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Studies of the Synthesis and Characterisation
of Some Polyacrylamides

by

R. BIRAN

SUPERVISOR : DR. J.V. DAWKINS

Submitted for the degree of Doctor of Philosophy
of Loughborough University of Technology.

July, 1978

Department of Chemistry

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ORIGINALITY

All the work presented in this thesis has been carried out by the author, except where otherwise acknowledged and has not previously been presented for a degree at this University or any other Institution.

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To my wife

DOOLIN

and to my two daughters

NADIA ROMA

and

CELIA USHA

ABSTRACT

Polyacrylamides have been synthesised by a solution polymerisation process using water as the solvent. The radical polymerisation performed under a nitrogen blanket was initiated by the thermal decomposition of potassium persulphate. The influence of monomer and initiator concentrations, temperature and reaction time on the polymerisation conversion of monomer into polymer and on polymer molecular weight has been investigated.

Average molecular weights of the polymers were determined by solution viscometry and membrane osmometry. A procedure for obtaining reproducible viscosity data has been developed using the Ubbelohde capillary type viscometer. Because of a degassing problem with water as a solvent and membrane breakdown with formamide as a solvent, it was found that reliable osmotic pressure results were only obtained with difficulty for polymers dissolved in formamide/water (1:3) mixtures.

Polyacrylamide samples have been separated by analytical gel permeation chromatography with silica packings. Various modified silicas and several eluents were investigated with the aim of reducing the adsorption of polyacrylamide onto the chromatographic packing. Studies were performed with physically coated phases such as polyethylene oxides, Aerosol OT, with chemically bonded phases such as hexamethyldisilazane and n-propylamine, and with eluents such as distilled water, formamide/water (1:5), 1% 880 and ammonia/formamide. Experimental results have shown that satisfactory separations of polyacrylamide dependent solely on a permeation mechanism were only obtained with a porous silica having a covalently bonded aminopropyl phase at the pore surfaces and with a mixed eluent of formamide/water (1:5). This GPC system was calibrated with polyacrylamide fractions prepared by fractional precipitation. Molecular weight distributions were determined from the chromatogram for a fraction and a whole polymer. The

distribution for the unfractionated polyacrylamide was in reasonable agreement with distributions predicted from the mechanism of polymerisation.

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CHAPTER 1

INTRODUCTION

Polyacrylamide is an important polymer which is used in such major areas as flocculating aqueous suspensions (1), in paper treating resins (2) and as gelling and stabilizing agents for soils and muds (3). Commercially available polyacrylamides are manufactured to high conversion and invariably contain additives which are present for various reasons. Dainton and Tordoff (4) showed that k_p and $k_p/k_t^{\frac{1}{2}}$ (where k_p is the propagation rate constant and k_t is the termination rate constant) for the polymerisation of acrylamide with a radical initiator are extremely large compared to other monomers. The transfer rate to the monomer is small. Hence, acrylamide will polymerise very quickly to give polymers with molecular weights in the millions and many of the important properties of polyacrylamide result from the extremely high molecular weight. Polymerisation at high pH proceeds more slowly, but there is little change in chain length because the ratio $k_p/k_t^{\frac{1}{2}}$ is almost constant.

One of the objectives in this research was to develop gel permeation chromatography for characterizing polyacrylamides. This required the synthesis of polyacrylamides prepared to low conversion and having well defined molecular weights between 10^4 and 10^6 . It is also desirable that the molecular weight distribution should not be too broad and that the polyacrylamides should be free of stabilizers, emulsifiers or additives which might have been used during the polymerisation. Since there are no synthetic water-soluble polymer standards commercially available, it was hoped that polyacrylamides produced in the laboratory would be suitable for calibrating an aqueous GPC system.

Gel permeation chromatography is a form of liquid chromatography which has been developed rapidly in recent years for polymer characterization. The technique has been given different names from the time of its inception up to the present time (5). Porath and Flodin (6) who were the first workers to prepare porous organic networks with well defined pore diameters suitable for separating polymers in aqueous media called the technique gel filtration. In 1964 Moore (7) who was the first worker to prepare porous cross-linked organic particles with well defined pore diameters suitable for separating synthetic polymers in organic media used the term gel permeation chromatography. Gel filtration with soft gels (xerogels) which are lightly cross-linked and swell in the eluent is used for biochemical applications, usually in aqueous eluents. Gel permeation chromatography is used for synthetic polymers in organic eluents with supports (aerogels) which are semi-rigid or rigid in nature. Both xerogels and aerogels are used as chromatographic supports for the separation of solutes by a size-exclusion mechanism, assuming no interaction effects between solute and gel.

For polyacrylamide in water it might be expected that the xerogel supports such as dextrans, polyacrylamide and agarose would be the most suitable for characterisation. Dextran (e.g. trade name Sephadex) (8) is a polysaccharide which is cross-linked with epichlorhydrin to form glyceryl links between the chains, thus forming a gel with a three-dimensional network. The polysaccharide is initially obtained from the fermentation of sucrose using the bacteria *Leuconostoc mesenteroides*. The amount of swelling of the gel in the solvent is proportional to the amount of cross-linking agent present. Polyacrylamide gel (e.g. trade name Bio-Gel) is synthetic and is obtained by the copolymerisation of acrylamide monomer and methylene bis acrylamide which is the cross-linking agent (9, 10). Agarose gel (e.g. trade name Bio-Gel A and

Sepharose) is a mixture of linear polysaccharides composed mainly of D-galactose and 3,6-anhydro-L-galactose residues (9, 10).

The above xerogels are classified by their manufacturers according to their fractionation ranges. The two types of compounds that are normally used to determine the fractionation ranges of the gel are first polypeptides and globular proteins which are very compact molecules and contain very little solvent and second dextrans which are flexible chains which are highly solvated and consequently contain a large amount of solvent. The manufacturer's hand book (11) refers to the highest molecular weight range that can be achieved by separating dextrans. With the Sephadex G200 support, dextrans in the molecular weight range 1000 and 200,000 can be separated. The polyacrylamide gel P-300 separates globular proteins in the molecular weight range 100,000 and 400,000. The agarose gel, e.g. Bio-Gel A-150m, separates globular proteins in the molecular weight range up to 150,000,000.

The xerogels are normally used under hydrostatic pressure employing a gravity feed system. Agarose A-150m because of its large pore sizes cannot be used with a hydrostatic head greater than 30 cm of water because of the gel compacting under its own weight and finally resulting in a breakdown of the gel matrix. Sephadex cannot be used at low pHs because of hydrolysis of the glucosidic linkages. Bio-Gel P cannot be used at extreme pH because of hydrolysis of the amide groups (9). On hydrolysis, carboxyl groups are produced which give the gel ion-exchange properties. Agarose has a considerable number of charged groups such as sulphate and carboxyl. Consequently it is necessary to work at high ionic strength in order to minimise ion exchange effects. Therefore, these gels are not suitable for separating polyacrylamide solutes of the specified molecular weights.

Gel filtration with xerogels is normally performed with aqueous eluents. However, xerogels may be modified so that they are compatible

with organic eluents. In the case of Sephadex, organic eluents such as glycols, formamide, dimethyl sulfoxide and acetone have been used (11). However, the degree of swelling of these modified gels was less than that with water (11), and so the fractionation range is used to separate lower molecular weights. The first preparation of cross-linked polystyrene particles for separations with organic eluents was separated by Vaughan (12) in 1960. However, his packings only covered a limited molecular weight fractionation range. In 1964, Moore (7) reported semi-rigid xerogels based on cross-linked polystyrene which successfully separated solutes in the fractionation range from monomer to molecular weights of several million. This led to the development of styragel packings, which are cross-linked particles of styrene and divinyl benzene and which are marketed by Waters Associates. Although these packings have been widely used for separations with organic eluents such as tetrahydrofuran, chloroform, toluene and o-dichlorobenzene, they are not compatible with water and therefore are not suitable for polyacrylamide. Rigid inorganic aerogels such as silica and porous glass do not swell in the eluent and may be used with both aqueous and organic eluents (13, 14). Examples of such packings are Porasil and Spherosil which are porous silica beads manufactured by Rhone-Progil of France and distributed by Waters Associates. Because of the rigidity, inorganic packings can be used under high pressures. The disadvantage of silica is that some solutes in certain liquids separate by an adsorption mechanism as well as by the size exclusion mechanism. The adsorption which can be reversible or irreversible is due to surface hydroxyl groups on the surface of the silica. These surface hydroxyl groups are sometimes termed "active sites" and may be reduced by techniques such as selecting a very polar eluent, coating the surface of the support with a physically bonded phase, bonding chemically on the surface of the support, or adding a surfactant or a surface active compound to the eluent. A further problem is the slow dissolution (p.p.m. concentration) of silica in water, resulting in the

formation of silicic acid ($\text{Si}(\text{OH})_4$) which can cause the reversible or irreversible adsorption of polyacrylamide (15).

The only paper that has been published on the GPC of polyacrylamide was by Hamielec (16, 17) who described the determination of the molecular weight distribution of polyacrylamide with columns of Bio-Glas and Controlled Pore Glass.

The eluent was a solution of 0.15% (w/v) potassium bromide in water but most of his experimental details were quite vague. A review by Cooper (18) demonstrates that GPC separations of polymers in aqueous media with aerogels has been a neglected area.

Further characterisation in order to determine the molecular weight of the polyacrylamide requires such techniques as light scattering, membrane osmometry and viscometry. Light scattering and membrane osmometry have not been used extensively for synthetic polymers in water. Silberberg (19) reported some light scattering measurements of aqueous polyacrylamide solutions. No experiments or results have been described for polyacrylamide in a membrane osmometer. Viscometry is a simple technique and has been widely used for polyacrylamide solutions, but there still exist several difficulties in performing the measurements (116).

Because so little characterisation data has been reported for polyacrylamide a major aim at the outset of this project was to investigate GPC separations of whole polymers and fractions of polyacrylamide in aqueous media in order to find experimental conditions such that the separation is effected by an exclusion mechanism. This necessitated a study of the synthesis of polyacrylamide in order to provide polymers having well defined molecular weights in the range of 10^4 to 10^6 by a low conversion polymerisation process. Work has also been performed in order to obtain reliable characterisation data for these polymers by osmometry and viscometry techniques. The provision of calibration fractions for

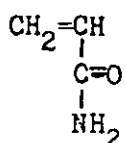
gel permeation chromatography has required a study of the fractionation of polyacrylamide by fractional precipitation.

CHAPTER 2

THEORY

2.1 ADDITION POLYMERISATION OF ACRYLAMIDE MONOMER

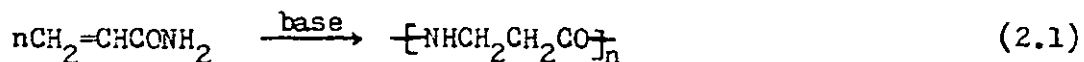
Acrylamide monomer contains two functional groups, the double bond and the amide group.



The carbon to carbon double bond is susceptible to activation by a free radical or ionic initiator. The active centre then propagates a kinetic chain which leads to the formation of a macromolecule whose growth is terminated by a suitable mechanism. This type of polymerisation is known as an addition polymerisation, which is characterised by three distinct stages:

- (1) Initiation - when the active centre is created.
- (2) Propagation - kinetic chain growth involving repeated addition of monomer to the growing chain.
- (3) Termination - where the growth of the polymer chain is halted either by combination or termination.

Polymerisation of acrylamide monomer can be activated by different types of initiators. Radical sources are the most common type of initiator for the polymerisation of acrylamide monomer. Free radicals are usually obtained by the thermal or photochemical decomposition of compounds such as inorganic or organic peroxide-type compounds. On the other hand, anionic polymerisation of acrylamide yields a polymer of entirely different structure, poly- β -alanine (nylon 3) (20).



This polyamide is crystalline; has a higher softening point and lower solubility than polyacrylamide obtained by a free radical polymerisation.

Before the synthesis of polyacrylamide is described, the theory of the kinetics of radical addition polymerisation will be presented.

2.1.1 Mechanism of Addition Polymerisation (21)

Initiators (I) on decomposition will produce radicals (X^\bullet) with a velocity constant k_d .



The addition of a monomer, denoted by M, will form a radical M^\bullet with a velocity constant k_a



The rate of initiation V_i (thermal initiation) is then the rate of production of chain radicals.

$$V_i = \frac{d[XM^\bullet]}{dt} = 2k_d f[I] \quad (2.4)$$

where f represents the efficiency of conversion of these radicals into propagating chains. Propagation is the addition of monomer to the growing radical



The rate of the bimolecular propagation reaction is assumed to be the same for each step

$$V_p = k_p [M][M^\bullet] \quad (2.6)$$

where $[M^\bullet]$ represents the concentration of the propagating chains and $[M]$

is usually low at any particular time. Termination is also a bimolecular process depending only on $[M^*]$. The rate of termination V_t is given by

$$V_t = 2k_t[M^*][M^*] \quad (2.7)$$

The rate constant k_t can be obtained from two possible mechanisms, combination or disproportionation. In the polymerisation of many monomers by the thermal decomposition of radical initiators, the mechanism is usually by combination (21).

A steady state is reached when the rate of radical formation is exactly counterbalanced by the rate of destruction, i.e.

$$V_i = V_t \quad (2.8)$$

For a polymerisation involving the thermal decomposition of a radical initiator, it follows from equations (2.4) and (2.7) that

$$2k_t[M^*]^2 = 2k_d f[I] \quad (2.9)$$

Therefore, the radical concentration is given by

$$[M^*] = \left\{ f k_d [I] / k_t \right\}^{\frac{1}{2}} \quad (2.10)$$

Because the radical concentration is too small to be determined in conventional polymerisation experiments, it is replaced in equation (2.6) by substitution of equation (2.10), giving

$$V_p = k_p \left\{ f k_d [I] / k_t \right\}^{\frac{1}{2}} [M] \quad (2.11)$$

Therefore, the rate of polymerisation is proportional to the monomer concentration and to the square root of the initiator concentration, if f is high. For a low efficiency initiator, f becomes a function of $[M]$, and the rate is proportional to $[M]^{3/2}$.

The average degree of polymerisation is given by

$$\bar{x}_n = \bar{M}_n / M_0 \quad (2.12)$$

where \bar{M}_n is the number average molecular weight and M_0 is the molecular weight of the monomer. The kinetic chain length \bar{V} is a measure of the average number of monomer units reacting with an active centre and is related to \bar{x}_n by

$$\bar{x}_n = 2\bar{V} \quad (2.13)$$

For termination by combination under steady state conditions, it follows that \bar{V} is given by (21)

$$\bar{V} = \frac{V_p}{V_i} = \frac{V_p}{V_t} = k_p^2 [M]^2 / 2k_t V_p \quad (2.14)$$

Therefore, the kinetic chain length is inversely proportional to rate of polymerisation. From an analysis of the temperature dependence of the rate of polymerisation (22), it follows that the rate of polymerisation will increase and the kinetic chain length will decrease on raising the temperature. The kinetic chain length is also inversely proportional to initiator concentration. Therefore, increasing the initiator concentration will decrease the kinetic chain length (i.e. molecular weight). The reaction kinetics described here are an over-simplification based on the assumption that termination occurs solely by a reaction between two growing chains, that no chain transfer takes place, and that there is negligible auto-acceleration in the rate of polymerisation (21).

If a chain transfer agent (SH) is deliberately added to reduce the value of \bar{x}_n , then the propagating radicals will react according to the equation



The rate of this reaction will influence \bar{x}_n which is given by (21)

$$\frac{1}{\bar{x}_n} = \frac{k_t \cdot V_p}{k_p^2 [M]^2} + \frac{k_{tr,s} [S]}{k_p [M]} \quad (2.16)$$

where $k_{tr,s}/k_p$ is the chain transfer constant, C_s . Chain transfer to monomer and initiator is assumed to be negligible in deriving equation (2.16).

2.1.2 Molecular Weight Distribution

For some types of polymerisation the resulting distribution of molecular weights can be calculated statistically. The distribution is usually presented as a plot of the weight of polymer of a given size against the chain length or molecular weight. Since a distribution of molecular weights exists in any sample of polymer, the experimental measurement of a molecular weight can give only an average value. The average molecular weights commonly measured are the number average molecular weight \bar{M}_n , the viscosity average molecular weight \bar{M}_v , and the weight average molecular weight \bar{M}_w . The positions of these averages on the molecular weight axis of the distribution are shown in Figure 2.1. The number average molecular weight \bar{M}_n which can be determined by membrane osmometry can be represented by the equation

$$\bar{M}_n = \frac{\sum_{i=1}^{\infty} w_i}{\sum_{i=1}^{\infty} N_i} = \frac{\sum_{i=1}^{\infty} N_i M_i}{\sum_{i=1}^{\infty} N_i} \quad (2.17)$$

where N_i is the total number of moles of i th species of molecular weight M_i and w_i is the weight of i th species. The weight average molecular weight \bar{M}_w which can be obtained from light scattering measurements can be represented by the equation

$$\bar{M}_w = \frac{\sum_{i=1}^{\infty} w_i M_i}{\sum_{i=1}^{\infty} w_i} = \frac{\sum_{i=1}^{\infty} N_i M_i^2}{\sum_{i=1}^{\infty} N_i M_i} \quad (2.18)$$

where N_i and w_i are defined as in equation (2.17). The value of \bar{M}_w is greater than \bar{M}_n as shown in Figure 2.1. The ratio \bar{M}_w/\bar{M}_n known as the polydispersity is used as a measure of the breadth of the molecular weight distribution. The viscosity average molecular weight \bar{M}_v can be represented by the equation

$$\bar{M}_v = \left[\frac{\sum_{i=1}^{\infty} N_i M_i^{1+a}}{\sum_{i=1}^{\infty} N_i M_i} \right]^{1/a} \quad (2.19)$$

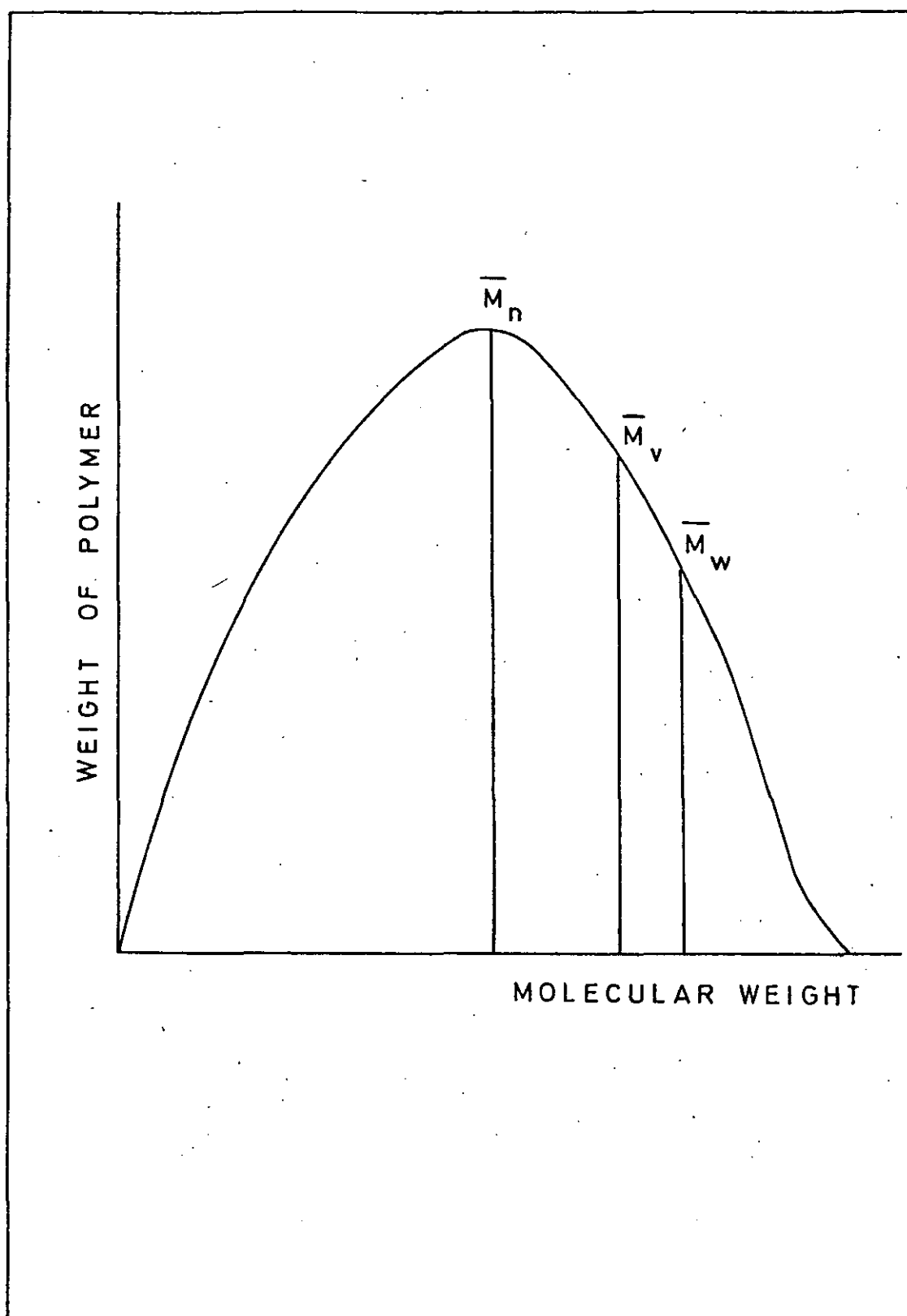
where a is the exponent in the Mark-Houwink-Sakurada equation, see equation (2.44) and is generally between 0.5 and 0.8. The value of \bar{M}_v is closer to \bar{M}_w than to \bar{M}_n , since equation (2.18) corresponds to equation with $a = -1$ and equation (2.19) corresponds to equation with $a = +1$. The molecular weight distribution of a polymer can be determined quickly by analytical GPC and with the advent of high performance GPC, analysis times can be improved tremendously (23).

The molecular weight distribution of a polymer is determined by the kinetics, mechanism and conditions of polymerisation. In a chain polymerisation the molecular weight distribution can be calculated and can be represented by an exponential distribution function provided the polymerisation is performed to low conversion so that there is little change in monomer and initiator concentrations (24). Thus, polystyrene prepared with a radical initiator has a differential weight distribution $w(M)$ as a function of molecular weight M given by

$$w(M) = \frac{4M^2}{\bar{M}_n^3} e^{-2M/\bar{M}_n} \quad (2.20)$$

and this function gives a polydispersity of 1.5. If a chain transfer agent is included in the polymerisation, then the differential weight distribution becomes:

FIGURE 2.1
DISTRIBUTION OF MOLECULAR WEIGHT OF A POLYMER



$$w(M) = \frac{M}{\bar{M}_n} \frac{1}{2} e^{-M/\bar{M}_n} \quad (2.21)$$

and this function gives a polydispersity of 2.0.

Hardly any work has been reported on the production of polymers with well defined molecular weight distributions from the radical polymerisation of acrylamide.

2.1.3 Polyacrylamide Synthesis

From the work of Dainton (4) and Suen (25) at 25°C, the rate constant for propagation is $1.8 \times 10^4 \text{ l mole}^{-1} \text{ sec}^{-1}$ and termination is $1.45 \times 10^7 \text{ l mole}^{-1} \text{ sec}^{-1}$, and for transfer to monomer is $2.2 \times 10^{-1} \text{ l mole}^{-1} \text{ sec}^{-1}$. The ratio $k_p/k_t^{1/2}$ exceeds that reported for any other monomer (26). This means the polymerisation is rapid and the molecular weights are high.

Bikales (27) has reviewed the chemistry of acrylamide monomer, Thomas (28) has reviewed polyacrylamide, and MacWilliams (29) has reviewed acrylamide chemistry. In these reviews the synthesis of polyacrylamides at low conversion and the determination of the molecular weight distribution by GPC were not discussed. Since low conversion polyacrylamides free from contaminants (e.g. surfactants and stabilisers) were required, then the right polymerisation process and experimental conditions must be chosen. In order to do this, a survey of all processes, catalysts and experimental conditions was performed. It was desirable early in the research to control the molecular weight distribution and average molecular weight of polyacrylamide by selecting the correct polymerisation conditions. Consequently the kinetics and mechanism of the process chosen should be well understood. The polymerisation of homogeneous aqueous acrylamide systems has been studied in more detail than heterogeneous systems.

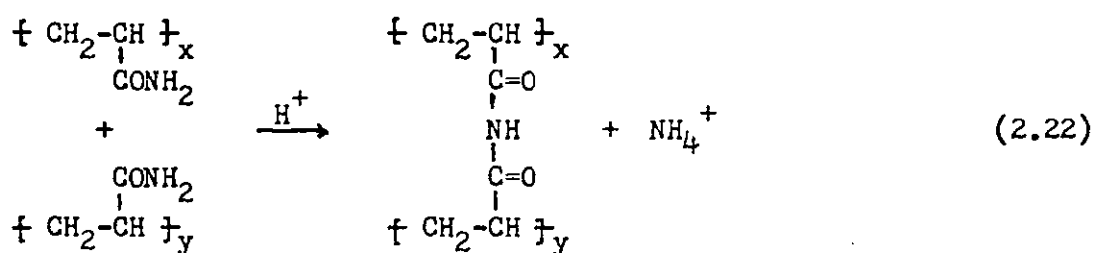
2.1.4 Solution Polymerisation

The presence of the solvent facilitates heat transfer and reduces the

viscosity of the medium. Water is cheap and non-toxic and is therefore used widely as a solvent. The acrylamide monomer and the initiator (e.g. potassium persulphate) are soluble in water and the chain transfer agent (e.g. propan-2-ol) is completely miscible with water. Conversion is controlled by reaction time and the molecular weight of the product is controlled by the concentrations of monomer, initiator, and chain transfer agent.

Polymerisations in aqueous solution are initiated by thermal or redox activated peroxide systems, by ultrasonic waves, by high energy radiation (e.g. γ rays) and photochemically. These methods reported by Schulz et al. (30) are indicative of the wide range of free radical sources which are effective. Schulz showed that γ rays yielded high molecular weight polyacrylamide, Fenton's reagent yielded low molecular weight polyacrylamide and ultrasonic waves polymerised the monomer and depolymerised the polymer.

As mentioned in Section 2.1.3, acrylamide monomer is easily polymerised. At extreme pH levels, different products may be formed (20). Polymerisation at pH 2.5 or below would result in imidization. Consequently, a cross-linked product as shown by the equation below may result.



2.1.4.i Initiation by peroxidic compounds

Nakano et al. (31) polymerised acrylamide monomer using an initiator of polyacrylamide peroxide. This peroxide was found in acrylamide which had been left standing in air for several weeks. The monomer polymerised spontaneously in water at room temperature in spite of the absence of an initiator. Takahashi et al. (32) showed that complexes of cerium(IV) with acrylamide monomer will initiate polymerisation. Narita et al. (33,

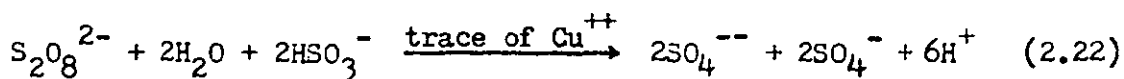
34, 35) performed a similar type of polymerisation using ammonium cerium(IV) nitrate as initiator. Rout et al. (36) initiated polymerisation of acrylamide monomer using a glycerol/cerium(IV) redox system. Kolodny (37) initiated polymerisation using a chlorate or bromate reduced by 3,3'-nitritoltris propionamide. Suen et al. (25) used a chlorate-sulfite initiator. Other workers have investigated various initiator systems. Pohleman et al. (38) used formaldehyde sufoxylate. Rodriguez and Giuey (39) used bisulphite. Loritsch (40) used a copper chelate or an organic peroxide reduced with ascorbic acid. Narita et al. (41) used cerium(IV) reduced with pinacol. Several workers have investigated electrochemical initiation. Skobets and Nestyuk (42) reduced persulphate electrolytically. Bhadani and Prasad (43) electrolysed acrylamide in sodium nitrate and N-N-dimethyl formamide which led to polymer forming simultaneously in the anode and cathode compartments. No added initiator was present.

Acrylamide monomer is so easily polymerised that compounds which have been referred to as retarders or inhibitors appear to initiate polymerisation when coupled to another compound or compounds. From some of the above examples Nakano's experiment (31) and the work of Bhadani and Prasad (42) appear to highlight the ease with which acrylamide monomer polymerises. On the other hand, copper ions, which have been referred to as retarders or inhibitors, initiate polymerisation when reduced with ascorbic acid (40), as reported by Loritsch.

Inhibitors which have been used in acrylamide synthesis can be found in references 44 to 50. These inhibitors were used at the time in order to inhibit polymerisation. On referring to references 51 and 52 metal ions were used by commercial manufacturers to terminate or to inhibit the polymerisation of acrylamide monomer in aqueous solution. However most redox catalysts used in the synthesis of polyacrylamide constituted some form of metallic ions, and it is obvious that some form of inhibition or retardation could occur. This system can be desirable in the production of low

conversion polymers as obtained by some of these authors (56-62). However, the effect of the presence of the metallic ions has not been considered by workers in the reaction mechanisms.

In Hoover's patent (53), the use of redox catalysts in the initiation of acrylamide monomer in aqueous solution was suggested. His technique of maintaining a constant increase in temperature on adding the catalyst was as follows. A large excess of oxidising catalyst is initially included in the monomer solution below the thermal activation temperature. The reducing agent is then added gradually in a controlled manner throughout the exothermic polymerisation reaction, and the temperature rise of the reaction mixture is controlled to a steady state. The preferred redox catalyst of Hoover was ammonium persulphate as oxidising catalyst and sodium metabisulphite as the reducing agent. His choice of pH was 7.5 because he believed that the pH had a significant effect on the rate of activation of catalyst. As the pH was lowered, the rate of reaction was decreased, or if the pH was increased the rate of reaction was increased. Therefore, to maintain constant free radical concentration the pH should be kept constant. However, the decomposition theory does not support this.



The role of metallic ions is not very clear since Hoover postulated that the presence of trace amounts of metals, such as ferrous, cupric, cobaltic, argentic or ceric ions, was essential to the generation of free radicals in a redox system. In 1967 Riggs and Rodriguez (54) used the persulphate/thiosulphate catalyst and showed that the rate of polymerisation increased with persulphate concentration and with the thiosulphate concentration. Also, the rate of polymerisation increased with monomer concentration. The molecular weights and the degree of conversion were quite high. Suen et al. (25) used chlorate and sulphite as a redox catalyst and found that this catalyst was only active under very acidic

conditions (pH 2.2). He found that quite high conversions were obtained. Suen and Schiller (55) claimed that hydrolysis in situ with a strong base may be used to produce polymers with some carboxylate groups. Of late new redox catalysts are being studied and these are described in references 56 to 62.

From this review of the literature on acrylamide polymerisation there are several observations which are not well understood.

There is a conflict of views concerning the use of metal ions in polyacrylamide synthesis. Metal ions are introduced in the form of metal salts, or in redox catalysts, or the slow leaching of electrodes in the electrolytic method. It has been stated that some metal ions are responsible for the generation of free radicals in solution and in other cases metal ions have been referred to as terminators and inhibitors.

Another important criterion is pH. From the chemistry of hydrolysis it is known that the amide groups can be hydrolysed at extreme pHs to form carboxylate groups. Consequently, some workers have assumed they have synthesised polyacrylamides by working at low pHs. It is possible that copolymers of polyacrylamide and polyacrylic acid have been produced instead. At high pH or with an anionic initiator (e.g. butyl lithium), nylon 3 is produced from acrylamide monomer.

It seemed therefore that the use of a single peroxy initiator in this research work would be more advantageous than using a redox catalyst. The single initiator chosen in this research was potassium persulphate.

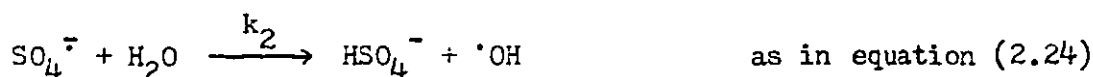
Decomposition of Potassium Persulphate

Green and Masson (63) were the first to show that the persulphate decomposition in aqueous solution follows a first order law. Evidence that fission of the persulphate took place was provided by Eager and Winkler (64) in their study of the oxidation of mercaptans by potassium persulphate. Bartlett and Cotman (65) proposed the following mechanism



These results were confirmed in a study by Kolthoff and Miller (66) who, using ^{18}O -labelled solvent, showed that the oxygen evolved came from the water.

Riggs and Rodriiguez (54) in their work stated that it was evident that the thermal decomposition of persulphate yielded two species capable of initiating polymerisation, the sulphate radical-ion and the hydroxyl radical. In the presence of acrylamide monomer, the equations can be considered as follows:



Riggs and Rodriiguez (54) obtained values of the relationship between rate of polymerisation and the monomer and initiator concentrations as

$$V_p = k_{1.25} [\text{M}]^{1.25} [\text{I}]^{0.5} \quad (2.30)$$

where $k_{1.25}$ is the rate constant of the reaction. The experiments of Chou Kwang-Fu (67) suggested that hydroxyl radicals were not formed. Consequently

he suggested that the initiating species was the sulphate radical anion $\text{SO}_4^{\cdot-}$.

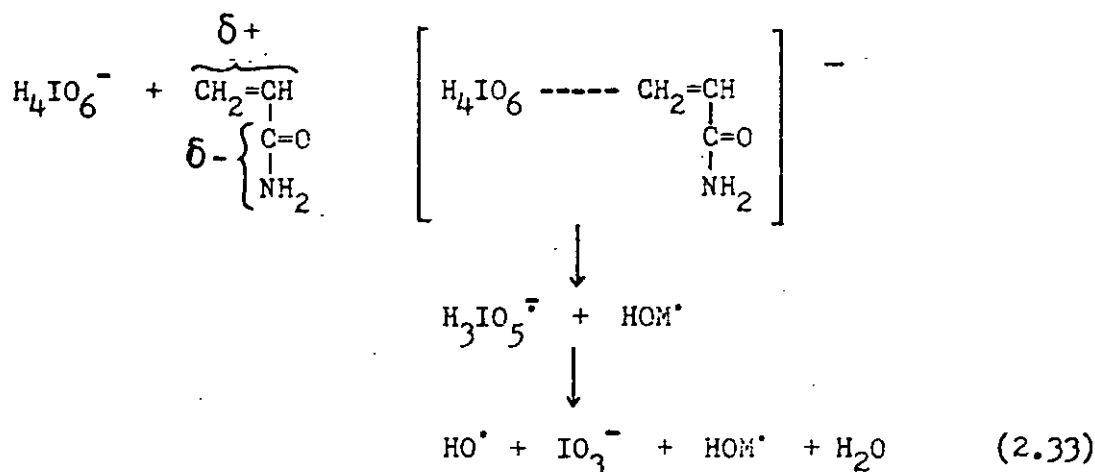
In this research the degree of polymerisation (\bar{x}_n) was of more interest than the rate of polymerisation. It follows from equations (2.13) and (2.14) that \bar{x}_n and V_p are related by

$$V_p \propto \frac{1}{\bar{x}_n} \quad (2.31)$$

Thus, increasing the rate of polymerisation would effectively increase conversion and lower the molecular weight. From the literature survey many of the syntheses of polyacrylamides have been carried out to high conversion with initiation with radical sources or by radiation. The reactions were performed dilatometrically so that the heat transfer is better than in a reaction flask. The kinetics of the reactions were best explained when the reactions were performed dilatometrically. Sorenson and Campbell (68) used a reaction temperature of 75-80°C. Bikales (20) claimed that at temperatures above 50°C branching and cross-linking reactions tend to occur. However, polyacrylamide synthesised by the method of Sorenson and Campbell (68) will dissolve in water, see Section 4.1. Branching tends to occur in polymerisations with high concentrations of polymer (69). Since low conversion was the objective in this work it was highly unlikely that branching would occur in the polyacrylamide synthesis using initiation below 80°C.

Chou Kwang-Fu (70) has studied the polymerisation of acrylamide monomer in detail. His polymerisations were performed with an aqueous solution of acrylamide at a pH of 5.4 with sodium metaperiodate as initiator at 40°C. The polymerisation was inhibited by oxygen and not affected by diffused daylight. When the monomer was absent, no thermal decomposition of sodium metaperiodate in an aqueous medium occurred. This behaviour is opposite to the usual self decomposition of an initiator such as potassium persulphate. The conversion data of Chou Kwang-Fu was quite low but no molecular weights were presented (70-73). The author postulated that

ionic species of sodium metaperiodate and acrylamide form a complex and that the primary decomposition of the complex produces primary radicals contributing to polymerisation initiation. The proposed mechanism is



Chou Kwang-Fu stated that the univalent anion is highly capable of forming a complex with the monomer (70). He studied the effect of pH on this polymerisation. He found that at pH 7 the rate of polymerisation was at its maximum, decreasing rapidly from pH 7 to pH 6 and becoming practically constant between pH 6 and pH 1. In alkaline solution, the rate of polymerisation decreased rather slowly with increasing pH. In acidic solutions, the degree of polymerisation remained nearly constant, irrespective of both pH and the polymerisation time, and was lower than degrees of polymerisation obtained in neutral and alkaline solutions. At about pH 7 the degree of polymerisation was virtually constant during the polymerisation.

However, in alkaline solution the degree of polymerisation increased as the polymerisation proceeded. The author explained the relation between the degree of polymerisation and pH in terms of various ionic acrylamide intermediates which may be formed in acidic and alkaline media.

Consequently the propagation constant (k_p) and termination constant (k_t) decreased as pH increased, but $k_p/k_t^{\frac{1}{2}}$ was constant regardless of pH.

Chou Kwang-Fu polymerised acrylamide in acidic aqueous solution (pH 2.0) using sodium metaperiodate as initiator at a temperature of 40°C (73).

He found that the rate of polymerisation was proportional to the second power of the acrylamide concentration, but independent of the initiator concentration. The initiation seems to be similar to the polymerisation performed at pH 5.4. However, termination occurred by undissociated periodic acid. Chou Kwang-Fu (74) polymerised acrylamide in alkaline aqueous solution. The conclusions were that a complex was formed from a univalent anion of sodium metaperiodate and an acrylamide molecule which participates in the initiation of polymerisation. The termination of polymerisation occurs between two polymer radicals by a bimolecular termination process. If the complex contained the bivalent anion of sodium metaperiodate, it seemed unlikely that the complex would participate in the initiation of polymerisation. Chou Kwang-Fu (67) polymerised acrylamide using aqueous hydrogen peroxide and using potassium persulphate in aqueous solution at a temperature of 40°C, and he compared his results with the sodium metaperiodate system. He showed that the polymerisation of acrylamide initiated by sodium metaperiodate, hydrogen peroxide and potassium persulphate in aqueous solution demonstrated a dependence of the rate of polymerisation on both the pH and the apparent first order decomposition rate constant of the initiator (k_{ap}). He showed that the decomposition rate constant of potassium persulphate in the presence of acrylamide monomer in aqueous solution was one hundred times greater than that for potassium persulphate in aqueous solution. Chou Kwang-Fu's experimental conditions were similar to Imoto's (75). However Chou Kwang-Fu's rate of polymerisation was twice and his molecular weight was a factor of ten lower than results reported by Imoto (75). The initiator hydrogen peroxide used in the same type of experimental conditions resulted in the degree of polymerisation being independent of pH at the beginning of the polymerisation. The increase in the degree of polymerisation was never found with potassium persulphate. It occurred only in alkaline solution in the case of sodium metaperiodate. The results were different for different initiators. The values of the

dissociation constants for the initiators became larger as follows:

potassium persulphate > hydrogen peroxide > sodium metaperiodate. Chou Kwang-Fu concluded that initiation with hydrogen peroxide resulted in an increase in the degree of polymerisation during the polymerisation which was independent of the pH value. In the case of potassium persulphate, the value of the degree of polymerisation was approximately constant during the polymerisation.

The rate of polymerisation of acrylamide initiated with azo catalysts exhibits the classic first order dependence on monomer concentration and half order dependence on catalyst concentration (76, 77). Sorenson produced polyacrylamides from the thermal decomposition of potassium persulphate (68). Ureta and Saloma (78) used the same method as Sorenson and showed that a relationship between initiator concentration and molecular weight existed. Riggs and Rodriiguez (54) showed that the thermally initiated polymerisation using persulphate followed the approximate rate law

$$V_p = k_{1.25} [K_2S_2O_8]^{0.5} [Acrylamide]^{1.25} \quad (2.34)$$

where $k_{1.25}$ is the rate constant for the reaction. The dependence of the rate on monomer concentration has been found to be exactly first power in photochemical studies (29). The higher order dependence on monomer concentration in the persulphate system is ascribed to a recombination of catalyst radicals. At high monomer concentrations the recombinations are fewer and the rate law approaches first order dependence in monomer. At low monomer concentration recombination is much greater and the order with respect to monomer approaches 1.5 (29). The rate law is

$$V_p = \frac{k[(ox)(red)]^{\frac{1}{2}} [M]^{5/2}}{M_o^{3/2}} \quad (2.35)$$

which applies to redox initiated polymerisations where the oxidant (ox) and reductant (red) are chlorate and sulphurous acid (39) or persulphate and metabisulphite (53). The rate of polymerisation using the persulphate-

thiosulphate redox initiation system is also non-linear in monomer concentration over most of the initiator concentration range (79). In cases where the initial monomer concentration and the high order dependence with respect to monomer concentration appear in the rate law expression, the behaviour of the initiation system may be explained by non-stationary state kinetics. The initiation reactions in all of these systems are chain processes, the paths of which are sensitive to other components of the system. It has been suggested that the polymer chain ends reduce both bisulphite and thiosulphate ions to radicals (29). These reactions are kinetically equivalent to a transfer to catalyst process. The presence of metal ions such as ferrous ion increases the rate of the reaction of the oxidant and reductant. Some other metals, for example, chromic ions are inhibitors. Gleason, Miller and Sheats (69) showed that the abstraction of hydrogen atoms from the polyacrylamide backbone occurs at 78°C but not at 50°C in the presence of a persulphate-bisulphite catalyst system. The identity of the species attacking the backbone is uncertain.

2.1.4.ii Initiation by Ionising Radiation

Collinson et al. (80) showed that the initiation of the polymerisation of acrylamide in aqueous solution using γ -rays or X-rays is a free radical process. Chambers, Collinson and Dainton (81) polymerised acrylamide, methacrylamide and N-t-butylacrylamide in aqueous solution with electrons from a Van de Graaf generator. The polymerisation was initiated by the reaction of a solvated electron, H^\bullet or HO^\bullet with the acrylamide. The radical half lives in dilute solutions of monomer are of the order of microseconds. Radiation studies have been useful in defining mechanisms. However, the technique is not important for the commercial preparation of polymers because of cross-linking before the monomer is completely polymerised.

2.1.4.iii Initiation by Photochemical Systems

Oster (82, 83) polymerised aqueous acrylamide solutions by irradiating a 10% solution with a tungsten source using 0.005% riboflavine phosphate as a sensitizer, a mild reducing agent, and a trace of oxygen. Shepp et al. (84), Chaberek et al. (85) and Chen (86) found oxygen to be deleterious in the thionine, methylene blue and eosin Y sensitized systems. The oxygen-containing systems are claimed to work through a redox mechanism in which hydrogen peroxide generated from oxygen and the photoactivated dye reacts with the reducing agent. Reducing agents are necessary in all of the dye-sensitized systems. A strong reducing agent in excess, for example ascorbic acid, will retard the polymerisation. Dainton and Tordoff (4) photopolymerised acrylamide in aqueous 0.12 M perchloric acid solution with ultra violet light using hydrogen peroxide or complex ferric ions as sensitizers. Publications by Natarajan and Santappa (87, 88, 89) led Bhaduri and Aditya to photopolymerise acrylamide using cobalt-ammine complexes (90). Kothandaraman and Santappa (91) also studied the photoinitiation of acrylamide and acrylic acid in presence of tetraamminediazido cobalt(III) complexes, where the basis of initiation was by a N_3^{\cdot} radical. Delzenne (92) also studied the photopolymerisation of acrylamide by chloro and aqua pentammine complexes.

2.1.5 Survey of Other Polymerisation Processes

The simplest polymerisation process is bulk monomer polymerisation, which is very useful for liquid monomers such as styrene. Acrylamide is a white crystalline solid which has a melting point of $84.5^{\circ}\text{C} \pm 0.5^{\circ}\text{C}$. This temperature would have to be exceeded before any form of bulk monomer polymerisation is to take place. In view of the fast rate of polymerisation, experiments with bulk monomer at elevated temperatures will not be easy to control. The disadvantages of bulk monomer polymerisation are minimised in homogeneous solution polymerisation and in heterogeneous polymerisations

such as inverse suspension and inverse emulsion.

2.1.5.i Inverse Suspension Polymerisation

The problem of heat dissipation in bulk monomer polymerisations may be reduced by suspending droplets of an aqueous solution of acrylamide in a hydrophobic phase, e.g. hexane, heptane, etc. The droplets about 0.01 to 0.5 cm are obtained by vigorous agitation of the system and may be stabilised by adding a protective colloid. The effect is a micro-bulk polymerisation which avoids the complications of heat and viscosity build-up. The hydrophobic phase, i.e. the continuous liquid medium, is a non-solvent for the monomer and the resulting polymer. Such a liquid medium should be volatile ($50^{\circ}\text{C} \rightarrow 110^{\circ}\text{C}$), non-toxic and a poor chain transfer agent. No work has been reported on the suspension of acrylamide droplets in a hydrophobic solvent with subsequent polymerisation. Friedrich et al. (93) described the bead formation of polyacrylamide by suspending solid monomer in a hydrophobic solvent (xylene). His method yielded low molecular weight polyacrylamides. Thomas and Friedlander (94) did similar work in synthesising polyacrylamide by suspending solid acrylamide monomer in a hydrophobic solvent.

2.1.5.ii Inverse Emulsion Polymerisation

In an inverse emulsion polymerisation a hydrophilic monomer, frequently in aqueous solution, is emulsified in a continuous oil phase using a water in oil emulsifier, and the monomer is polymerised using an oil-soluble initiator. The products are viscous latices consisting of sub-microscopic ($1\mu\text{m}$), water swollen, hydrophilic polymer particles colloidally dispersed in the continuous oil phase.

In conventional emulsion polymerisation an emulsifier is present at a concentration above the critical micelle concentration. These micelles are in equilibrium with the free emulsifier molecules. In the case of ionic

emulsifiers there are about 50-200 molecules in the micelles. In emulsion polymerisation the monomer is in the form of droplets stabilised by emulsifier. Part of the monomer is solubilised in the micelles. As free radicals enter the micelles the monomer is then polymerised and the polymer particles (latex particles) are formed. The emulsifier molecules are adsorbed at the surface of the particles and protect them from coagulation.

In inverse emulsion polymerisation the formation of micelles is uncertain, but is portrayed speculatively because insufficient study of these systems has been made. The hydrophilic part of the emulsifier molecule is oriented towards the hydrophilic dispersed phase (acrylamide) and the hydrophobic part towards the hydrophobic continuous phase (xylene). The initiation of polymerisation proceeds by a mechanism analogous to that of the conventional emulsion system (95).

In conventional latices, the colloidal stability of the particles arises from the predominance of the electrostatic forces of repulsion over the London-Van der Waal's forces of attraction. Therefore, in most particle-particle collisions, the particles repel one another, so that the London-Van der Waal's forces of attraction at large separation distances cannot overcome the electrostatic forces of repulsion, and so many conventional latices remain stable indefinitely without significant flocculation of the particles.

In inverse emulsion polymerisation a recommended non-ionic emulsifier is sorbitan monostearate and the initiator is an oil-soluble peroxide, as described by Vanderhoff (96). A similar procedure uses a water-soluble initiator as described by Lincoln (97). Polymerisations have been conducted in aromatic, aliphatic and halogenated hydrocarbons as described by Volk (98).

The inverse latices are less stable than the conventional latices; on standing their particles will settle out in a few hours to a few days.

In some cases, the agglomerated latices may be redispersed by gentle agitation. The non-ionic emulsifier will partially stabilise the particles by covering the particles' surface with a protective layer. It may not be easy to remove a protective colloid or emulsifier from the polymer. Despite the attractions of these processes, detailed studies of acrylamide polymerisations have not been reported. The differences between inverse emulsion polymerisation and inverse suspension polymerisation are outlined in Table 2.1.

Table 2.1

Characteristics of Inverse Emulsion Polymerisation
and Inverse Suspension Polymerisation

| Inverse Emulsion | Inverse Suspension |
|--|--|
| (1) The initiator is introduced into the continuous phase. | The initiator is introduced into the dispersed phase. |
| (2) Smaller particle sizes are obtainable (less than $1\mu\text{m}$). | Larger particle sizes are obtainable ($\sim 0.01 \rightarrow 0.05\text{ cm}$). |
| (3) The molecular weight is large (of the order of millions). | The molecular weight is low ($\sim 100,000$). |

2.1.5.iii Precipitation Polymerisation

Very little work has been reported on this process for acrylamide polymerisations. In this process the monomer is soluble and the resulting polymer is insoluble in the chosen solvent. Yoshizawa (99) described the preparation of acrylamide polymer in t-butanol. Monagle (100) described the preparation of acrylamide polymer in a mixture of t-butanol, water and salt. Jennes and Scriba (101) described the polymerisation of acrylamide in acetone. In most solvent systems the molecular weight of the

polymer obtained with this process is very low. Also, it is known in this type of process that side reactions such as popcorn polymerisation, when tough cross-linked nodules of polymer grow rapidly and sometimes foul the feed lines in industrial plants, may occur (28). The polymer obtained from these reactions is normally in the form of a fine powder. Because molecular weights of $10^5 \rightarrow 10^6$ are not achieved easily this type of process is undesirable.

Gromov et al. (77) polymerised acrylamide monomer in dimethylsulfoxide (DMSO), tetrahydrofuran (THF) and in water, initiated by the thermal decomposition of azobisisobutyronitrile (AIBN). The values of $k_p/k_t^{0.5}$, the degree of polymerisation in water at equivalent monomer concentration and initiation rate were 10 times higher than in DMSO and 66 times higher than in THF. The rates of polymerisation in organic solvents do not fall quite so dramatically because the rates of decomposition of AIBN increase 5- and 30-fold respectively, as compared to water. The rapid polymerisation in water as compared to that in the aprotic solvents was ascribed to formation of a protonated radical species consistent with the acceleration in acid solution (the rate constant for the chain growth for polymerisation of acrylamide at pH 1 at 25°C in aqueous solution is 18,000 which decreases with increase in pH) (77).

2.1.5.iv Solid State Polymerisation

Acrylamide monomer can be polymerised in the solid state using ionizing radiation. MacWilliams (29) reported that the "in source" polymerisation initiated at 25°C with ^{60}Co γ rays is sluggish. However, when acrylamide is irradiated at 5°C, there is very little conversion but frequently "post polymerisation" occurs violently upon warming. This type of polymerisation normally yields low molecular weight acrylamides in comparison with solution polymerisation (102). In solution polymerisation oxygen normally retards the rate of polymerisation. However in solid state polymerisation, oxygen has

little effect on the rate of polymerisation. Propionamide on the other hand retards the rate of polymerisation of acrylamide monomer (103). On the addition of the photosensitizer methylene blue for visible light, the rate of polymerisation is increased (104).

2.1.6 Conclusions

A major aim in this research was to prepare pure and well defined polyacrylamides. Consequently, it was desirable to minimise the number of components in the polymerisation. Heterogeneous polymerisations were ruled out because of the contamination of the polymer with surfactants and stabilisers and because hardly any fundamental studies have been reported on the dependence of molecular weights and molecular weight distributions on the variables in the polymerisation. Solution polymerisation was chosen because the kinetics of polymerisation have been studied in more detail. Potassium persulphate was used as the radical generating initiator. The kinetics of this reaction were described by Riggs and Rodriguez (54) despite some criticisms made by Chou Kwang-Fu (67). It was hoped to elucidate the polymerisation conditions necessary for low conversion in order to produce polymers with a well defined molecular weight distribution close to that expected from the polymerisation mechanism. The mechanism for initiation involving two or more components is likely to be more involved and may give rise to undesirable side reactions. It would then be difficult to predict the molecular weight distribution from the polymerisation mechanism.

2.2 Solution Viscosity

From the measurement of solution viscosity, the size or extension in space of polymer molecules may be determined. With a capillary viscometer the ratio of the time t of a solution to the time t_0 of the solvent is called the relative viscosity and is denoted by η_r .

$$\eta_r = t / t_o \quad (2.36)$$

As this has a limiting value of unity, a more useful quantity is the specific viscosity η_{sp} , defined by

$$\eta_{sp} = \eta_r - 1 = (t - t_o) / t_o \quad (2.37)$$

The specific viscosity defined by η_{sp}/c expresses the contribution of solute molecules at concentration c to the viscosity. Similarly the inherent viscosity η_{inh} , defined by

$$\eta_{inh} = (\ln \eta_r) / c \quad (2.38)$$

expresses the contribution of solute molecules at concentration c to the viscosity. At infinite dilution both the specific viscosity and the inherent viscosity give the intrinsic viscosity $[\eta]$

$$[\eta] = \lim_{c \rightarrow 0} \frac{\eta_{sp}}{c} \quad (2.39)$$

$$[\eta] = \lim_{c \rightarrow 0} (\ln \eta_r) / c = \lim_{c \rightarrow 0} \eta_{inh} \quad (2.40)$$

The concentration c is expressed in grams of solute per 100 mls of solution (or percentage concentration). The intrinsic viscosity is expressed in the reciprocal of these units, i.e. decilitres per gram ($dl \ g^{-1}$).

The relationship between dilute solution viscosity and polymer concentration has been described by various functions all of which have been used to obtain $[\eta]$ by extrapolation to infinite dilution. Huggins (105) proposed the equation

$$\eta_{sp}/c = [\eta] + k' [\eta]^2 c \quad (2.41)$$

where k' is called the Huggins slope constant, which is usually a constant for a given polymer-solvent system. Some attempts to give a molecular interpretation to k' have been reported. For example, Gillespie (106) examined polystyrene in various solvents and related k' to the interaction

parameter for two coiling molecules. He showed that k' diminishes for polystyrenes in better solvents, corresponding to an increase in molecular entanglement as the polymer molecules become more extended. An alternative expression for the dependence of solution viscosity on polymer concentration is due to Kraemer (107)

$$\ln \eta_{r/c} = [\eta] - \beta [\eta]^2 c \quad (2.42)$$

where the slope β is called the Kraemer constant. Equations (2.41) and (2.42) may be combined on the same plot, as shown in Figure 2.2. Since both lines have the same ordinate intercepts, k' and β are related by the equation

$$k' + \beta = 0.5 \quad (2.43)$$

Van Oene and Cragg (108, 109) pointed out that slopes of the plots in Figure 2.2 can be seriously affected by adsorption or wall effects and have suggested methods by which $[\eta]$ and k' can be accurately evaluated.

The intrinsic viscosity of a polymer solution is a measure of the capacity of a polymer molecule to enhance the viscosity, which depends on the size and shape of the polymer molecule. The intrinsic viscosity increases with the molecular weight and is given by the Mark-Houwink-Sakurada equation (110)

$$[\eta] = KM^a \quad (2.44)$$

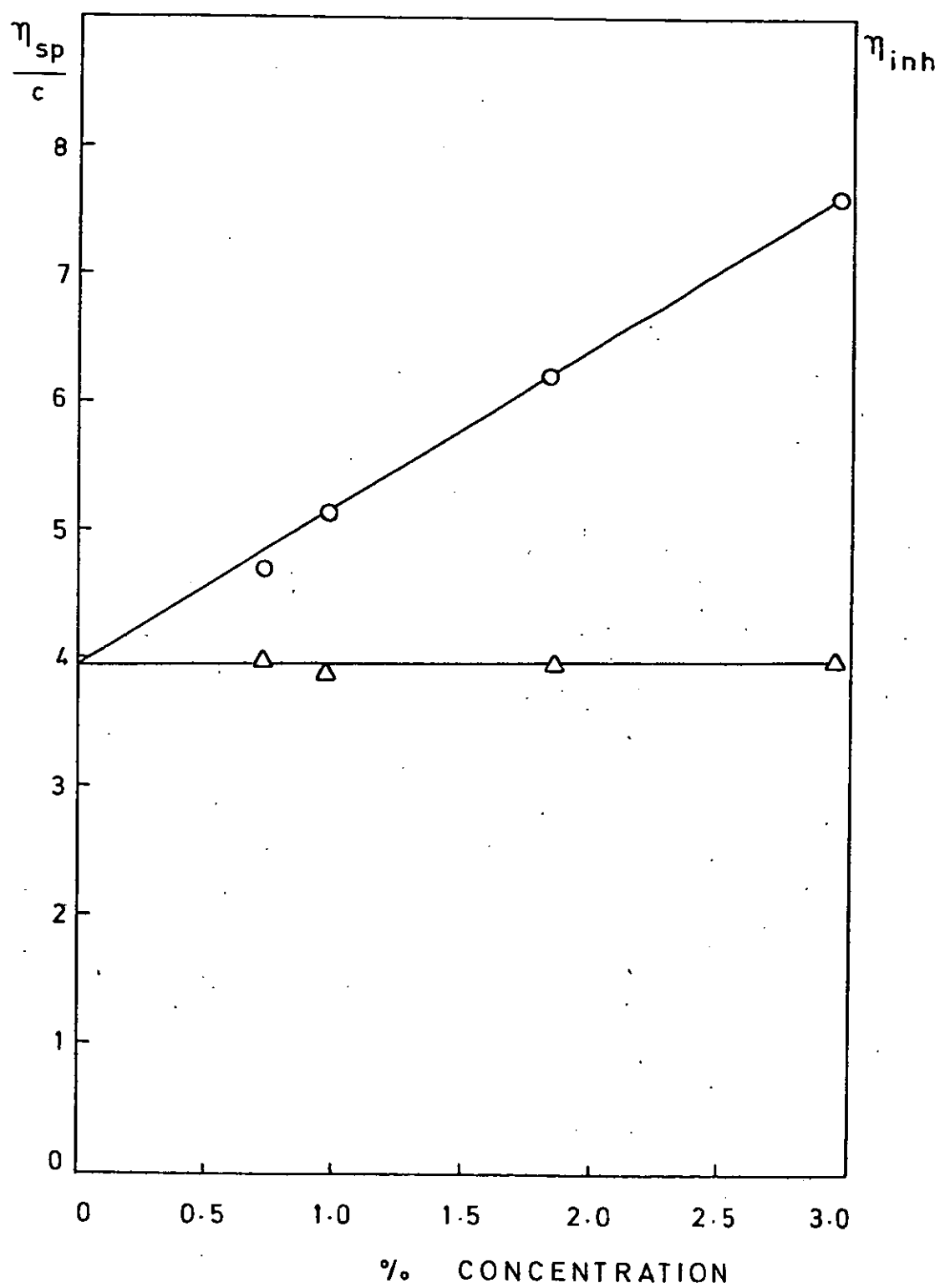
where K and a are constants for a particular polymer and solvent.

2.2.1 Interpretation in Terms of Polymer Conformation

The dimensions of a linear chain molecule are usually expressed in terms of the end-to-end distance r . For a given structure of the basic chain, the mean square value of r is determined by the nature of hindrance to internal rotation and by Van der Waals or other types of interactions

FIGURE 2.2

SOLUTION VISCOSITY OF PA53 IN WATER



between non-bonded groups which are separated in the basic structure by many valence bonds. This latter interaction is called long-range interaction, while the hindrance to internal rotation is called the short-range interaction (22). If the interactions are absent, then the so-called "freely rotating chain" is obtained. Its dimensions can be easily estimated from the data of the given bond lengths and bond angles.

A freely jointed chain is defined as a polymer not affected by short-range or long-range interactions and having all possible values for the valence angle between main chain bonds. The mean-square end-to-end distance, $\langle r^2 \rangle_f$ for such a linear chain is given by (22).

$$\langle r^2 \rangle_f = x l^2 \quad (2.45)$$

where x is the number of bonds each having a length l . If the valence bond angle is fixed but the linear chain is still unaffected by both types of interaction, the mean-square end-to-end distance is given by

$$\langle r^2 \rangle_{of} = 2x l^2 \quad (2.46)$$

when the main chain backbone is composed of carbon atoms. The subscript f indicates free rotation about main chain bonds. For one polymer chain many different conformations are possible, which explains why average dimensions must be considered. The mean values in equation (2.46) may be calculated from a normal or Gaussian probability function.

Short-range interactions lead to restricted rotation about main chain carbon-carbon bonds, so that end-to-end distances larger than the values calculated with equation (2.46) are preferred. A chain with fixed valence bond angle and restricted rotation is known as an unperturbed chain with mean-square end-to-end distance $\langle r^2 \rangle_o$. According to Flory (22), the unperturbed dimensions are given by

$$\langle r^2 \rangle_o = C x l^2 \quad (2.47)$$

in which C is known as the characteristic ratio. Values for C may be compared for various polymers; for example, C is 2×7.29 for polyacrylamide, 2×5 for polystyrene, and 2×3.35 for polyethylene (22). Therefore, the short-range interactions increase the end-to-end distance for polyacrylamide compared with polystyrene which in turn is more extended than polyethylene. The value of x is proportional to molecular weight M , so that it follows from equation (2.47) that $\langle r^2 \rangle_0 / M$ is a constant independent of molecular weight for a given polymer. Values of $\langle r^2 \rangle_0$ and $\langle r^2 \rangle_0 / M$ may be determined from measurements of solution properties with theta solvents, defined as solvents in which the polymer chain has dimensions unaffected by long-range interactions.

The influence of long-range interactions is to expand the chain because two segments of the chain separated by many main-chain bonds cannot occupy the same volume in space. This excluded volume effect is molecular weight and solvent dependent. The influence of long-range interactions on polymer dimensions is simply represented by

$$r^2 = \alpha^2 \langle r^2 \rangle_0 \quad (2.48)$$

where α is the linear expansion factor which is greater than unity for the excluded volume effect in good solvents and is exactly unity for theta solvents.

The chemical interpretation of viscosity measurements is due to Einstein who considered the behaviour of solid spheres. The intrinsic viscosity can be related to the density of the sphere ρ_2 by the equation

$$[\eta] = 2.5 / \rho_2 \quad (2.49)$$

This equation (2.50) may be expressed in terms of the volume of the solid sphere, giving

$$[\eta] = \frac{10 \pi N R^3}{3M} \quad (2.50)$$

where N is Avogadro's number, K is molecular weight and R is the radius of the solid sphere. Flory (22) in his theory of the frictional properties of polymer molecules suggested that the form of equation (2.50) should still apply, so the intrinsic viscosity should be proportional to the effective hydrodynamic volume of the polymer molecule in solution. If it is assumed that the hydrodynamic radius is directly proportional to the root-mean-square end-to-end distance of the polymer chain, then equation (2.50) according to Flory becomes

$$[\eta] = \Phi \langle r^2 \rangle^{3/2} / M \quad (2.51)$$

in which Φ is a universal constant. Substitution of equation (2.48) into equation (2.51) and rearrangement gives

$$[\eta] = \Phi \left[\frac{\langle r^2 \rangle_0}{M} \right]^{3/2} \alpha^3 M^{1/2} \quad (2.52)$$

where $\Phi \langle r^2 \rangle_0 / M^{3/2}$ is a constant. For a theta solvent α is unity so equation (2.52) becomes

$$[\eta] = K_{\theta} M^{0.5} \quad (2.53)$$

This equation may be compared with equation (2.44). Clearly, a is 0.5 for theta solvents, but may be as high as 0.8 for good solvents because of the dependence of α on molecular weight.

2.2.2 Viscosity of Polyacrylamide

Polyacrylamide is non-ionic and is completely soluble in water. The solubility is not greatly influenced by temperature and appears to be limited at any temperature only by the high viscosity of the solution as the concentration increases (111). Consequently water has been a popular solvent for studies of the solution properties of polyacrylamide. Collinson and co-workers (80) suggested the following relation

$$[\eta] = 68 \times 10^{-5} M^{0.66} \quad (2.54)$$

for fractions of polyacrylamide in water.

Kotera et al. (112) performed capillary viscometry work on commercial samples of polyacrylamides of molecular weights 300×10^4 , 30×10^4 and 12×10^4 , using formamide as the solvent. They found no degradation in molecular weight with time at operating temperatures of 30°C and 60°C . On plotting $\log [\eta]$ vs. \bar{M}_w , they found that the K value was 1.08×10^{-3} and the a value was 0.54.

$$[\eta] = 1.08 \times 10^{-3} M^{0.54} \quad (2.55)$$

These results suggest that polyacrylamide in formamide is close to the theta state, so that the polymer chains have a similar conformation to the unperturbed state. From equation (2.54) water is a "good" solvent for polyacrylamide so that the chains are more expanded in water than in formamide.

Kotera compared his results with polyacrylamide in aqueous electrolyte solutions. Krotkina et al. (113) measured the intrinsic viscosity of polyacrylamide in 10% aqueous sodium chloride. Kurata and Stockmayer (114) reported measurements with 1N sodium nitrate. Significant differences between the K and a parameters were obtained, as outlined in reference (113).

Sheats and Linke (115) observed that their aqueous solutions of polyacrylamide of molecular weight two million and more were degraded on standing at room temperature. They showed that adding up to 10% of non-solvent (e.g. glycols and alcohols) helped in stabilising polyacrylamide solutions from degradation. Narkis and Rebhun (115) showed that a decrease in intrinsic viscosity occurred in polyacrylamide solutions on standing. However, on re-precipitating the polymer from solution the initial intrinsic viscosity was obtained. They concluded that a decrease in viscosity of a polymer solution on standing does not necessarily indicate degradation. It is likely that the long extended polyacrylamide molecules are difficult to

disentangle during dissolution. They suggested that at least fifteen days were needed for a polyacrylamide solution to reach constant intrinsic viscosity values. Patat et al. (117) suggested that anomalous behaviour of intrinsic viscosity measurements using a capillary viscometer was due to polymer adsorption into the walls of the viscometer. Chinai and Schneider (118) suggested that the concentration of the dissolved polymer is an important factor since chain entanglements are a function of the size and number of molecules in solution. Silberberg et al. (19) on evaporating solutions of polyacrylamide to dryness over phosphorous pentoxide obtained values of 8 to 10% higher than the initial value. They attributed this to water being very strongly held to the chain. They also obtained negative slopes of the plots η_{sp}/c vs. c and postulated that aggregates of the polymer were formed which were more compact or more spherical than the individual molecule. They also showed that the viscosity increases appreciably as the rate of shear was lowered. In conclusion, they suggested that the addition of neutral salt up to 0.1 Molar had no influence on the viscosity of aqueous polyacrylamide solutions.

Nagashiro and Tsunoda (119) showed that aggregate formation during solution preparation could be minimised by stirring. However, the stirring rate should not be too high otherwise scission of the high molecular weight polyacrylamide will occur. At a stirring speed ~ 7000 r.p.m. degradation of polyacrylamide took place. After a certain length of time the molecular weight remained constant. When the solvent of the stirred solution was evaporated and the polymer was dissolved in the same type of solvent, the viscosity of the solution was found to be equal to that of the initial stirred solution and not to the original solution before high speed stirring. This suggested that the decreased viscosities due to high speed stirring were irreversible which resulted from chain scission. Abdel Alim and Hamielec (17) performed similar experiments with a high-shear couette viscometer, identifying a loss in viscosity because of degradation. All

these problems were considered in preparing solutions and in performing measurements of solution viscosity.

2.3 Membrane Osmometry

Two components of closely similar shape, size and chemical nature when mixed may form an ideal solution which obeys Raoult's law:

$$p_1 = p_1^{\circ} x_1 \quad (2.56)$$

where p_1 and p_1° are the partial pressures of solvent vapour in equilibrium with the solution and the pure solvent respectively and x_1 is the mole fraction of this component in the solution given by

$$x_1 = \frac{n_1}{n_1 + n_2} \quad (2.57)$$

where n_1 is the number of molecules of solvent and n_2 is the number of molecules of solute.

The total free energy of mixing ΔG for solvent (1) and solute (2) is given by

$$\Delta G = -kT (n_1 \ln x_1 + n_2 \ln x_2) \quad (2.58)$$

where k is Boltzmann's constant and T is the temperature ($^{\circ}$ Absolute). For an ideal solution the enthalpy of mixing ΔH is zero and the entropy of mixing is therefore given by

$$\Delta S = -k (n_1 \ln x_1 + n_2 \ln x_2) \quad (2.59)$$

Since ΔS is positive and since ΔH is zero, it means that the molecules of both components may replace one another indiscriminately.

The relative lowering of vapour pressure of the solvent due to the addition of non-volatile solute depends on the mole fraction of the solute, i.e. the number of molecules present. Vapour pressure lowering is a

colligative property from which the average molecular weight obtained for a poly-disperse polymer is the number average molecular weight (\bar{M}_n). Other colligative properties for determining \bar{M}_n are boiling point elevation (ebulliometry), depression of freezing point and osmotic pressure.

The first two techniques are used for low molecular weight polymers with molecular weights below 10,000. Vapour pressure osmometry is applicable to the same low molecular weight range. However, membrane osmometry is applicable to polymers in the molecular weight range 20,000 \rightarrow 500,000. Polymers of molecular weights lower than 20,000 may have a tendency to diffuse through the membrane.

The polymer solution is separated from the pure solvent by a membrane, permeable to solvent molecules only. Initially, the chemical potential μ_1 of the solvent in the solution is lower than that of the pure solvent μ_1^0 . Solvent molecules tend to pass through the membrane into the solution in order to attain equilibrium. This causes a build-up of pressure in the solution compartment, until at equilibrium, the pressure exactly counteracts the tendency for further solvent flow. This pressure is the osmotic pressure.

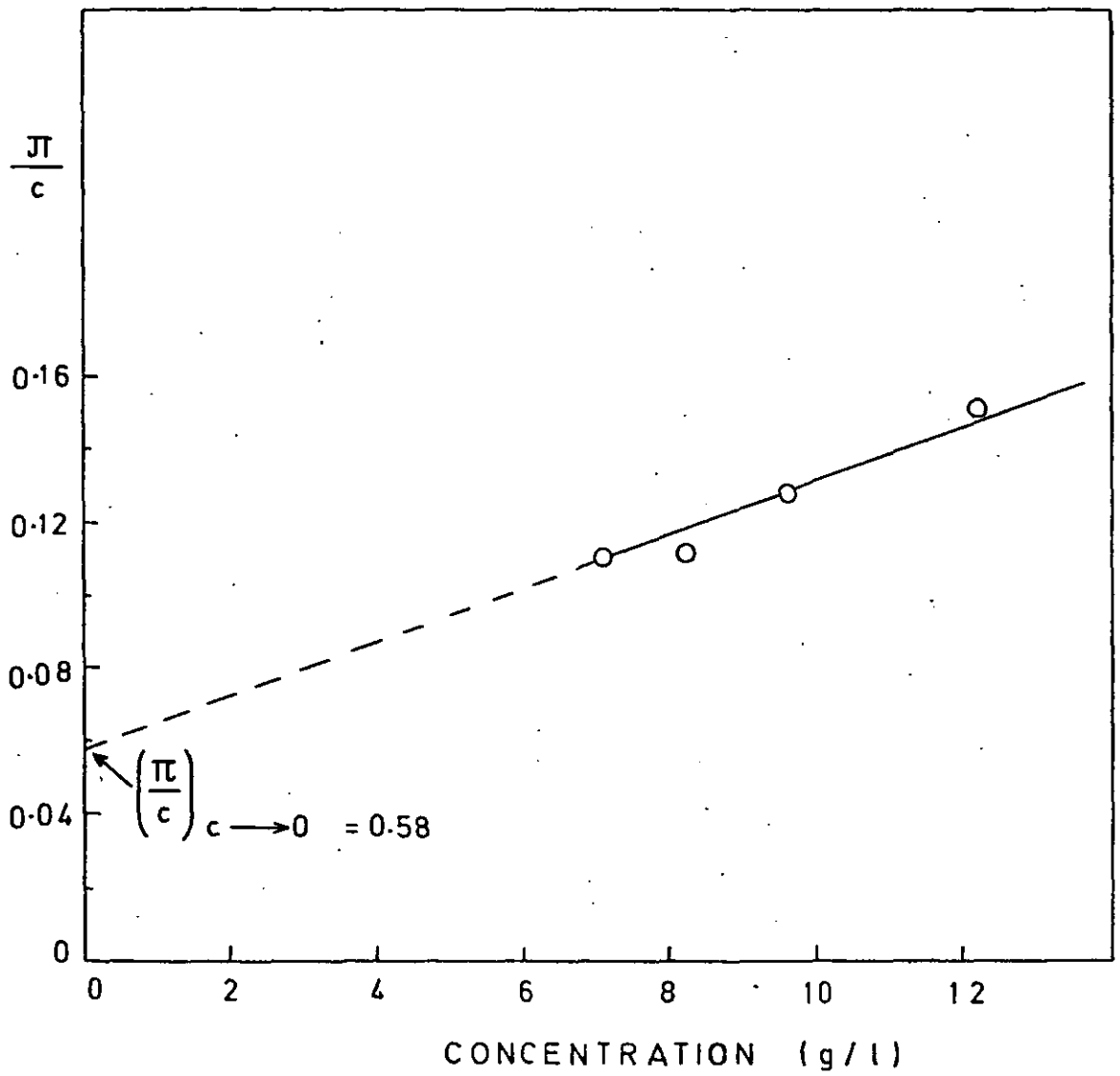
The correct value of temperature is the membrane temperature in degrees Kelvin. The gas constant R has the value of 0.08208 litre-atmosphere/degree mole. Because the 502 membrane osmometer reads in centimetres of solvent as a pressure unit rather than atmospheres, the appropriate value of R is then calculated, multiplying by the height in centimetres of a column of liquid corresponding to a pressure of one atmosphere. (1 atmosphere = 1033 cm of water where density of water = 1 g/cc.) In the new parameters for R and corrected for the density of liquid, d

$$R = \frac{0.08208 \times 1033}{d} \quad (2.60)$$

where d is the solvent density in gm/cc.

FIGURE 2.3

MEMBRANE OSMOMETRY ON PA 43 IN FORMAMIDE/WATER (1:3)



The free energy change $\Delta \bar{G}_1$ of a solvent added to a solution is given by

$$\Delta \bar{G}_1 = RT \ln a_1 \quad (2.61)$$

where R is a gas constant, T is the absolute temperature and a_1 is the activity of the solvent. The free energy change $\Delta \bar{G}_1$ is related to osmotic pressure by

$$-\Delta \bar{G}_1 = \pi V_1 \quad (2.62)$$

Therefore

$$-\ln a_1 = \pi V_1 / RT \quad (2.63)$$

If the solution is sufficiently dilute, a_1 is identical with x_1 , and since x_1 is very near to unity, then

$$-\ln a_1 \cong -\ln x_1 \cong 1 - x_1 \cong x_2 \quad (2.64)$$

where x_2 is moles of solute, V_1 is the volume of solvent and x_1 is the mole fraction of solvent.

$$\frac{\pi}{RT} = \frac{x_2}{V_1} = \frac{n_2}{n_1 V_1} \quad (2.65)$$

Now

$$n_2 = \frac{w_2}{M_2} \quad \text{and} \quad n_1 V_1 = \frac{w_1}{m_1} \frac{M_1}{\rho_1} = V \quad (2.66)$$

$$\therefore \frac{\pi}{RT} = \frac{w_2}{V} \cdot \frac{1}{M_2} = \frac{c_2}{M_2} \quad (2.67)$$

$$\therefore \frac{\pi}{c_2} = \frac{RT}{M_2} \quad (2.68)$$

For an ideal solution M_2 for the solute is evaluated from equation (2.69) in which c_2 is the concentration of solute.

Polymer solutions generally exhibit deviations from ideal behaviour because of a large difference in size between the polymer and solvent. It is found that Π/c_2 in equation (2.69) is concentration dependent and may be expressed in the form of a virial equation.

$$\Pi/c_2 = RT \left(\frac{1}{\bar{M}_n} + A_2 c + A_3 c^2 + \dots \right) \quad (2.69)$$

where A_2 and A_3 are the second and third virial coefficients. The values of A_2 and A_3 depend on polymer/solvent interactions. Generally A_3 will be zero when a plot of Π/c_2 vs. c_2 may be extrapolated as a straight line to zero concentration. An example for polyacrylamide is shown in Figure 2.3, so for polymer solutions the following relation holds

$$(\Pi/c_2)_{c_2 \rightarrow 0} = \frac{RT}{\bar{M}_n} \quad (2.70)$$

The slope from the plot of Figure 2.3 gives a value of A_2 which will be positive for non-ideal solutions and zero for an ideal solution.

It is possible that A_3 will be non-zero in which case the plot of Π/c_2 vs. c_2 will not be a straight line. Curvature of the plot causes uncertainty in extrapolation to zero concentration. Then the square root plot of $(\Pi/c_2)^{1/2}$ vs. c_2 may produce a straight line suitable for extrapolation (110).

2.4 Gel Permeation Chromatography

The molecular weight distribution (MWD) is the most important property of a polymer since it affects solution properties, melt flow characteristics and mechanical properties. In recent years, the most popular technique for analytical fractionation has been gel permeation chromatography (GPC).

The molecular weight distribution obtained from GPC can show subtle differences between polymers, see Figure 2.4.

For example, two samples of a polymer having the same average molecular

FIGURE 2.4

CHROMATOGRAMS HAVING SAME AVERAGE MOLECULAR WEIGHT
BUT DIFFERENT MOLECULAR WEIGHT DISTRIBUTION

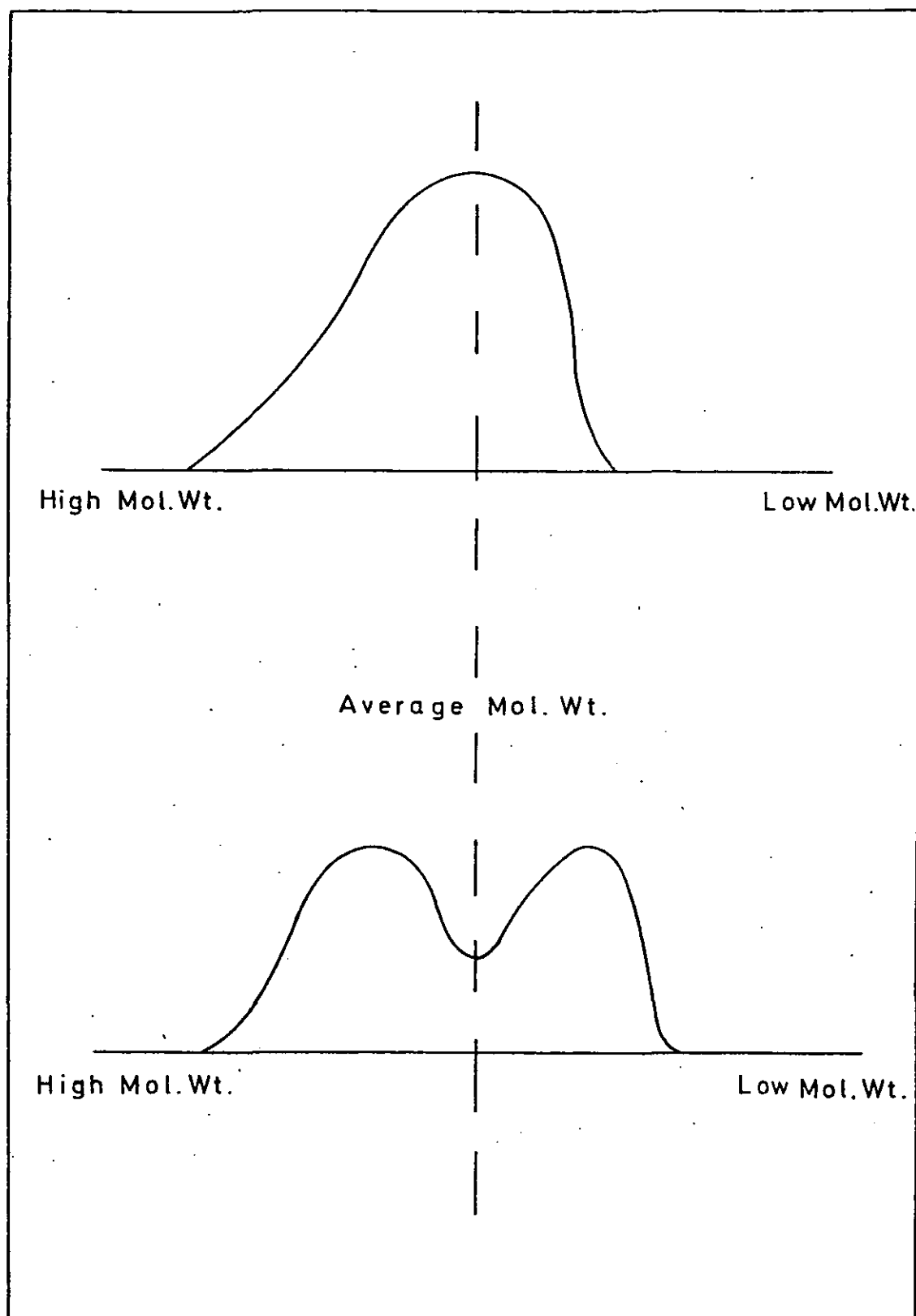


FIGURE 2.5

CHROMATOGRAMS OF TWO DIFFERENT POLYMERS

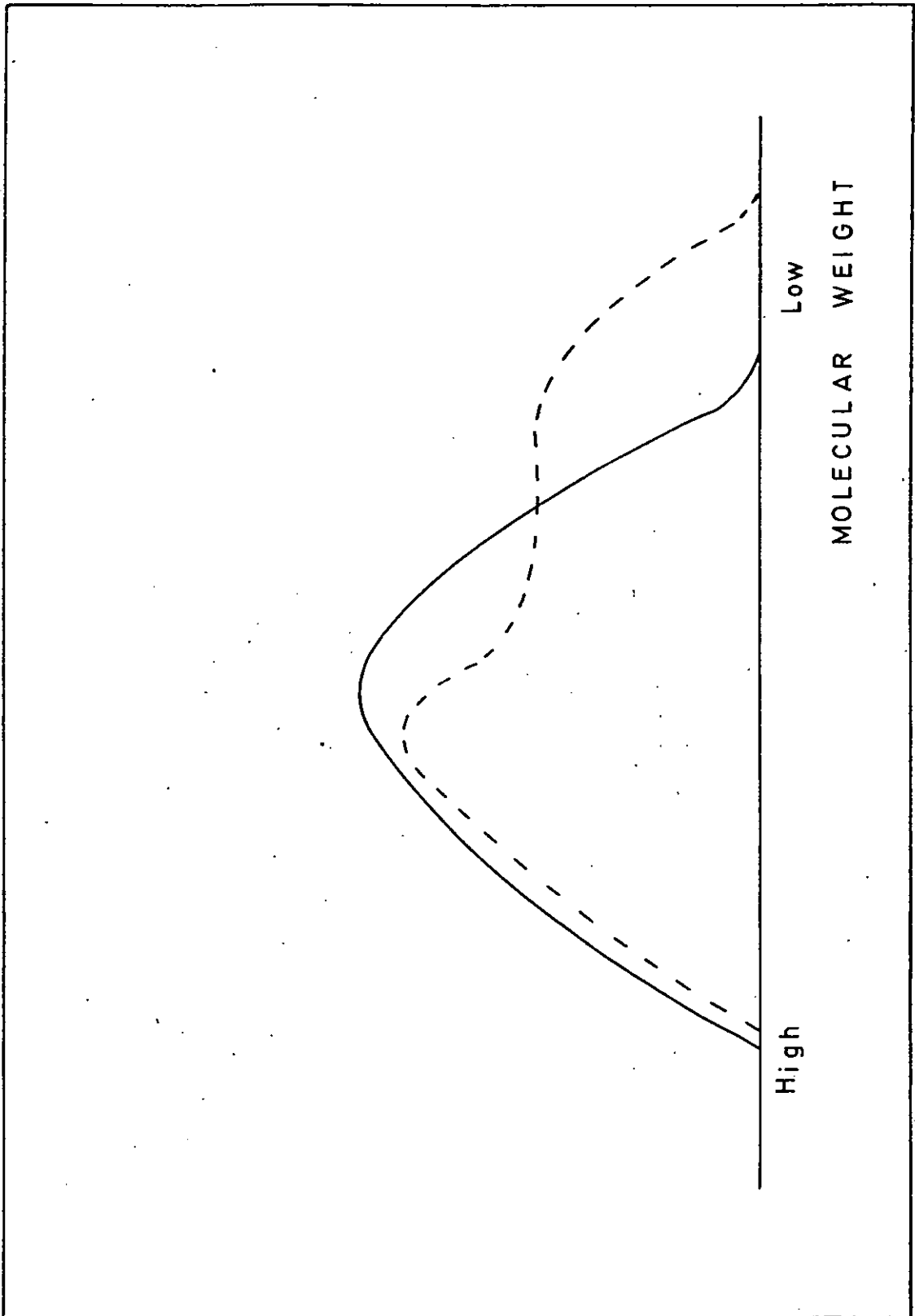
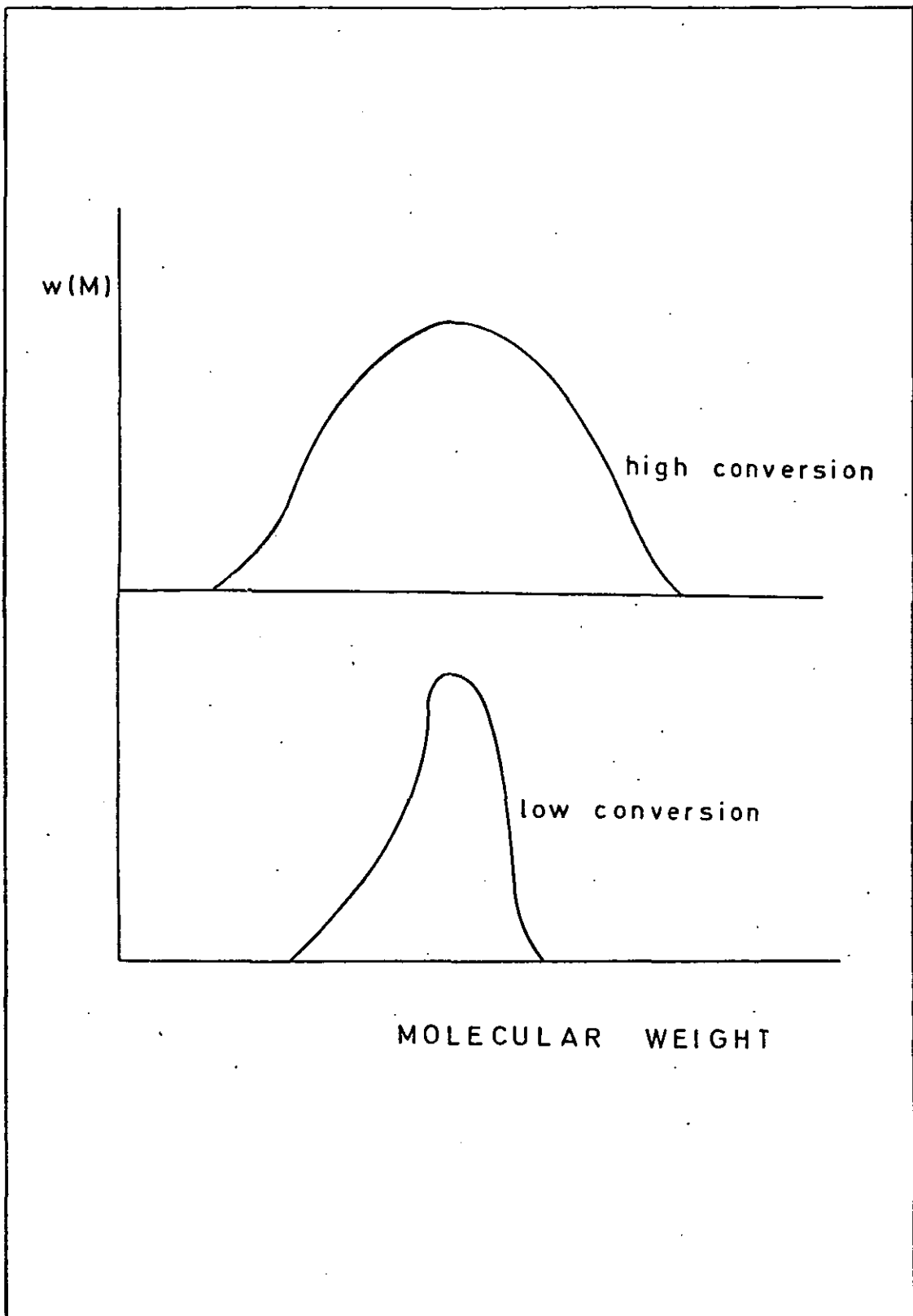


FIGURE 2.6

CHROMATOGRAMS OF A HIGH AND LOW CONVERSION POLYMERS



weight but different molecular weight distributions can have different tensile strengths and melt viscosities, see Figure 2.5.

In order to interpret these chromatograms a calibration curve obtained from narrow molecular weight distribution standards is needed. Consequently low conversion polymers would yield narrow molecular weight distribution as opposed to high conversion polymers yielding broad molecular weight distribution, see Figure 2.6.

2.4.1 Primary Mechanism of Separation

This mechanism of separation is effected by selective permeation of solute sizes in solution through various pores and pore networks of the gel (120-122), see Figures 2.7 and 2.8.

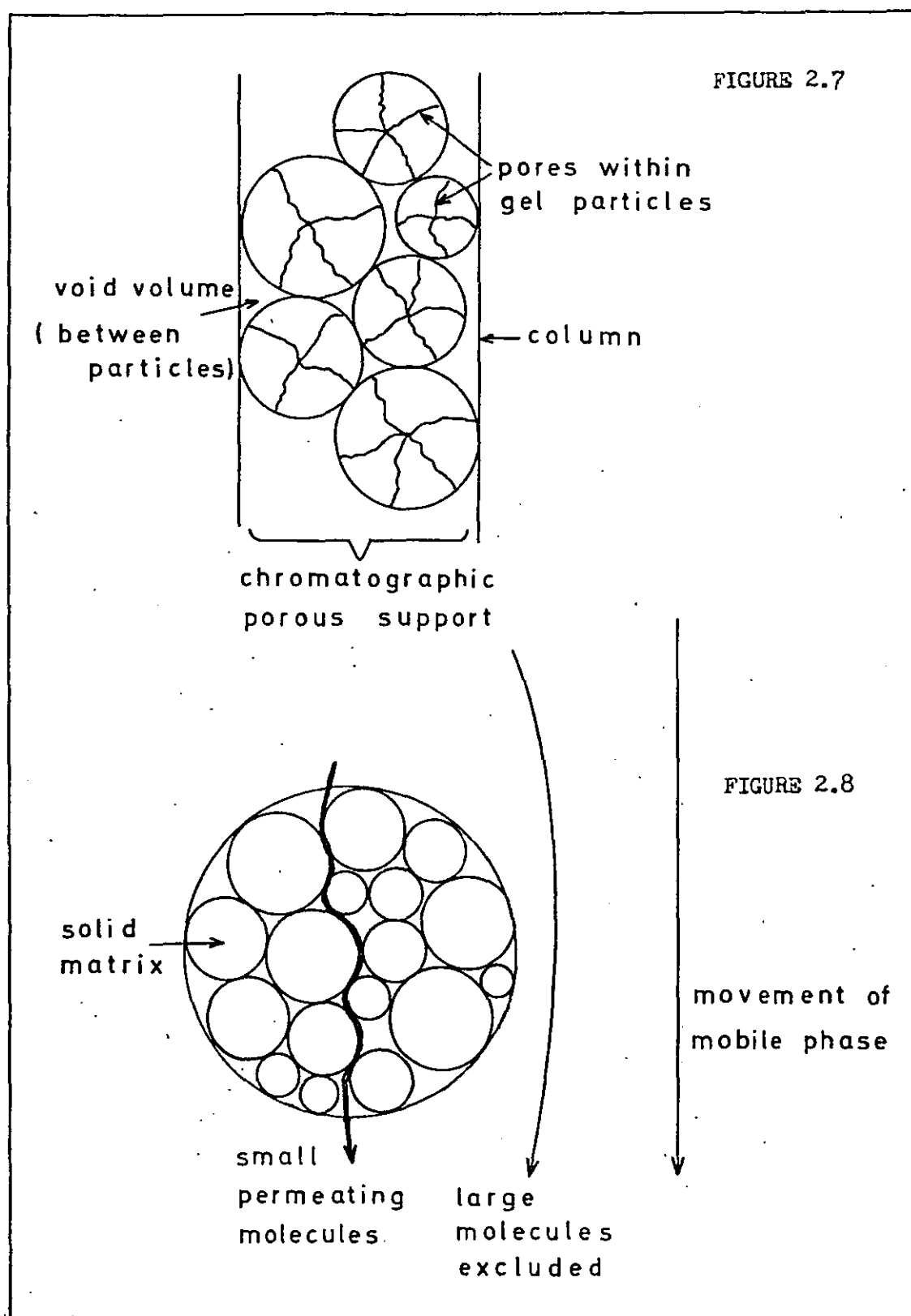
The small molecules can permeate into the pores of the packing (porous chromatographic support), whereas the large molecules cannot enter the pores and consequently are confined to the void volume of the gel. Intermediate sized molecules can permeate some passages in the particles but not others (123). This separation depends on the pore size distribution of the gel and the solvent used.

Therefore, molecules of different sizes injected at the same time travel different distances down the column. The small molecules travel longer distances through the tortuous paths within the gel thus resulting in a larger retention volume. Large molecules flow shorter distances between the particles and consequently have smaller retention volumes. For clarity the void volume of the gel will be denoted by V_o and the pore volume of the gel V_p . Large molecules elute at the void volume V_o and totally permeating molecules elute at $V_o + V_p$. Intermediate molecules elute between V_o and $V_o + V_p$ as shown in Figure 2.9.

The fundamental retention equation for any chromatographic process is,

$$V_e = V_o + K_d V_p \quad (2.71)$$

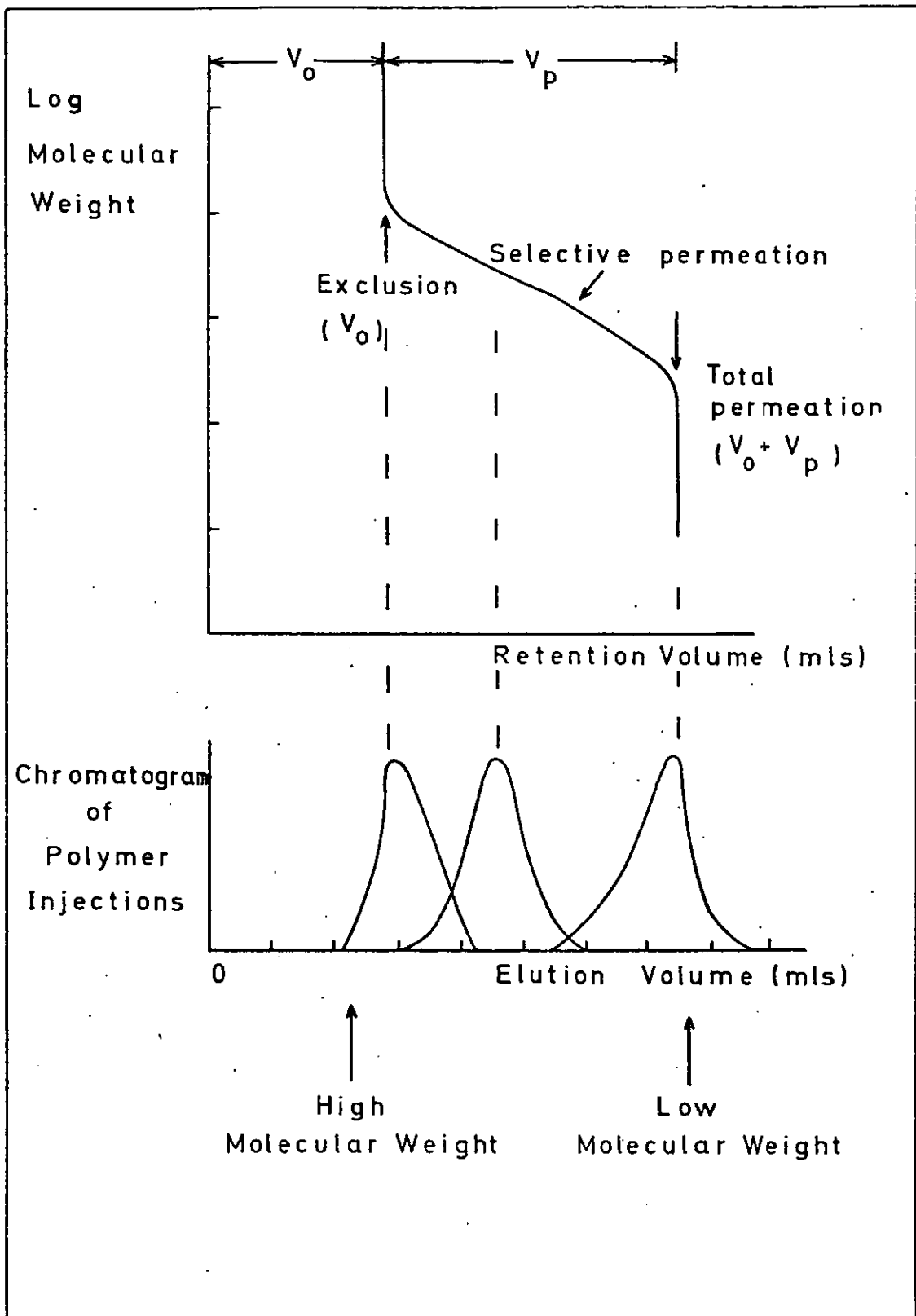
SCHEMATIC DIAGRAM SHOWING PACKING OF PARTICLES IN COLUMN



SCHEMATIC REPRESENTATION OF FLOW PATH OF MOBILE PHASE AND SOLUTE

FIGURE 2.9

CALIBRATION CURVE FROM POLYMER CHROMATOGRAMS



where V_e is the elution volume of a component, V_o is the column void volume, V_p is the column pore volume (i.e. volume of stationary phase), and K_d is the equilibrium distribution coefficient, where $K = 0$ at V_o and $K = 1$ at $V_o + V_p$.

The object of gel permeation chromatography is to separate, which is measured in terms of resolution (124-126).

$$R_s = \frac{1}{4} [(\alpha - 1) / \alpha] (N_{\text{eff}})^{\frac{1}{2}} \quad (2.72)$$

$$N_{\text{eff}} = 16 [(V_2 - V_o) / W_2]^2 \quad (2.73)$$

where

$$\alpha = (V_2 - V_o) / (V_1 - V_o) \quad (2.74)$$

where R_s is the resolution, N_{eff} is the effective number of plates, V_o is the column void volume, V_1 is the elution volume of component 1, V_2 is the elution volume of component 2 and W is the width of peak (in volume). In this equation (2.72) α is the ratio of the elution volumes of two components. To increase the resolution of separation the V_p term in equation (2.71) should be large. Another way of increasing resolution is to increase the effective number of plates (N_{eff}) in equation (2.73). This is a measure of column efficiency and is affected by parameters such as particle size, shape of packing, inside diameter of column, linear velocity of solvent and packing procedure of column. Since V_p is the value which dictates how much of the column is available for separating, the expression V_p/V_o is a measure of the maximum capacity of the column expressed in terms of the void volume. Therefore the higher the value of V_p/V_o up to the point where the physical characteristics of the packing is accepted, the better is the separating capability. Packings which have a wide distribution of pore sizes will have wide usable ranges, but as the range increases, the separating power within that range decreases proportionally. Thus, packings which are not effective

in the range of interest would decrease the overall resolution that is obtained. As the sample traverses an extra irrelevant column, the separated peaks will undergo spreading and destroy the previously attained resolution.

2.4.2 Secondary Mechanism of Separation

In the primary mechanism separation was performed by an exclusion mechanism where no interaction between polymer and support occurred. Hydrodynamic volume was the size parameter upon which the steric exclusion mechanism was based. Dawkins and Hemming suggested the equation (127-130)

$$K_d = -A \log [\eta] M + B \quad (2.75)$$

where A and B are constants and $[\eta] M$ is the hydrodynamic volume according to equation (2.75).

Dawkins and Hemming (127-130) showed that under certain circumstances secondary mechanisms such as adsorption and partition can occur. For particular polymer-solvent systems, if the value of a in the Mark-Houwink equation (2.44) falls below 0.65, i.e. the solvent is either a poor or a theta solvent, then solute-gel interactions give rise to a partition mechanism (where solutes have a different solubility in the mobile phase compared to the stationary phase) or an adsorption mechanism (when the stationary phase is regarded as the surface area within the gel pores). The retention volume of a solute can be represented by the equation

$$V_R = V_o + K_d K_p V_p \quad (2.76)$$

where K_p is the distribution coefficient for solute-gel interaction effects which are assumed independent of molecular weight. When a good solvent for a polymer is used ($a \geq 0.65$), then $K_p = 1$, but for poor or theta solvents K_p is greater than 1 (131). Dawkins (132) reviewed the dependence of the adsorption/partition effects with polystyrene gels on the enthalpy change on solute transfer to the organic gel. For example, polyvinylpyridine is

irreversibly adsorbed on polystyrene gel with chloroform but separates according to steric exclusion with N,N-dimethylacetamide. However, some solute-gel interactions still occur with some polar polymers, e.g. in dimethylformamide (133). With inorganic packings, polystyrene was separated by Moore and Arrington (131) using a binary theta solvent mixture of butanone and iso-propanol. No solute-gel interaction took place because iso-propanol was preferentially adsorbed onto the surface of the silica. On the other hand, polystyrene in benzene will separate by steric exclusion and solute-gel interactions, because solute and eluent have similar affinity for the surface sites. Dawkins (134) stated that studies of polymer adsorption from solution onto non-porous adsorbents also suggest that, if preferential solvent-adsorbent interactions are absent, then the extent of adsorption increases as polymer-solvent interaction decreases. In aqueous GPC using porous silica as support, polyanions in the presence of a simple salt separated by a mechanism dominated by steric exclusion (135). However, all polycations and many polyampholytes and non-ionic polymers were irreversibly bound to the silica support. Dubin (133) suggested that polar organic eluents appear most attractive for these applications on silica supports rather than sulphonating polystyrene gels which is quite tedious and time consuming for use with aqueous systems. From these observations, it is likely that a polar polymer such as polyacrylamide in water is likely to show solute-gel interaction effects with silica packings.

2.4.3 Calibration

Analytical GPC is not an absolute technique for measuring the molecular weights of polymers or polymer fractions. Consequently, a calibration curve is necessary in order to determine the molecular weight of an unknown polymer sample. Calibration curves are obtained from the injection of polymer standards of narrow molecular weight distribution normally obtained from fractionation using a suitable technique (136). Narrow molecular

weight distribution polystyrenes are commercially available (137). The logarithm of the peak molecular weight of each fraction versus their respective elution volumes give a plot as shown in Figure 2.9. This plot is satisfactory for determining the molecular weights of further polystyrenes (123). At present there are no suitable aqueous GPC polymer standards commercially available.

Benoit et al. (138) proposed a universal calibration procedure based upon the hydrodynamic volume $[\eta]M$, see equation (2.77), of a polymer molecule in solution, so that the plot of $\log [\eta]M$ versus elution volume will be the same for all polymers, i.e.

$$\log [\eta]_p M_p = \log [\eta]_{ps} M_{ps} \quad (2.77)$$

where p denotes the unknown polymer and ps denotes polystyrene.

Coll (139) suggested that $[\eta]M$ can be used as a universal calibration parameter for linear, flexible molecules and probably also for star-branched molecules (140). This has been confirmed for many linear polymers (138, 139, 141). Dawkins (142, 143) produced a universal calibration using the end-to-end distance of a molecule, a term related to hydrodynamic volume, equations (2.77) and (2.52). His universal calibration equation is

$$\frac{M_p}{M_{ps}} = \left[\frac{\bar{r}_o^2}{M} \right]_{ps} \left[\frac{M}{\bar{r}_o^2} \right]_p \left[\frac{\alpha_{ps}}{\alpha_p} \right]^2 \quad (2.78)$$

Generally α_{ps}/α_p is close to unity, so M_p may be calculated from M_{ps} with the constants on the right hand side of equation (2.78).

It is possible to use equations (2.77) and (2.78) to find a molecular weight calibration for polyacrylamide. The $[\eta]_{ps} M_{ps}$ curve could be established with polystyrene standards in tetrahydrofuran. These values could be used to find M_p for polyacrylamide in water provided the dependence of $[\eta]_p$ on M_p had been determined. This procedure assumes that the pore

size and pore size distribution do not change on changing from tetrahydrofuran to water and that solute-gel interactions do not occur. Although the former assumption holds for silica packings, the latter is not valid for polyacrylamide. Consequently, it is preferable to calibrate directly with narrow molecular weight distribution standards of polyacrylamide.

In this research, polyacrylamide fractions have been prepared by fractional precipitation. If these same fractions have a narrow molecular weight distribution, then any average molecular weight may be used in plotting a GPC calibration curve, since

$$\bar{M}_v \cong \bar{M}_n \cong \bar{M}_w \cong M_{\text{peak}} \quad (2.79)$$

where M_{peak} is the molecular weight at the peak of the chromatogram. Errors may arise for broad molecular weight distribution fractions when plotting GPC calibration curves because M_{peak} may not be identical to any of the experimental average molecular weights. Dawkins et al. (144) observed that fractions obtained by fractional precipitation of PDMS (polydimethyl siloxane) did not obey equation (2.79) and that on the basis of a logarithmic normal function the value of \bar{M}_v was close to M_{peak} . For such a function the average molecular weights are related to M_{peak} by Dawkins (145)

$$\bar{M}_n = M_{\text{peak}} e^{-\beta^{2/4}} \quad (2.80)$$

$$\bar{M}_v = M_{\text{peak}} e^{a\beta^{2/4}} \quad (2.81)$$

$$\bar{M}_w = M_{\text{peak}} e^{\beta^{2/4}} \quad (2.82)$$

where β is a parameter related to the breadth of the molecular weight distribution and a is the exponent in the Mark-Houwink dilute solution viscosity equation, see equation (2.44). Consequently it was decided to assume that \bar{M}_v was close to M_{peak} for the polyacrylamide fractions.

2.4.4 Chromatogram Broadening

A low molecular weight compound when injected into a GPC instrument gives a broadened Gaussian peak rather than a narrow rectangular peak. Snyder and Kirkland (146) have reviewed the theory of broadening which depends on three major factors

- (i) Flow path irregularities between the particles in the column.
- (ii) Axial diffusion of solutes in the mobile phase.
- (iii) Mass transfer of solutes between the mobile phase and the particles.

The equation of Van Deemter, Klinkenberg and Zuiderweg (147) was derived showing the dependence of the height equivalent to a theoretical plate H on the three mechanisms (i), (ii) and (iii). Their expression may be written in the form

$$H = A + (B / u) + Cu \quad (2.83)$$

where u is the mean linear velocity of the mobile phase and the constants A , B and C refer to mechanisms (i), (ii) and (iii) respectively. The value of H is also given by

$$H = L / N \quad (2.84)$$

in which L is the length of the column and N is the number of theoretical plates which is determined experimentally from

$$N = \left(\frac{4V_e}{w} \right)^2 \quad (2.85)$$

where w is the width of the chromatogram at the baseline.

Flow paths through the column should be as similar as possible, necessitating spherical particles of the same size packed into a uniform array. Ideally, the particles should be packed in a hexagonal array. If packing irregularities are reduced H should be minimised. In the Van Deemter equation the flow path irregularity term does not depend on u .

Axial diffusion is due to the random motion at the molecular level. Because of this motion the individual molecule may lead or lag behind the mean position by an amount which increased with time in the column. Thus, the faster the mobile phase velocity the shorter the time available for molecules to diffuse away from the mean position and hence the inverse relationship between H and u . The interphase mass transfer contribution to H arises because the transfer of the solute molecule to the stationary phase abruptly brings the progress of the molecule to a halt. Whilst held in the gel the molecule lags further behind the other molecules which are in the mobile phase. The faster the mobile phase is moving, the greater the gap between these molecules leading to an increase in band broadening. Hence, there is a direct relationship between H and u .

The Van Deemter equation (147) in its full form is

$$H = 2\lambda d_p + \frac{2VD_m}{u} + \frac{8}{\pi^2} \frac{K'}{(1+K')^2} \cdot \frac{d_f^2}{D_s} \cdot u \quad (2.86)$$

where λ , V are parameters relating to packing irregularities and varying path lengths, d_p is the mean particle diameter of the packing, D_m , D_s are molecular diffusion coefficients of the solute in the mobile and stationary phases respectively, u is the mean mobile phase velocity, K' is the retention coefficient of a particular solute, and d_f is the thickness or depth of stationary phase which approximates to d_p , the particle diameter of the packing. It follows from equation (2.86) that an increase in column efficiency will result if the diameter of the particles is decreased, provided that the other parameters are held constant. Flow paths through the column should be as similar as possible, necessitating regular particles with a narrow size distribution which may be packed in a uniform array by a suitable method. It is also clear from equation (2.86) that column efficiency will decrease at high flow rates and for very high molecular weight polymers with low diffusion coefficients. Further, the design of the instrumentation is also important for high column efficiencies. Narrow

columns should be avoided because of wall effects and the injector should not contain large pockets of dead volume.

2.4.5 Silica Supports

In Chapter 1 the support suggested for the separation of polyacrylamide was a silica aerogel as opposed to xerogels. There is a wide variety of silica supports commercially available, some of which have been described by Dark and Limpert (148). Janak et al. (149) made a complete study of all possible supports. Heitz et al. (150) looked at silica packings with large pore sizes. Holdoway (151) compared the physical properties of both silica and alumina packings that are commercially available. In this research Porasil and Spherisorb (spherical particles) were studied. The behaviour of silicas uncoated and bonded will be discussed generally.

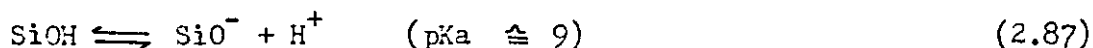
Silica gel is one of the most common gels used as a chromatographic support. It is classified as a polar adsorbent because the polarity is due to the surface hydroxyl groups. The magnitude of the specific surface area is inversely proportional to the adsorbent pore diameter. Adsorbents with a specific surface area greater than $500 \text{ m}^2/\text{gm}$ usually have a mean pore diameter below 100 \AA . For a specific surface area of $30 \text{ m}^2/\text{gm}$ the mean pore diameter is about 400 \AA , and for a silica gel with a specific surface area of $5 \text{ m}^2/\text{gm}$, the mean pore diameter is 2500 \AA . Snyder (152) demonstrated that the formation of hydrogen bonds with surface hydroxyl groups is the mechanism of adsorption that occurs most often on silica gel. Two types of hydroxyl groups may be considered as shown in Figure 2.10

- (i) The free type; this represents an adsorption centre on which adsorption may take place.
- (ii) The reactive type; this refers to association by hydrogen bonding taking place between the hydroxyl groups bound on the surface.

The thermal activation of the adsorbent reflects the differences of

these groups. Above 200°C, physically bound water is completely removed. At a temperature above 400°C a molecule of water may be eliminated from a reactive type to form a siloxane group as shown in Figure 2.10. This group is less active to adsorption than the above two types.

To remedy the problem of adsorption of polar solutes on silica supports a number of techniques have been used. Electrolyte exclusion has been used when a non-electrolyte in water needs to be separated. An electrolyte such as sodium chloride is added to the aqueous eluent to interact with the ionic sites on the silica surface. Then, the non-electrolyte separates by a permeation mechanism with a retention volume between V_o and $V_o + V_p$ (152). Jane (153) referred to silica itself as a cation-ion exchanger where the reaction is



Some authors (154, 155, 156) have discussed the extent to which separations occur by ion-exchange compared to other mechanisms on micro-particulate silica-based materials.

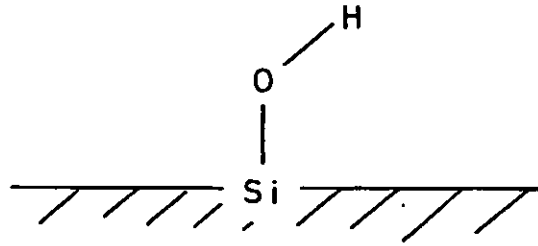
Another technique of removing active sites from the surface is to physically or chemically bond a suitable phase onto the surface of the silica. The concept is that all surface silanols should be reacted to give a mono-molecular layer of the bonded species.

Bristow (152) summarised the complications that become apparent as follows:

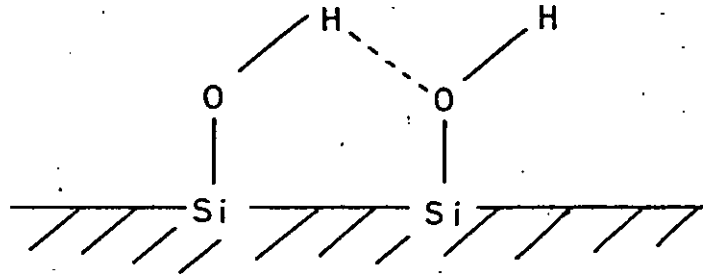
- (i) New silanol groups can be made by hydrolysis of siloxane groups on the surface.
- (ii) Not all silanols will, or can, react, partly for steric reasons.
- (iii) Eluents may remove some bonded groups, for example by hydrolysis.
- (iv) Eluents can dissolve the silica at high pH.
- (v) Reagents may polymerise and produce a thicker coating. This is

FIGURE 2.10
TYPES OF SILICA SURFACES

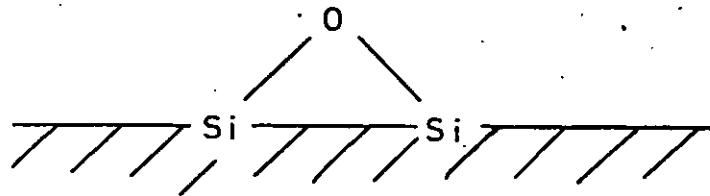
The Free Type



Reactive Type



Siloxane Type



prevalent with di- and tri-chloro silanes which cross-link with any water molecules present.

Hemetsberger et al. (157) and Majors et al. (158) deduced from infra-red spectra that Si-OH groups are still present even after the reaction with long alkyl chloro silanes is complete, and yet these groups cannot react with trimethylchlorosilane (TCMS). Halasz et al. (159) managed to react all these hydroxyls with a C_1 silane, whereas half the hydroxyls were only removed using a C_{18} chain length silane. At the same time long chain lengths were reported to be best in separation (158, 159, 160).

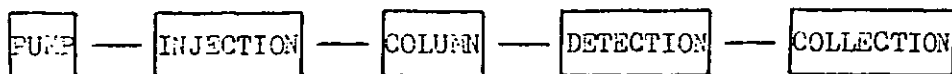
Knox and Pryde (155) and Kikta and Grushka (161) reported how the eluent composition in the pores was altered by the bonded phase. In an organic-water system the less polar organic solvent will solvate the bonded alkyl layer creating a zone in the pore which is organic-rich.

A liquid which dissolves a polymer for GPC characterisation should also have a low viscosity, high boiling point and should not dissolve, react with, or degrade the column packing. While compatibility of the solvent with the sample and the gel are important, compatibility of the solvent with the detection system is essential. With a refractometer as a detector to monitor the sample as it emerges from the column, the sample must have a different refractive index to that of the solvent such that the differential signal can be monitored. In the case of using an ultra-violet detector, then the solvent must be transparent at the wavelength being used. Thus, the sensitivity of the detector increases as the difference in the physical property between sample and solvent increases.

2.4.6 Instrumentation for Polyacrylamide GPC Analysis

The heart of the chromatograph is the packing in the stainless steel columns. The rest of the hardware is essential for pumping the liquid through the column and monitoring and recording the signals from the detection system.

Schematically this can be represented as:



In High Performance Liquid Chromatography, pumps of constant flow rate, syringe injection and small particles $\sim 10 \mu\text{m}$ are essential for efficient separation. In gel permeation chromatography, solutions of synthetic and natural polymers tend to be more viscous. The pumping system could either be constant flow or constant pressure. The injection system is valve loop injectors for most cases, so that a larger loading (1 or 2 mls) of the sample on the column is possible. The packings can vary in size. If high performance GPC is necessary, then smaller particles would be essential such that the efficiency of the column would be higher. However, if peak volume is all that is required, then larger particles such as Porasil E1500 ($37\text{--}75 \mu\text{m}$) can suffice. In this research Porasil E1500 and other related Porasils were used which had a particle size range of 37 to $75 \mu\text{m}$. In the case of Spherisorb SG120, the particle size was $10 \mu\text{m}$. The particle size and pore size distribution for this gel were quite narrow (151). The two most popular detectors in gel permeation chromatography are refractometry and ultraviolet photometry.

Polyacrylamide shows no absorbance in the visible and near UV region. There is a weak absorbance which increases in intensity with decreasing wavelength in the region below 240 nm (162). The refractometer is the best choice for monitoring the differential signal of polyacrylamide. However, dissolved air and other impurities can give undesirable detector signals. Therefore, a suitable technique such as degassing the eluent thermally and flushing the column at a higher temperature would aid in expelling the trapped air. The concentration of polymer eluting from the column is monitored by the detector with a suitable recorder. The slide wire potentiometer pen recorders are suitable for recording the signal on chart paper. Before injecting the polymer solution onto the column, the solution must be

filtered to avoid blockage of the injection valve and/or the inlet to the column.

2.5 Fractional Precipitation of Polyacrylamide

To establish a calibration curve for the gel permeation chromatography of polyacrylamide, fractions of narrow molecular weight distribution from polyacrylamide are required. Accurate calibration of retention volumes in terms of log molecular weight is established with fractions (or standards) having narrow molecular weight distributions. Since the position of the molecular weight calibration curve is dependent on structural variables which determine the molecular size of polymers in solution, it was necessary to prepare fractions of polyacrylamide.

Fractional precipitation involves the stepwise decrease of the solvent power resulting in the first fraction of highest molecular weight and the succeeding ones of progressively decreasing molecular weights. This form of precipitation can be achieved by any of the following three methods:

- (i) Addition of non-solvent (or precipitant).
- (ii) Elimination of solvent by evaporation.
- (iii) Lowering the temperature of the system.

Method (i) does not require special equipment and has been attempted previously with aqueous polyacrylamide solutions. Venkatarao and Santappa (163) used iso-propanol as non-solvent in fractionating an aqueous polyacrylamide 1% solution. No experimental details were reported. Baysal and co-workers (164, 165) used methanol as non-solvent at a constant temperature of 30°C; again no experimental procedure was reported. An experimental technique for the present fractionations was established as described in Chapter 3.

Flory (22) theoretically expressed the solvent power in terms of the "polymer-solvent interaction constant, χ ". A solvent for a given polymer

should have a χ value below 0.5, whereas a liquid having a χ value above 0.5 will be a non-solvent. Phase separations will occur when the value of 0.5 is exceeded. The critical value χ_c will depend upon the molecular weight of the dissolved polymer molecules. If the size of a molecule is expressed in terms of its degree of polymerisation, x (22), then χ_c is given by

$$\chi_c = \left(\frac{1}{2}x\right) (1 + x^{\frac{1}{2}})^2 \approx \frac{1}{2} + \frac{1}{x^{\frac{1}{2}}} \quad (2.88)$$

Thus the addition of non-solvent with large χ will cause the χ value of the system to exceed the χ_c value for each component. The component will then precipitate in order of the decreasing value of the degree of polymerisation, x .

In choosing solvent/non-solvent systems, factors such as flammability, toxicity, vapour pressure, peroxide formation, etc., have to be considered. Also, a non-solvent with a moderate precipitating power is far better than one with a strong precipitating power. It would be expected, based on tabulated values of solubility parameters (26), that methanol ($\delta = 14.5$) would be a more moderate precipitant than iso-propanol ($\delta = 11.5$) for aqueous solutions of polyacrylamide.

CHAPTER 3

EXPERIMENTAL

A series of polyacrylamides were required with well defined average molecular weights and molecular weight distributions. Consequently, well defined conditions had to be established both in the synthesis and characterisation work. Also, an aqueous GPC system had to be developed with a suitable porous support in order to separate polyacrylamides predominantly by a permeation mechanism.

3.1 Polymerisation

3.1.1 Purification of Reagents

Acrylamide monomer used in these experiments was obtained commercially from BDH. It was possible that the manufacturers may have added certain inhibitors or retarders to inhibit polymerisation of acrylamide monomer during storage and transportation. Recrystallisation was carried out in order to reduce possible contaminants.

3.1.2 Recrystallisation of Acrylamide (Monomer)

Acrylamide monomer (250 gms) with a BDH minimum assay of 98.5% was dissolved in a minimum amount of methanol (350 mls). All purification and polymerisation procedures involving acrylamide monomer were performed with careful safety precautions, see Appendix (1). Magnetic stirring was employed in bringing about dissolution. No form of heating was used because of the ease with which acrylamide polymerises. Excess methanol was then removed using a rotary evaporator at room temperature. The solution was then filtered through a glass funnel using a fast speed filter paper (Whatman's grade 4) in order to remove insoluble impurities. The filtered

solution was then stoppered into a 500 ml round bottom flask and stored in a refrigerator at -20°C overnight.

The contents of the flask were allowed to thaw out for about two hours before filtering into a Buchner flask using grade 4 Whatman's filter paper. The product was washed with ice cold methanol. The white crystals of monomer were then placed in a vacuum desiccator, connected to a vacuum pump and dried overnight at room temperature. The vacuum desiccator was wrapped with aluminium foil in order to prevent light entering. The crystals were then weighed and a yield of 210.8 g (84.2%) was obtained.

3.1.3 Recrystallisation of Potassium Persulphate (Initiator)

Potassium persulphate (BDH, Analar grade) was dissolved in a minimum amount of distilled water with the aid of magnetic stirring. No form of heating was used, because aqueous potassium persulphate dissociates easily with rise in temperature forming potassium sulphate and hydrogen peroxide.

The solution was stoppered in a flask and placed in a refrigerator overnight. The frozen mixture was then allowed to thaw out and filtered into a Buchner flask using grade 4 Whatman's filter paper. The product was washed with ice-cold water. The white crystals were then allowed to dry under vacuum at room temperature. A 66% recovery of potassium persulphate was obtained.

3.1.4 Isopropanol (Chain Transfer Agent)

Isopropanol (Analar grade) obtained from BDH was used as received.

3.1.5 Solution Polymerisation of Acrylamide Monomer

The initial polymerisation runs were performed according to the procedure described by Sorenson and Campbell (68). A typical example was the method used for polymerisation run 6.

Acrylamide (5.1746 gms) was dissolved in distilled water (46.5 cm^3)

and placed in a 100 ml reactor flask. The solution in a nitrogen atmosphere was heated to 68°C. Potassium persulphate (0.0111 gms) and isopropanol (0.7785 gms) were added. The temperature of the reaction was kept within the range 75-80°C by heating with an iso-mantle. After a reaction time of two hours, the viscous solution was poured into methanol (industrial grade) in order to precipitate the polymer. The polyacrylamide was isolated and dried in a vacuum oven at 50°C for 24 hours.

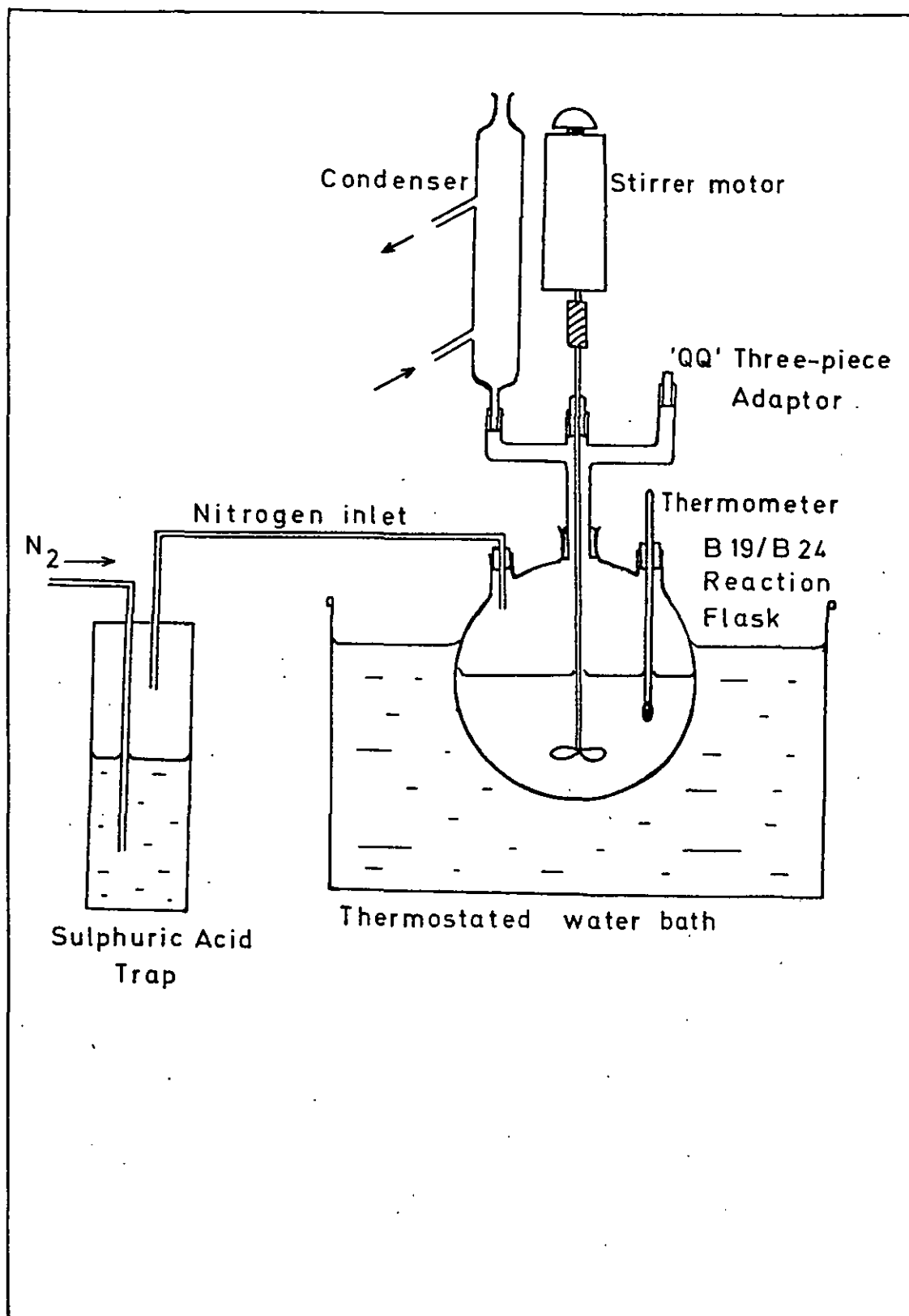
In this polymerisation procedure, it was found to be quite difficult to control the exothermic nature of the reaction using the iso-mantle as a source of heat.

From polymerisation 12 onwards, the reactor shown in Figure 3.1 was used. A water bath heated at constant temperature replaced the iso-mantle giving better dissipation of the heat of reaction. The sulphuric acid trap removed moisture from the nitrogen stream and acted as a flow gauge (70-80 bubbles per minute).

The initiator was introduced as an aqueous solution. Stirring was by mechanical means using a Voss stirrer motor turning at approximately 120 r.p.m. A typical example is the method for polymerisation run 24. The reaction flask of 500 ml capacity containing the aqueous acrylamide solution (125 mls) was flushed with nitrogen continuously and immersed in a water bath maintained at a constant temperature of 45°C. The solution was stirred and potassium persulphate (0.9869 gms) dissolved in distilled water (5 cm³) was added. After a reaction time of 40 minutes, the viscous solution was poured into methanol (industrial grade) in order to precipitate the polymer. The polymer was left precipitated in the methanol for 7 hours, such that unreacted monomer and initiator would have sufficient time to enter into solution. The polyacrylamide was isolated and dried in a vacuum oven at 50°C for 24 hours. Afterwards, the polymer was crushed and stored in stoppered perspex tubes for future characterisation work.

FIGURE 3.1

REACTOR FOR SYNTHESIS OF POLYACRYLAMIDE



3.2 Viscometry

Ubbelohde suspended level viscometers having flow times for water of 1000 s and 83 s were used at 25°C. The viscometers were thoroughly cleaned using chromic acid before use. Initially, a polyacrylamide solution of known concentration was prepared and agitated on a flask shaker overnight in order to achieve a homogeneous mixture. The solution was then filtered using a Whatman's grade 1 filter paper. A known volume of this solution was transferred to the viscometer and the mean of several flow-times was determined.

3.2.1 Dilutions within the Viscometer

The Ubbelohde suspended level viscometer having a flow-time for water of 83.0 s was used in a thermostatted water bath at 25°C. The viscometer support was levelled using a spirit level gauge. The cleaning of the viscometer was done as before. The top ends of the viscometer were modified, to accommodate B14 quick-fit 'U' pieces, such that foreign matter could not enter the viscometer. Polyacrylamide solutions were prepared with filtered distilled water and agitated on a flask shaker for 24 hours in order to achieve a homogeneous mixture. After complete dissolution of the polyacrylamide in water, the solution was filtered using Whatman's filter paper (grade GF/C). The polyacrylamide concentration in the filtrate was determined gravimetrically and was used in subsequent calculations of the intrinsic viscosity $[\eta]$. A known volume of a filtered solution was transferred to the viscometer and the mean of several flow-times was recorded after leaving the solution for about 15-20 minutes to attain thermal equilibrium.

Solutions of decreasing polyacrylamide concentrations were prepared within the viscometer by adding known volumes of water. After each dilution the mean of several flow-times was recorded for the polyacrylamide solution, after leaving the solution for about 15-20 minutes to attain thermal equilibrium.

librium. The procedure tended to produce anomalous results when plotting data according to equations (2.41) and (2.42). The anomalous behaviour was probably due to inadequate mixing of the polyacrylamide solution and the water during the time scale of the flow-time determinations on the diluted solutions.

3.2.2 Dilutions external to Viscometer

Consequently, all solutions with various concentrations of polyacrylamide have been prepared by the same procedure outside the viscometer in order to achieve better equilibrium of polyacrylamide with water. The flow-time of the most dilute polyacrylamide solution was determined first, followed by solutions with increasing polyacrylamide concentration. Between solutions, the viscometer was washed with distilled water and then with the next solution. The polyacrylamide solutions were prepared such that η_r did not exceed 3.0. The data were extrapolated by equations (2.41) and (2.42) to find $[\eta]$.

The viscosity average molecular weight \bar{M}_v was calculated using the Mark Houwink equation (equation (2.44)).

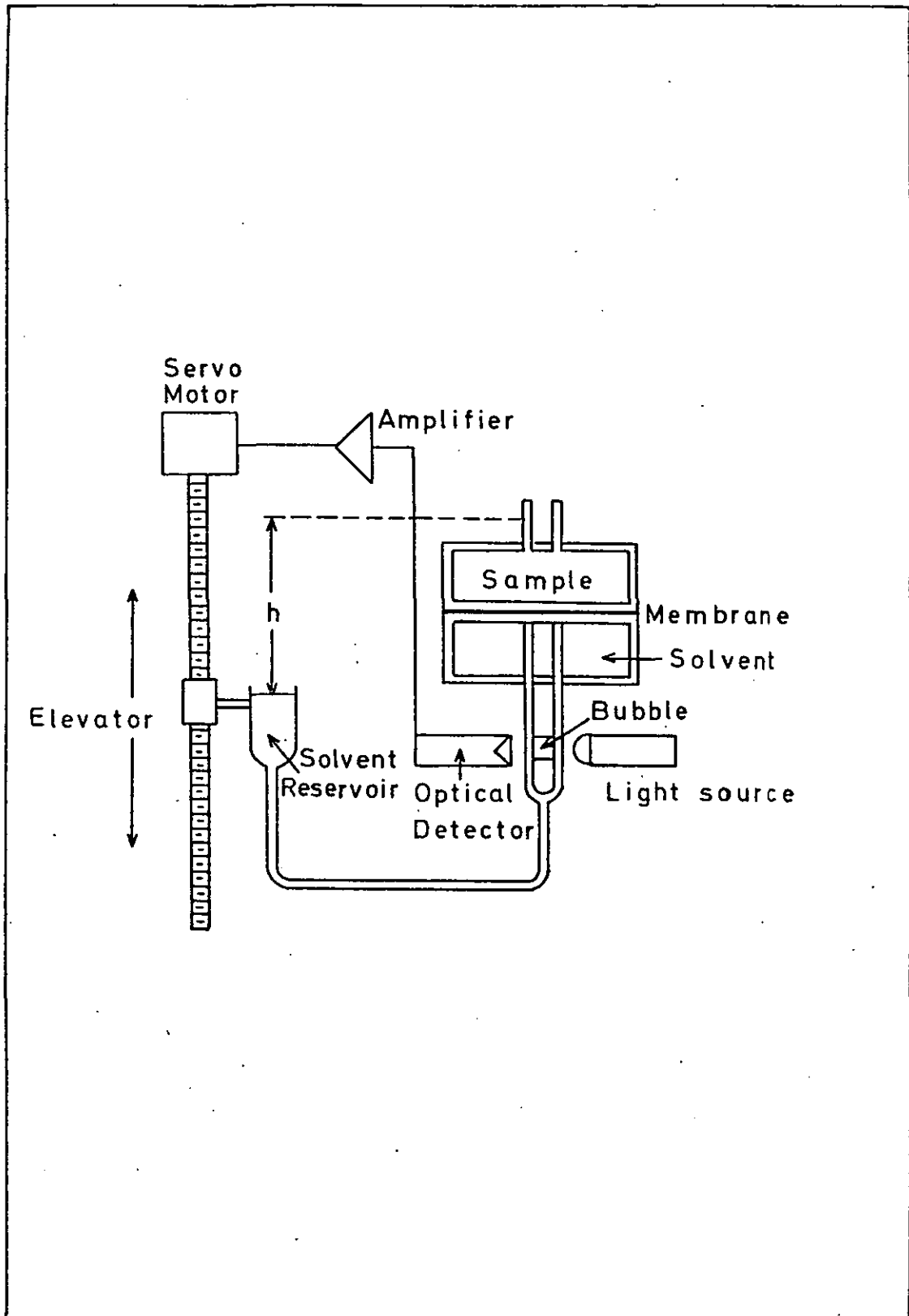
In the gravimetric determination of the concentration of some polyacrylamide solutions after filtration, large losses of polyacrylamide were recorded with cellulose filter paper. Lower losses were found with glass fibre filter paper (GF/C), as documented in Chapter 4.

3.3 Membrane Osmometry

The Mechrolab Model 502 membrane osmometer was used for determinations of the osmotic pressure of polyacrylamide solutions. A schematic diagram of the osmometer is shown in Figure 3.2. The technique relies on a stable air-bubble in a capillary. Consequently, the solvent and all solutions must be thoroughly degassed. However, a drift in the osmometer head reading was observed with aqueous polyacrylamide solutions, presumably because of the

FIGURE 3.2

SCHEMATIC DIAGRAM OF A MECHROLAB RAPID MEMBRANE OSMOMETER



solution "sticking" in the capillary owing to surface tension phenomena. For organic systems, toluene is normally used as the solvent in membrane osmometry experiments, e.g. for polystyrene. Toluene itself has a very low surface tension (27.7 dynes/cm at 10°C) and is also very easy to degas, whereas water has a very high surface tension (73.05 dynes/cm at 18°C). On looking for another possible solvent for polyacrylamide, it appeared that formamide had a lower surface tension than water (58.2 dynes/cm at 20°C), but on experimenting with formamide as a solvent, it was observed that both aqueous membranes (B19) and non-aqueous membranes (0-8) disintegrated. It was found that the B19 membrane did not disintegrate in a mixture of formamide and water (1:3). This liquid mixture produced stable readings in the osmometer and also for polyacrylamide solutions. The formamide and water were degassed separately before mixing in the correct ratio for osmometry. Formamide was degassed under reflux in a nitrogen atmosphere, and water was boiled. The dismantling and setting up of the membrane osmometer were performed according to the instructions in the manufacturer's handbook (166).

3.3.1 Aqueous Operation

A glass capillary of capillary no. 18561A and aqueous membranes type B19 (hp 18528A) were used for the hp 502 membrane osmometer. Bubble formation or entrapment was known to produce sluggish or erratic instrument operation owing to dirt, oil or grease which act as potential sites for bubble formation. Therefore, cleanliness was most important in the handling of all components, membranes and solvents. All components were cleaned thoroughly with water and acetone. All glassware including the capillary was washed with chromic acid and rinsed with degassed distilled water. Bacterial growth can cause membrane deterioration, as well as evolution of gases, resulting in unstable osmotic pressure readings. Therefore, all membranes were conditioned and stored at a temperature of 5°C in a refrigerator. The solvent (binary) was thoroughly degassed and stored in a screw-top bottle.

3.3.2 Pre-conditioning and conditioning of aqueous membranes (B19)

Aqueous membranes, type B19, were wet packed at the Hewlett Packard factory in 25% isopropanol/water. The membranes were thoroughly rinsed several times in distilled water and at no time were they allowed to become dry. The membranes were then soaked in a formamide/water (1:3) mixture for at least 24 hours, changing the solvent several times afterwards. The membranes were then stored at a temperature of 5°C in a refrigerator. This step was known as pre-conditioning.

Before use, several pre-conditioned membranes were placed in a fresh amount of water/formamide (3:1) and warmed to a temperature of 40°C for 30 minutes. This is known as membrane conditioning. The solution was agitated occasionally by swirling the flask to remove gas bubbles on the surface of the membranes. The membranes in the solvent were covered and allowed to cool to 4 or 5 degrees above room temperature. The operating controls, recorder range setting, the solvent introduction, optical system alignment, adjustment of reference photocell, the bubble introduction, the membrane installation and activation of the servo system were well documented in the operating and service manual with reference to schematic and pictorial diagrams (166).

3.3.3 Establishing the solvent reference value, P_0

When the bubble reached the control level and the servo system started to operate, the solvent level in the glass stack was checked to make sure that the bottom of the meniscus was at the scribe line on the glass. Also, the solvent level was checked in the solvent reservoir (sometimes called elevator reservoir) to correspond with the scribe line on the glass.

The instrument was left alone until equilibrium had been established at room temperature, as indicated by a steady reading. The time for equilibrium varied from half an hour to four hours. After a stable balanced reading had been attained, the solvent in the upper chamber was replaced by

filling the sample stack and drawing the level down to the mark. A stable reading should be reached which may take as long as half an hour to achieve. This stable reading is P_0 , the reference value for the solvent.

3.3.4 Measuring the solution reference, P

The most dilute solution was used first, followed by increasing concentrations in successive measurements. The following procedures were used:

- (a) The teat pipette was filled with sample solution.
- (b) The sample solution was introduced into the osmometer by the procedure recommended in the manufacturer's manual.
- (c) The above step was repeated twice again.
- (d) On the last addition, the sample level was drawn to the scribe mark on the glass sample stack, aligning the bottom of the meniscus with the scribe. The stable reading at equilibrium was noted as P_1 .
- (e) The above step was repeated, and the stable reading was noted as P_2 . The average reading P from P_1 and P_2 was used in the calculation of number average molecular weight \bar{M}_n as shown in Chapter 2.3.

3.4 Gel Permeation Chromatography of Polyacrylamide (GPC)

Initially, analytical and preparative GPC techniques were investigated. The columns used for preparative GPC were glass columns similar to the arrangement described by Mulder and Buytenhuys (167). They employed a gravity feed system for their separations with soft gels as their GPC support.

3.4.1 Preparative GPC

From possible organic gels that are commercially available which may effect separations of polyacrylamide of molecular weights $10^5 \rightarrow 10^6$, the lightly cross-linked agarose (Bio-Gel A-150) was chosen. Because of the sensitivity of these gels to even slight pressures, only slow flow rates

($2 \rightarrow 4 \text{ cm}^3/\text{hr}$) were possible with a gravity feed of degassed distilled water as eluent. Also, the gel bed tended to compact when the hydrostatic pressure was greater than 30 cms of water. Since supports based on swollen organic gels seemed to be unsatisfactory, porous inorganic silicas which are more rigid were investigated. The length of the glass column was 50 cm and the internal diameter was 2.2 cm. The inorganic packing was retained in the column by a glass sinter of porosity 4 ($5 \rightarrow 15 \mu\text{m}$) which was supported inside a polythene cup and sealed to the column by a gasket and plastic end-fitting. The support was held firm by a plunger at the top end of the column. The column packing was Bio-Glas 1500 (particle size $37 \times 75 \mu\text{m}$) which consisted of irregular shaped particles. The Bio-Glas was coated with polyethylene oxide (molecular weight 800) by the solution technique as described in reference (10). The packing was added as a slurry in small increments at a time whilst placing a vibrator on the tube. A hydrostatic pressure in excess of 1 metre was used to give a flow rate of $1 \text{ cm}^3 \text{ min}^{-1}$. Problems were encountered with a decreasing flow rate as a function of time. Because of the appearance of a growing void volume between the top of the support and the undersurface of the plunger, the gel appeared to be compacting under its own weight, thus generating more constricted flow paths between the particles (irregular shaped). Also, fine particles smaller than $10 \mu\text{m}$ were discovered between the sinter and the cup in the bottom end-fitting. These could have been produced by fragmentation of the Bio-Glas by the vibrator during packing. The polymer solution was introduced into the column by a syphon arrangement as described by Mulder and Buytenhuys (167).

20 ml aliquots of eluent were collected, and from each aliquot a sample was injected into the sample cell of the refractometer, with the reference cell containing degassed distilled water. The refractometer and recorder were set at maximum sensitivity. Polyacrylamide appeared to be eluting at 130 mls, reaching a peak maximum of 160 mls and tailing off to its original base line at a retention volume of 190 mls. The reduced peak heights could

be due to the fact that considerable dilution of the sample was taking place or because of some retention of the sample on the unreacted active sites of the Bio-Glas support. It was decided that since no synthetic water soluble polymer standards were commercially available, an analytical GPC should be explored extensively in order to establish a size exclusion separation of polyacrylamide. Once an analytical technique had been effected, fractions could then be prepared either by preparative GPC or by fractional precipitation.

3.4.2 Analytical GPC Instrumentation

The instrumentation consisted of the following:

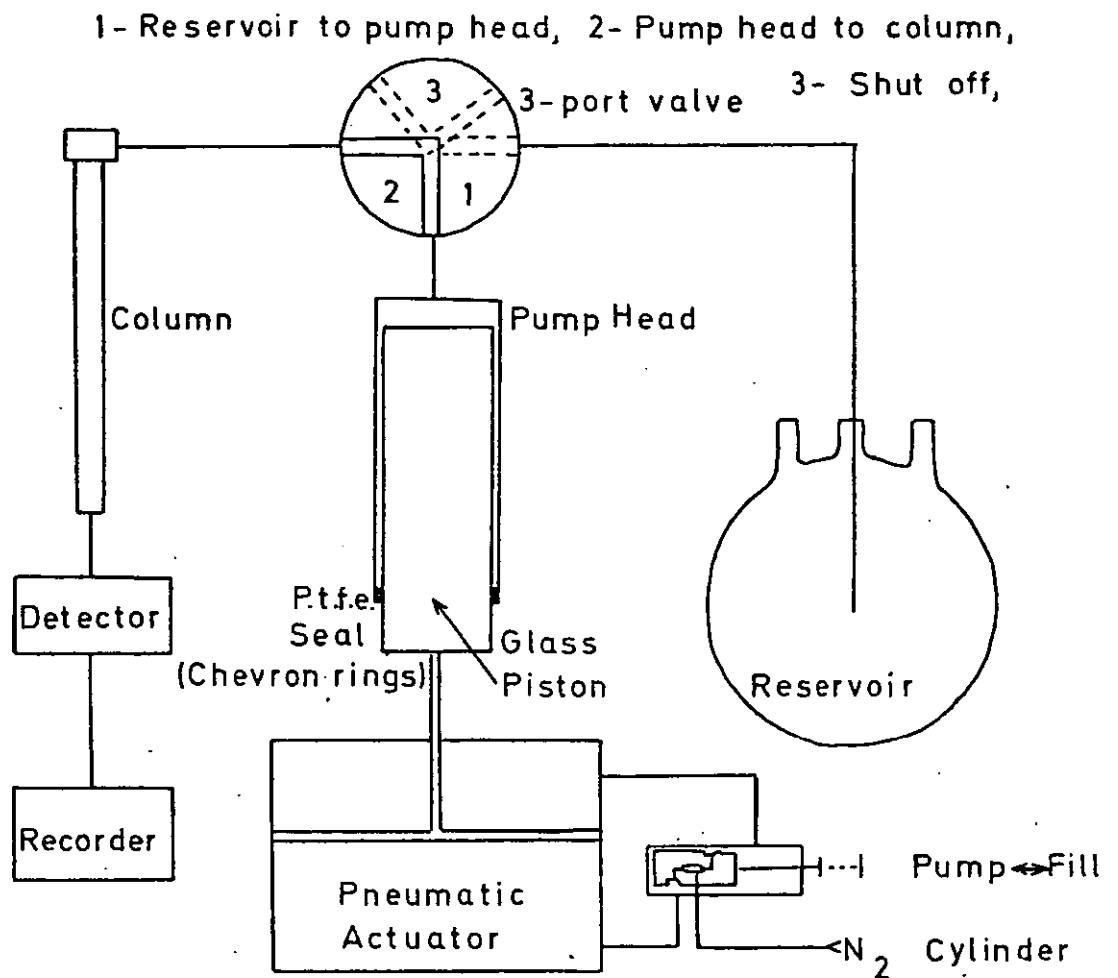
- (a) A constant pressure pump (750/01) manufactured by Applied Research Laboratories Limited, Luton.
- (b) Stainless steel columns from 1 ft \rightarrow 2 ft in length, and 3/8" internal diameter.
- (c) A Laboratory Data Control Refractometer, model 1107.
- (d) A Vitatron UR 404 linear recorder of 0-10 mV full scale deflection.
- (a) The constant pressure pump consisted of a pneumatic actuator driving a pump head. The solvent reservoir was mounted outside the cabinet of the pump as shown in the schematic diagram Figure 3.3. The pump which could be filled manually with a slow delivery stroke and fast return was used with externally mounted columns at ambient temperature. The controls on the pump were STOP/START and FILL/DELIVERY to the column.

Pneumatic Actuator: The actuator was operated from a compressed nitrogen cylinder.

Pump Head: The pump head consisted of a polished glass piston within a stainless steel cylinder. A long-life PTFE seal (Chevron rings) ensured minimum friction. The glass piston was never in contact with the cylinder, and wear on the piston was thus virtually eliminated. The gas supply to

FIGURE 3.3

SCHEMATIC OF PRESSURE PUMP



the actuator was controlled by a pressure regulator. The diaphragm of the actuator was nine times larger in area than the glass piston, resulting in the liquid pressure being nine times greater than the gas pressure. Thus, the gauge attached to the pressure regulator was scaled to indicate the liquid pressure at the pump head outlet and not the gas pressure to the actuator. A three-position valve was mounted at the outlet of the pump head so that it could be shut off, connected to the reservoir for refill, or to the column. The capacity of the pump head was 60 mls; the solvent level was indicated on the front panel of the instrument. The delivery outlet was connected via a 1/16" (i.d.) stainless steel tubing.

Solvent Reservoir: The solvent reservoir was a standard Quickfit three-necked 1 litre flask, designed so that the solvent could be degassed by either vacuum or reflux methods. A PTFE tube connected the reservoir to the pump head.

Valve loop injector: The loop injector was a 6 port valve containing a loop of 2 ml capacity and a syringe inlet to accommodate a 10 ml syringe. This off-column type of injection means that the sample was not injected on to the surface of the silica support. Also, the flow of solvent does not have to stop in order to inject the sample. The disadvantage was of course that the sample would be diluted, dependent on injection time, before it reached the support in the column.

(b) Stainless steel columns: Experiments were performed with inorganic porous silicas (principally Porasil) packed into stainless steel columns of dimensions 61.0 cms x 0.75 cms using the dry packing method described by Kirkland (146). The packing was retained by a stainless steel mesh of poresize 5 μ m, supported by a 3/8" \rightarrow 1/16" reduced end piece which was held in place by a Swagelock nut. The top end of the column was retained by a stainless steel mesh held in position by Swagelock fittings connected to the loop injector valve via a 1/16" (i.d.) stainless steel tubing.

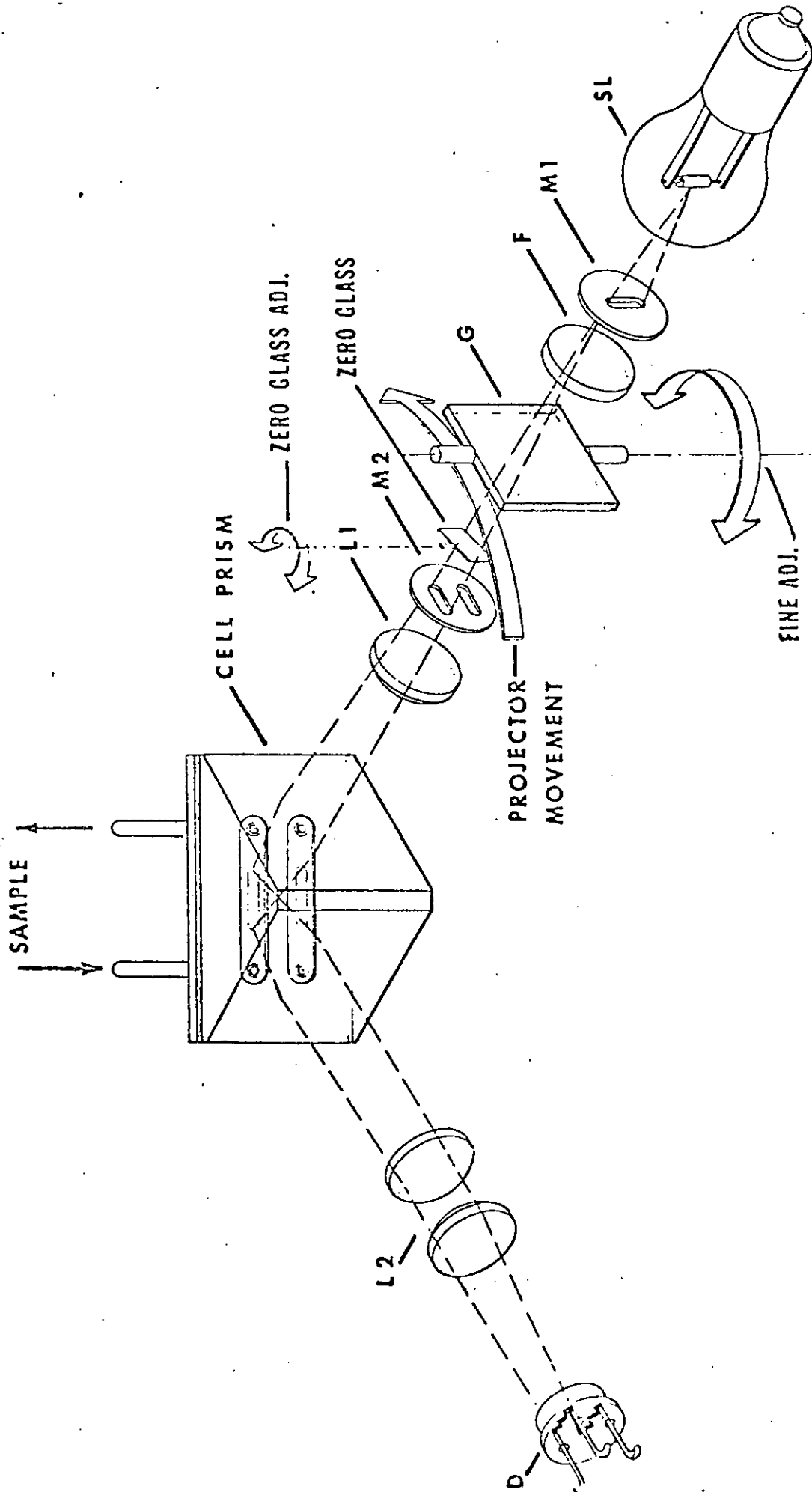
(c) Refractometer: The refractometer, model 1107 LDC refractomonitor, was constructed of two units: an optical unit containing the refractometer cell and located just under the analytical streams, and the control unit which is cable-connected to the optical unit. The inlet and outlet connections to the sample cell were made through two 1/16" (i.d.) stainless steel capillary tubes; the reference cell was through two 1/8" (i.d.) stainless steel capillary tubes. The capillary tubes emerged from the prism through the top of the optical unit cover. A low index prism was used giving a solvent refractive index range between 1.31-1.44. The cells were made up of a standard 0.002" Teflon gasket which was clamped between the bottom side of the prism and the top side of the stainless steel backing plate. The cell volumes were 0.5 microlitres each. The heat exchanger in the optical unit was never used. Operations were performed at ambient temperature.

Principle of Operation: This operation was based on Fresnel laws, see Figure 3.4) which relate the transmittance and reflectance of the interface to the angle of light incidence and the refractive indices of the two materials forming the interface. The interface was formed between the glass prism and the liquid whose refractive index was to be measured. The differential refractomonitor model 1107 was unique for two reasons:

- (1) a single axis optical system was used to illuminate the two interfaces.
- (2) the transmitted, rather than the reflected, light was used in the measurement.

In Figure 3.4, reproduced from reference (168), a tungsten filament having a 10,000 hours life span was used as a light source (L). Light from the source lamp (SL) passed through source mask (M1), infra-red blocking filter (F), fine adjusting glass (G), zero glass (Z), aperture mask (M2), and was collimated by lens (L1). Mask (M2) defined two collimated beams which entered the cell prism and impinged upon the glass to liquid interface as shown. Components SL through L1 were mounted on a separate optical bench in an assembly known as the projector. In adjusting the angle of incidence

FIGURE 3.4



to accommodate solvents of various refractive indices, the projector was rotated about a pivot point. Fine adjustment of the angle of incidence was performed by rotating the fine adjusting glass (G) which slightly displaced the apparent position of the source lamp (SL) and changed the angle of incidence slightly. Light from the two beams, which was reflected from the liquid to glass interface, did not enter the detector lens assembly (L2), and was discarded. Light which was transmitted through the two liquid to glass interfaces passed through the liquid film and impinged on the surface of the cell backing plate. The cell backing plate had a finely ground light diffusing layer, where the transmitted beams appeared as two spots of light. The detector lens assembly (L2) forms an image of these spots on the light sensitive resistors of dual photodetector (D).

When the angle of incidence was properly adjusted to slightly less than the critical angle for the solvent contained in both cell chambers, the same amount of light will impinge on the photodetectors (D). If the refractive index of the liquid in one chamber was changed (e.g. a solute entering into the sample chamber), the partition of the total light incident on that interface into reflected and transmitted beams will be changed in accordance with the Fresnel laws. As a result the amount of light impinging on each element of dual detector (D) will no longer be the same, indicating a difference in refractive index between the two liquids.

Throughout all experiments, the eluent from the columns was mobile through the sample cell. In the reference cell degassed eluent was kept stationary by connecting a length of polythene tubing between the inlet and outlet.

(d) Recorder: A Vitatron UR 404 recorder with universal input attenuator was used. This recorder had a sensitivity of 10 mV for full scale deflection in the linear range. This was later converted to 1 mV full scale deflection. The incoming signal (voltage) from the refractometer was com-

pared with a reference voltage on a resistor in the form of a slide wire.

3.4.3 Analytical GPC Experimentation

The analytical GPC experiments which were performed are presented in Table 3.1. The silica gel Porasil was commercially available from Waters Associates. The SG 120 (Spherisorb) was kindly provided by A.E.R.E., Harwell. In experiments 1 \rightarrow 8, the columns were dry-packed. They were flushed with degassed distilled water in experiments 1 \rightarrow 4, or with the appropriate eluents in subsequent experiments, as shown in Table 3.1. Small molecular weight solutes, e.g. ethanol, acetamide and iodo-acetamide, were injected into the columns, so that the total permeating volume could be determined. Aqueous polyacrylamide solutions ($\sim 0.3\%$) were prepared and filtered using a GF/C filter paper. Separations were performed at eluent flow rates between 0.5 and 2.5 cm³ min⁻¹. In the experiments using binary eluents, polyacrylamide solutions were prepared with the same mixture of liquids.

3.4.3.1 Experiment 1

The Porasil was dry packed in the column by "tamping". The gel was not treated in order to reduce active sites. Distilled-degassed water was used as eluent. In the second part of the experiment, 0.15% w/v KBr solution was used as eluent with the untreated Porasil E1500, as employed by Hamielec (17).

3.4.3.2 Experiment 2

The Porasil was treated with polyethylene oxide in order to reduce active sites on the surface of the silica. Two techniques were used in the coating process, a solution technique and a suction technique.

Solution technique: Hiatt et al. (169) and Hawk et al. (170) suggested the coating of inorganic oxide supports with polyethylene glycol in order to minimise interaction effects which lead to high retention volumes. 35 cm³

TABLE 3.1

Analytical GPC Experiments with Silica Packings

| GPC experiment | Silica | Pore size Å | Surface Coating | Eluent |
|----------------|-----------|--------------------|-----------------|--|
| (1) (a) | Porasil E | 1500 | Uncoated | Water |
| (b) | " | " | " | 0.15% w/v KBr |
| (2) (a) | " | " | PEO 20,000 | Water |
| (b) | " | " | PEO 6,000 | " |
| (c) | " | " | PEO 800 | " |
| (d) | " | " | PEO 200 | " |
| (3) | " | " | Decoated | " |
| (4) | Porasil F | 2000 (decoated) | Aerosol OT | " |
| (5) (a) | " E | 1500 | Uncoated | Formamide/water |
| (b) | " C | 400 | " | " |
| (c) | " D | 1000 | " | " |
| (6) (a) | " E | 1000 | " | 1% 880 NH ₃ |
| (b) | " F | 2000 | " | " |
| (c) | " E | 1500 | " | " |
| (7) (a) | " D | 1000 | " | 1% 880 NH ₃ /HCONH ₂ |
| (b) | " C | 400 | " | " |
| (c) | " B | 250 | " | " |
| (8) (a) | " E | 1500 | HMDS | Water |
| (b) | " E | " | " | THF/Water |
| (9) | SG 120 | 1200 | Aminopropyl | Water |
| (10) | " | " | " | Water/HCONH ₂ |
| (11) | Porasil F | 2000 | " | " |

of dry gel was mixed with 100 ml of 0.05% aqueous solution of polyethylene oxide (molecular weight 800). This was left in solution for 60 minutes, after an initial (15 mins.) swirling by hand. Vigorous stirring was avoided in order to minimise the formation of small particles by fragmentation. The excess polyethylene glycol was decanted off and the gel was washed six times with distilled water (600 cm^3). Any fine particles in suspension were removed by decanting. The gel was then dried in a vacuum oven at 60°C for 24 hours.

Suction technique: The column containing the support was attached to the pump via the injection valve. A 0.5% aqueous solution of polyethylene glycol (molecular weight 800) was pumped through the column. The column was flushed with 400 cm^3 of distilled water before attempting fractionation of polyacrylamide.

3.4.3.3 Experiment 3

Bio-Glas coated with polyethylene glycol was decoated using hot concentrated nitric acid (10). The procedure used in decoating Bio-Glas which consists of irregular shaped particles within the particle size range $37\text{--}75 \mu\text{m}$ should be just as effective in decoating the polyethylene oxide from Porasil which is a porous silica of spherical particles within the size range $37\text{--}75 \mu\text{m}$.

3.4.3.4 Experiment 4

Porasil F 2000 (35 cm^3) was coated using the solution technique with 100 cm^3 of 0.3849% Aerosol OT in aqueous solution. The mixture was swirled by hand for 10 mins., and then left standing on the bench for 60 minutes. The excess Aerosol OT was decanted off and the gel was washed with distilled water (600 cm^3) using 200 cm^3 aliquots each time. The gel was dried in a vacuum oven at 60°C for 24 hours. The column was dry packed by the tamping method.

3.4.3.5 Experiment 5

Uncoated Porasil E 1500, C 400 and D 1000 were packed into three separate columns. The eluent was a binary mixture of formamide (1 part) and water (5 parts). Formamide in the mixture was chosen because it is a suitable organic solvent for polyacrylamide (171, 112). Formamide was degassed by refluxing under a nitrogen blanket for two hours. Water was boiled using a hotplate and the two components were then mixed in the correct ratio in the reservoir. The mixture was then placed under vacuum to remove any dissolved air. The mixture was then pumped through a column containing the gel support under investigation.

3.4.3.6 Experiment 6

Porasil E 1500, F 2000 and D 1000 (all gels uncoated) were dry packed into three separate columns. The eluent was 1% 880 ammonia. This eluent is a colourless liquid which is quite volatile. As a consequence, the water was boiled and stored in the reservoir until the temperature was about 25°C. Then, the right volume of 880 ammonia was added to the water in the reservoir to give a 1% 880 ammonia solution. The flask was not placed under vacuum because the ammonia concentration in the mixture would decrease owing to the higher vapour pressure compared to water.

3.4.3.7 Experiment 7

Porasil D 1000, C 400 and E 1500 (uncoated) were dry packed into three separate columns. The eluent was 1% 880 ammonia in a water/formamide mixture. Water was boiled on a hot plate, and formamide was degassed under reflux using a nitrogen blanket. The water was allowed to cool to room temperature in the reservoir. The correct volume of 880 ammonia was then added to give an aqueous solution of 1% 880 ammonia. Formamide at a temperature of 25°C was added to the 1% 880 ammonia solution in the reservoir to give a ternary mixture of 1% 880 ammonia:formamide in the ratio of 5:1.

3.4.3.8 Experiment 8

Porasil E 1500 was chemically bonded with hexa-methyl disilazane (HMDS) by Mr. M. Holdoway at A.E.R.E., Harwell. Details of this type of reaction and the experimental procedure can be obtained from the literature, such as in reference (172). The gel was dry packed into a stainless steel column.

The water was degassed by boiling. Tetrahydrofuran was distilled and stabilised with 0.1% w/v Quinol. Quinol acts as a scavenger in removing any form of peroxides which are explosive when isolated.

3.4.3.9 Experiments 9, 10, and 11

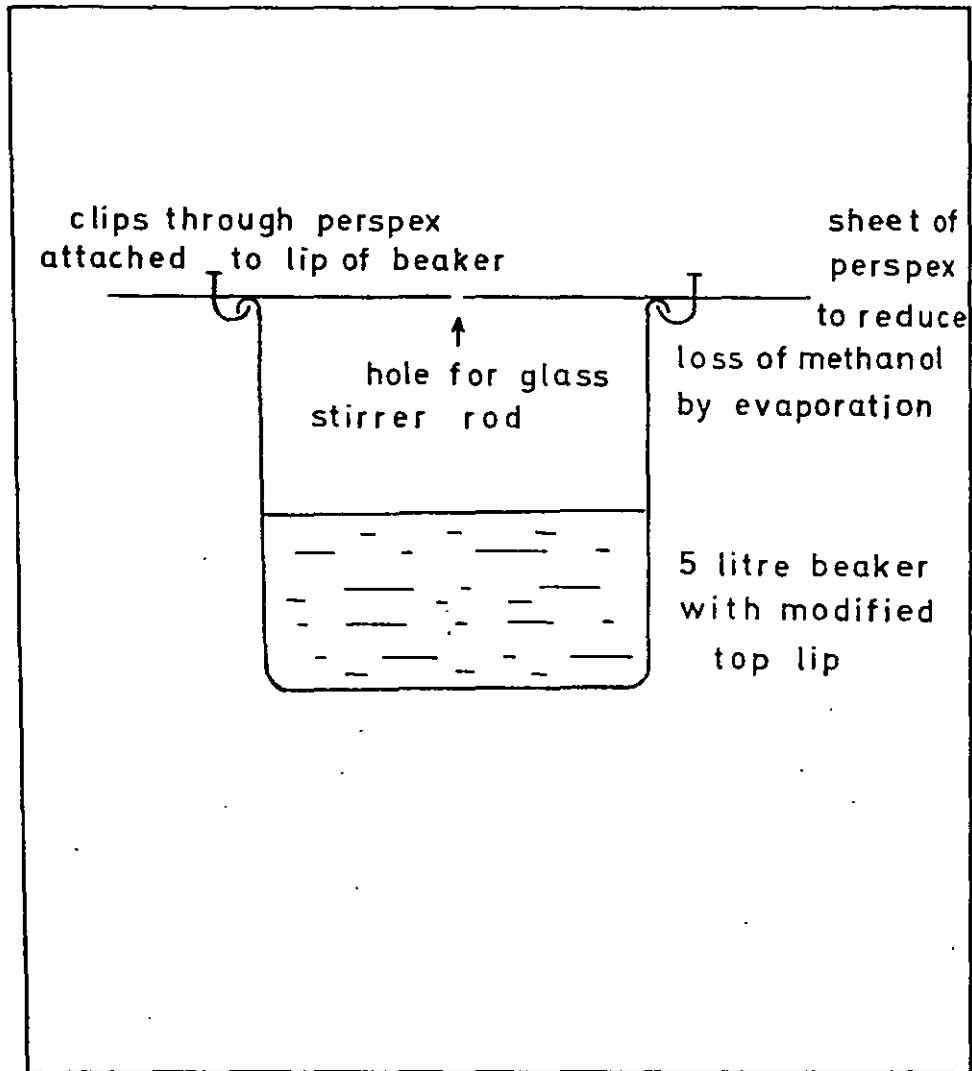
SG 120 is a silica gel kindly provided by Dr. J. Ramsay at A.E.R.E., Harwell (173, 174). The chemical bonding of the aminopropyl phase to the silica was performed by Mr. M. Holdoway. The column, one foot in length was slurry packed in methanol under pressure at Harwell. Porasil F was chemically bonded with n-propylamine at Harwell by the same procedure. The column was slurry packed in methanol under gravity control at Loughborough. Water and water/formamide (5:1) were used as eluents. The technique of degassing was the same as described before.

3.5 Fractional Precipitation

The initial preparative GPC experiments described in Section 3.4.1 were not completely satisfactory. It was decided to prepare fractions by fractional precipitation involving non-solvent addition at constant temperature. The standard fractionation flask for fractional precipitation as described in Cantow's book (175) was unsuitable for polyacrylamide. Swollen polyacrylamide precipitates are very sticky and adhere to glass very easily. Therefore, it was decided to work with a modified apparatus involving a 5 L beaker, as shown in Figure 3.5. After precipitation of the first fraction, the supernatant was decanted into a second beaker in the thermostatted water bath. The precipitate was removed from the first beaker and further non-

FIGURE 3.5

FRACTIONATING FLASK



solvent addition to precipitate the second fraction was performed in the second beaker. The non-solvent used here was methanol.

3.5.1 Precipitation with Heating and Cooling Cycles

The standard procedure in fractional precipitation is to add non-solvent at constant temperature, e.g. methanol at 25°C, in order to precipitate the first fraction and then to raise the temperature, e.g. to 40°C, in order to dissolve the precipitate. Subsequent cooling down to 25°C allows the precipitate to form under equilibrium conditions at constant temperature over a long period of time, e.g. overnight. After the removal of the precipitate, the whole procedure may be repeated for each subsequent fraction. Such a fractionation was performed with an aqueous solution (1 dm³) of polyacrylamide PA47 (0.9% w/v) and methanol as non-solvent. Several difficulties were encountered with this procedure. Firstly, a fraction having formed on addition of methanol did not re-precipitate after heating and cooling. Secondly, although 98.8% of the polymer was recovered, the order of fractions with respect to molecular weight was not always in the correct sequence.

3.5.2 Evaluation of Weight of Precipitate vs. Volume of Non-Solvent

It was therefore decided to perform a fractional precipitation experiment with the heating and cooling cycles omitted. The precipitation conditions were determined from small scale experiments to find the weight of polymer precipitated as a function of the volume of methanol added.

Six boiling tubes were placed in a thermostatted water bath at 25°C. To each tube containing an aqueous solution (5 cm³) of polyacrylamide PA49 (1.172%), known volumes of methanol were added. The solution in the tubes was stirred, and then each tube was stoppered. The tubes were left overnight in a water bath thermostatted at 25°C and then the supernatant was decanted off the following morning. The precipitate was dried for 24 hours at a temperature of 50°C under vacuum. A plot of polymer precipitated vs.

volume of methanol added for two separate experiments, as shown in Chapter 4, revealed the threshold value of methanol for initial and complete precipitation.

3.5.3 Precipitation, omitting Heating and Cooling Cycles

The fractionation of PA49 is typical. An aqueous solution (95 cm^3) of PA49 (0.922%) was placed in a fractionation flask in a thermostatted water bath at 25°C . The required volume of methanol, determined from the small scale experiments, was added slowly with stirring. The supernatant was removed the following morning and the precipitate was dried in a vacuum oven at 50°C for 24 hours. Further fractions were isolated by repeating the procedure with further additions of methanol. The final fraction was obtained by evaporating the liquids in the fractionation flask. 98% of the polymer was recovered in fractions. The molecular weights of the fractions were determined by solution viscometry using the external dilution method. The fractions were also examined by analytical GPC using columns of SG 120 silica and Porasil F (aminopropyl bonded) separately and in series, with water/formamide (5:1) as eluent.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Polymerisation of Acrylamide

In Chapter 1 it was stated that a major aim was to synthesise low conversion polyacrylamides which were free from contaminants for GPC studies. Most commercially available polyacrylamides are synthesised to high conversion and contaminants, such as emulsifiers, are present. The initial experiments were performed with an isomantle as the source of heat. Typical results are shown in Table 4.1 for polymerisation times of two hours.

Polymer 4 prepared in the absence of chain transfer agent had a high molecular weight. The molecular weight may be reduced by including the chain transfer agent in the polymerisation, creating more short chains (see equation (2.16)) and a broader molecular weight distribution. However, both polymers in Table 4.1 were produced at high conversions of monomer. Furthermore, the exothermic nature of the reaction was not easy to control with the isomantle arrangement. Although the results in Table 4.1 demonstrated the preparation of polyacrylamide with molecular weights below one million, it was felt a better control of the reaction conditions was required in order to produce low conversion polymers.

In all subsequent work a water-bath was used to allow a better dissipation of the heat of reaction. The chain transfer agent was omitted because of its tendency to broaden the molecular weight distribution (see equation 2.16). Control of conversion and polymer molecular weight in acrylamide polymerisations will then depend on initiator concentration, monomer concentration, reaction time and reaction temperature. Initial experiments on the influence of temperature are given in Table 4.2 for polymerisations performed for two hours.

Table 4.1

Synthesis of polymers using isomantle as source of heat

| Polymer | [M] moles l ⁻¹ | [I] × 10 ⁻³ moles l ⁻¹ | [SH] moles l ⁻¹ | % conversion | Temp. °C | \bar{M}_v |
|---------|------------------------------|---|-------------------------------|--------------|-------------|-------------|
| 3 | 1.759 | 0.612 | 0.309 | 58.3 | 75 → 80 | 168,000 |
| 4 | 1.762 | 0.612 | - | 74.2 | 75 → 80 | 516,500 |

Table 4.2

Effect of temperature on polymer yield

| Polymer Sample | [M] moles l ⁻¹ | [I] × 10 ⁻³ moles l ⁻¹ | % conversion | Temp. of reaction °C | \bar{M}_v |
|-------------------|------------------------------|---|--------------|-------------------------|-------------|
| 12 | 0.155 | 0.047 | 36.8 | 75 | 47,000 |
| 13 | 0.159 | 0.054 | 33.8 | 75 | 40,700 |
| 14 | 0.238 | 0.954 | 38.3 | 75 | 13,000 |
| 15 | 0.238 | 0.952 | - | 45 | - |
| 16 | 0.238 | 0.952 | - | 45 | - |

In polymers 12→16 inclusive as tabulated in Table 4.2, there exists a difference in varying the reaction temperature. The similar reaction conditions for polymers 12 and 13 give almost the same values for conversion and molecular weight. For polymer 14 the decrease in molecular weight arises from the large increase in the initiator concentration rather than the much smaller change in the monomer concentration, see equation (2.14). The lack of polymer in experiments 15 and 16 was rather surprising. This suggested that lower temperatures of polymerisation might be a way of producing acceptable polymers at low conversions. This was tested by performing polymerisations with higher monomer and initiator concentrations at the reaction temperature of 45°C. The results are outlined in Table 4.3.

Polymers 17 and 18 were prepared under the same conditions except that the reaction time for polymer 17 was twice that for polymer 18. As expected, a higher conversion was obtained for polymer 17. All the polymers in Table 4.3 had very high molecular weights which were unacceptable for GPC studies. The molecular weight may be reduced by increasing the initiator concentration, see equation (2.14), but the fast initiation rates which also result will raise the conversion. Polymerisations 22, 24, 27 and 28 performed for short times with high initiator concentrations were not successful in producing polymers with acceptable molecular weights for GPC, see Table 4.3. The dependence of conversion on time for these polymerisations is plotted in Figure 4.1. The low conversion for polymer 20 and for polymers 15 and 16 in Table 4.2 may be due to traces of residual stabiliser or metal ions in the monomer (Section 2.14).

It was concluded that lower polymerisation temperatures whilst reducing the conversion by appropriate control of initiator concentration and reaction time produced polyacrylamide chains which were much too long. In view of the molecular weight data in Table 4.2, it was decided to perform polymerisations at 70°C in order to find ways of reducing the conversion. All the conditions in Table 4.2 were held constant apart from the initiator

FIGURE 4.1

% CONVERSION VERSUS TIME

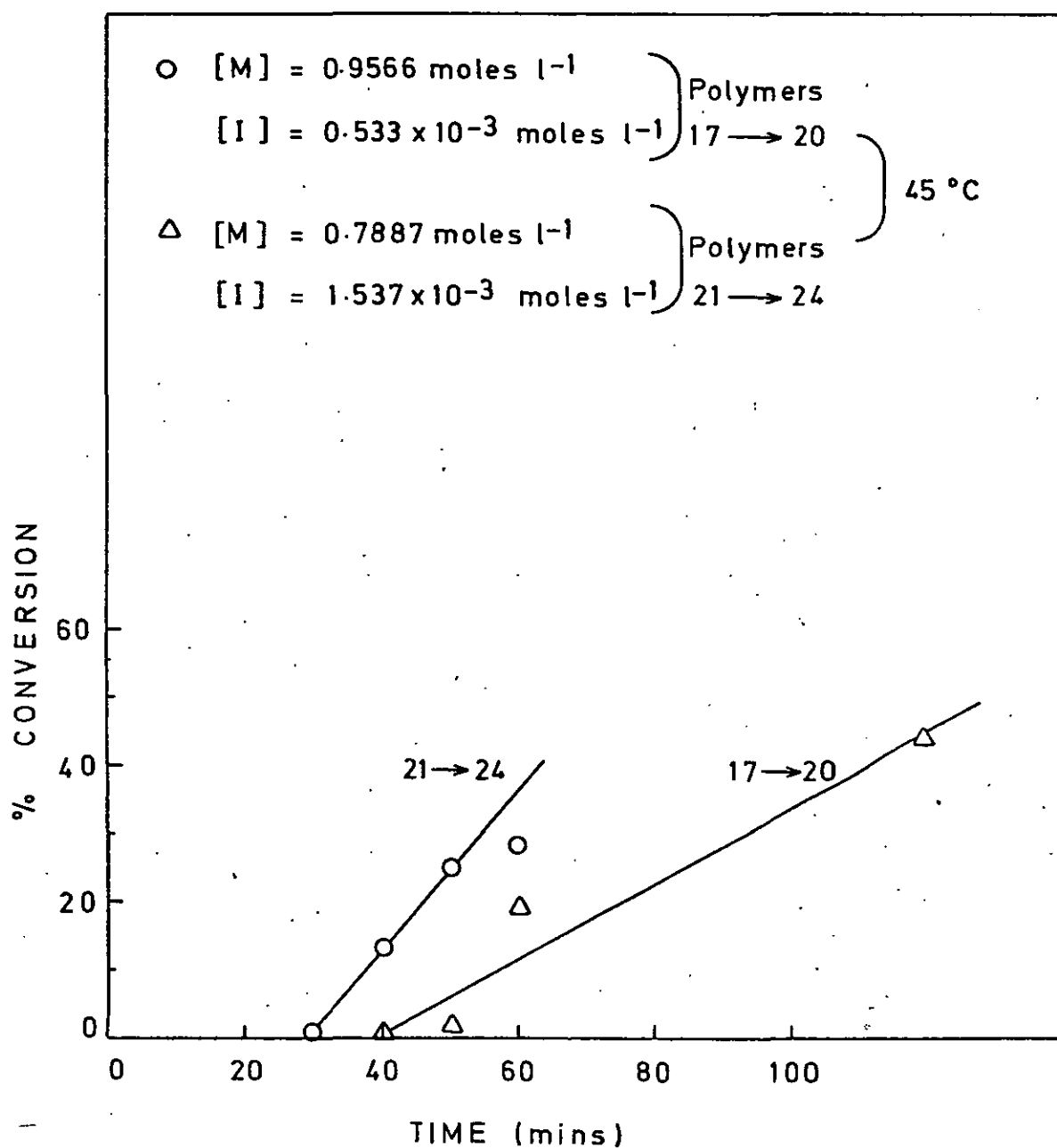


Table 4.3

% Conversion versus reaction time

| Polymer Sample | [M] moles l ⁻¹ | [I] x 10 ⁻³ moles l ⁻¹ | Reaction time (mins.) | % conversion | Temp. of reaction °C | \bar{M}_v |
|----------------|------------------------------|---|--------------------------|--------------|-------------------------|---------------------|
| 17 | 0.957 | 0.533 | 120 | 44.2 | 45 | 2 x 10 ⁶ |
| 18 | 0.957 | 0.533 | 60 | 19.2 | 45 | 2 x 10 ⁶ |
| 19 | 0.957 | 0.527 | 40 | - | 45 | - |
| 20 | 0.957 | 0.527 | 50 | 2.0 | 45 | 3 x 10 ⁶ |
| 21 | 0.789 | 1.537 | 60 | 28.1 | 45 | - |
| 22 | 0.789 | 1.537 | 50 | 24.8 | 45 | 3 x 10 ⁶ |
| 23 | 0.789 | 1.537 | 30 | - | 45 | - |
| 24 | 0.789 | 2.921 | 40 | 12.6 | 45 | - |
| 27 | 0.789 | 2.945 | 30 | 11.1 | 45 | 2 x 10 ⁶ |
| 28 | 0.758 | 2.814 | 30 | 7.7 | 45 | 2 x 10 ⁶ |

concentration, giving the results shown in Table 4.4. These data which are plotted in Figure 4.2 show that the increase in the rate of polymerisation and the decrease in the molecular weight as the initiator concentration is raised is in accordance with equations (2.31) and (2.14). Table 4.4 shows that polymers with acceptable molecular weights may be produced by low conversion (< 20%) polymerisation. An alternative investigation is to hold all conditions constant apart from the monomer concentration. The results of such experiments are shown in Table 4.5 and are plotted in Figure 4.3. These results are again in agreement with the theoretical equations (2.34) and (2.14) that the rate of polymerisation and the molecular weight of the polymer should increase on raising the monomer concentration.

These results demonstrate that polymerisations performed at 70°C will yield low conversion (< 20%) polymers with an average molecular weight in the range 10^4 to 10^6 , provided the monomer and initiator concentrations and reaction time are correctly chosen. This work is an improvement on the experiments reported by Sorenson and Campbell (66) and Riggs and Rodriguez (54) who were able to prepare polymers with molecular weights below one million but their monomer conversions were very high. Further examples of polymers suitable for GPC analysis are shown in Table 4.6. All these polymerisations were performed at 70°C for a time of 120 min. By restricting the polymerisation conversion below 20%, it is hoped that the molecular weight distribution will be close to one of the theoretical distribution functions, equations (2.20) and (2.21). The lowering of the polymerisation temperature to reduce the conversion does not appear to be advantageous because of the tendency to increase the degree of polymerisation, see Table 4.3.

4.2 Solution Viscosity of Polyacrylamide

As described in Section 2.2.2, several workers have reported that the viscosity of dilute polyacrylamide solutions may change depending on solvent,

Table 4.4

% Conversion and molecular weight versus initiator concentration

| Polymer Sample | % conversion | Molecular weight | Initiator concentration moles $l^{-1} \times 10^{-3}$ |
|----------------|--------------|------------------|--|
| 45 | 22 | 476,000 | 0.085 |
| 46 | 11.3 | 574,100 | 0.077 |
| 56 | 15.09 | 420,300 | 0.094 |
| 58 | 16.6 | 316,000 | 0.106 |

$$[M] = 0.235 \text{ moles } l^{-1} \text{ at } 70^{\circ}\text{C}$$

Table 4.5

% Conversion and molecular weight versus monomer concentration

| Polymer Sample | % conversion | Molecular weight | Monomer concentration moles l^{-1} |
|----------------|--------------|------------------|---|
| 55 | 11.72 | 60,000 | 0.149 |
| 57 | 15.63 | 90,500 | 0.155 |
| 46 | 11.3 | 574,100 | 0.221 |
| 42 | 36.0 | 308,000 | 0.235 |

$$[I] = 0.077 \text{ moles } l^{-1} \text{ at } 70^{\circ}\text{C}$$

Table 4.6Conditions necessary to prepare low conversion polyacrylamides

| Polymer Sample | [M] moles l ⁻¹ | [I] x 10 ⁻³ moles l ⁻¹ | % conversion | Temp. °C | Reaction time (mins.) | Molecular Weight |
|-------------------|------------------------------|---|--------------|-------------|-----------------------------|---------------------|
| 50 | 0.155 | 0.067 | 18.47 | 70 | 120 | 123,550 |
| 51 | 0.155 | 0.057 | 28.88 | 70 | 120 | 135,750 |
| 55 | 0.146 | 0.072 | 11.72 | 70 | 120 | 60,000 |
| 57 | 0.155 | 0.079 | 15.63 | 70 | 120 | 90,500 |

temperature, time and storage conditions. Various reasons have been proposed for the experimental results (115-119). Initially, results shown in Figures 4.4 and 4.5 were obtained, which do not correspond to the theoretical behaviour predicted by equations (2.37) and (2.38). Similar observations have been reported by other workers (115-119). Polymers PA7 and PA11 were high conversion polymers and would be expected to have a broad molecular weight distribution. Because of the possibility that very long polyacrylamide chains may be trapped in the GPC apparatus, all solutions were filtered before being examined by any solution characterisation technique. The loss of any polymer during this operation will change the concentration, so that the observations in Figures 4.4 and 4.5 could result from incorrect polymer concentrations. From the literature survey (32) it would appear that the monitoring of the concentration of polymer in the filtrate has not been considered previously. Further, polyacrylamide on mixing with aqueous solvents does not reach equilibrium very rapidly, so that insufficient time may have been allowed between the viscosity determinations for each diluted solution. Consequently, the filtration and dilution procedures were further investigated.

4.2.1 Filtration

A solution of a high conversion polymer PA5 ($\bar{M}_v = 668,000$) in water was prepared, as described in Section 3.2, and divided into four equal aliquots. Each solution was filtered through a Whatman's Grade A filter paper which is based on a cellulose material. The polymer concentration of each filtrate was determined gravimetrically and the results are given in Table 4.7. It is observed that there is a reproducible retention of some polyacrylamide on the filter paper.

Solution viscometry was then performed on each solution using the external dilution method, see Section 3.2.2. The results are given in Table 4.8. The viscosity plots obtained were of the conventional type and

FIGURE 4.2

POLYMERIZATION RATES AND POLYMER MOLECULAR WEIGHTS
ON INITIATOR CONCENTRATION

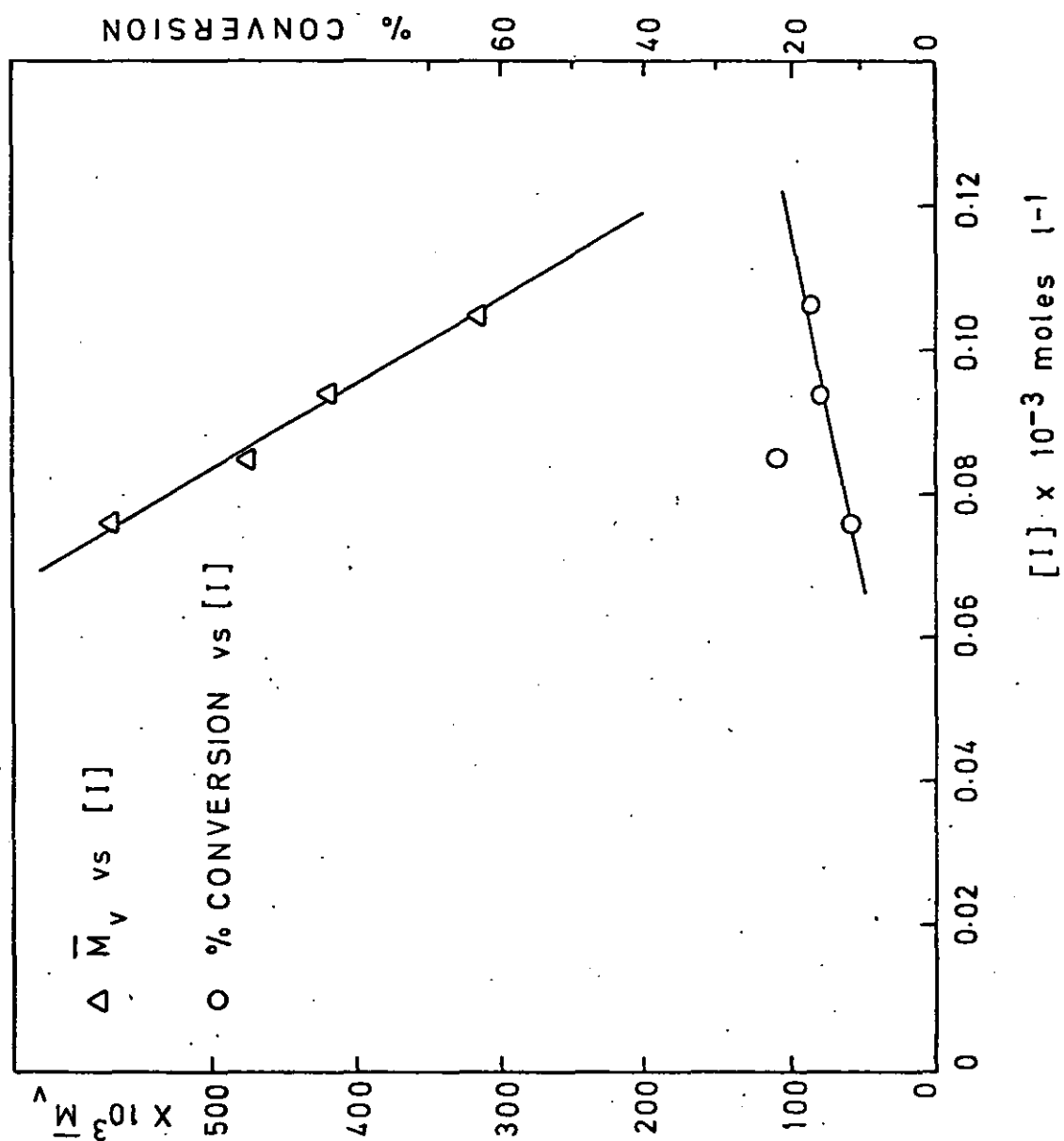


FIGURE 4.3

POLYMERIZATION RATES AND POLYMER MOLECULAR WEIGHTS
ON MONOMER CONCENTRATION

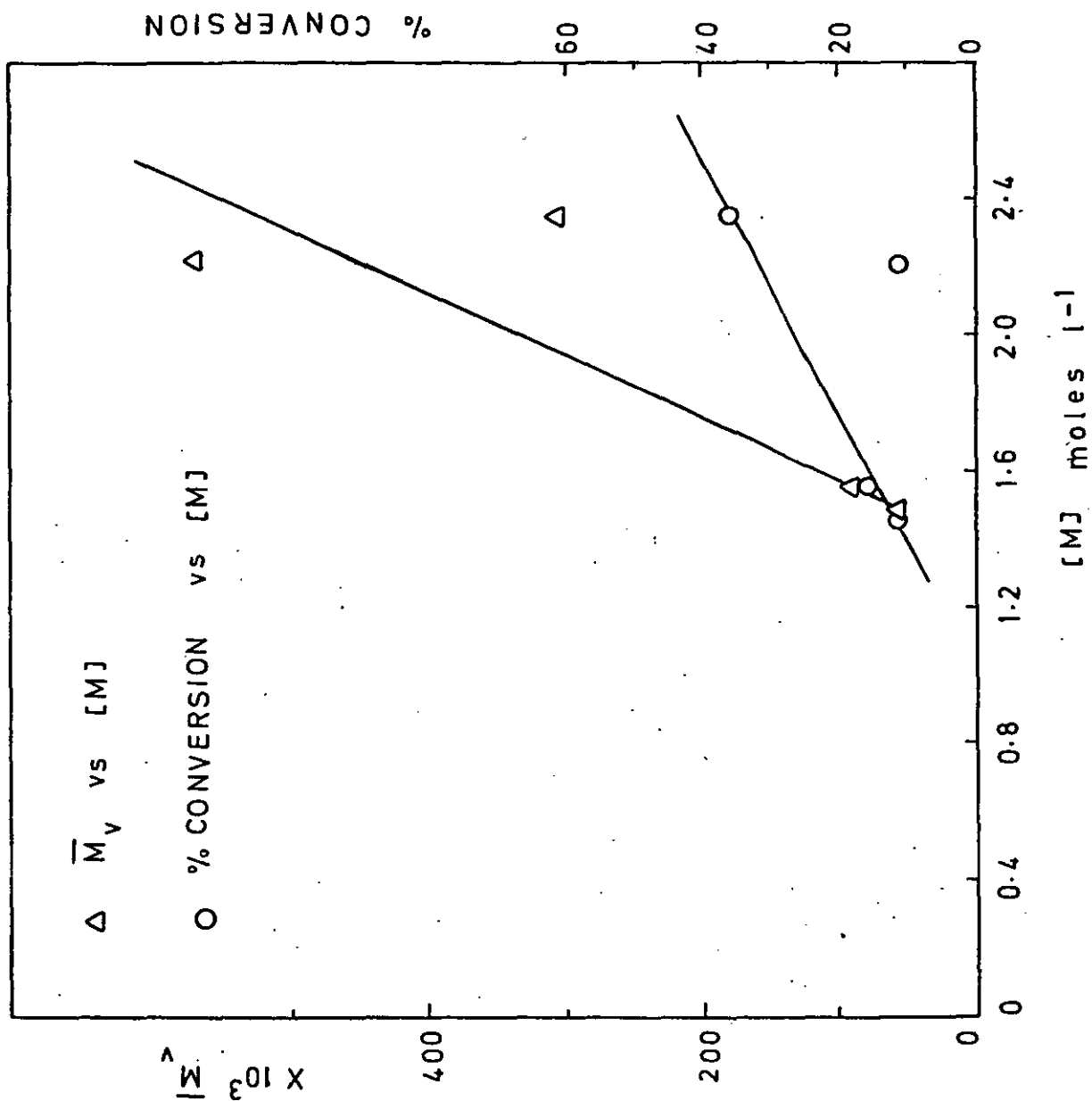


Table 4.7Polyacrylamide PA5 filtered through Whatman's Grade A filter paper

| Polymer PA5 solution | Initial concentration | Final concentration | % loss |
|----------------------|-----------------------|---------------------|--------|
| First | 0.418 | 0.310 | 25.86 |
| Second | 0.418 | 0.317 | 24.18 |
| Third | 0.418 | 0.318 | 23.94 |
| Fourth | 0.418 | 0.313 | 25.14 |

Table 4.8Viscosity analysis of PA5 solutions

| Polymer PA5 solution | $[\eta]$ | \bar{M}_v | K' | β | $K' + \beta$ |
|----------------------|----------|-------------|-------|---------|--------------|
| First | 3.80 | 476,100 | 0.573 | 0.023 | 0.596 |
| Second | 3.80 | 476,100 | 0.563 | 0.061 | 0.624 |
| Third | 3.90 | 495,200 | 0.480 | 0.097 | 0.577 |
| Fourth | 3.75 | 466,600 | 0.610 | 0.009 | 0.619 |

FIGURE 4.4

SOLUTION VISCOSITY OF PA 11 (INTERNAL DILUTION)

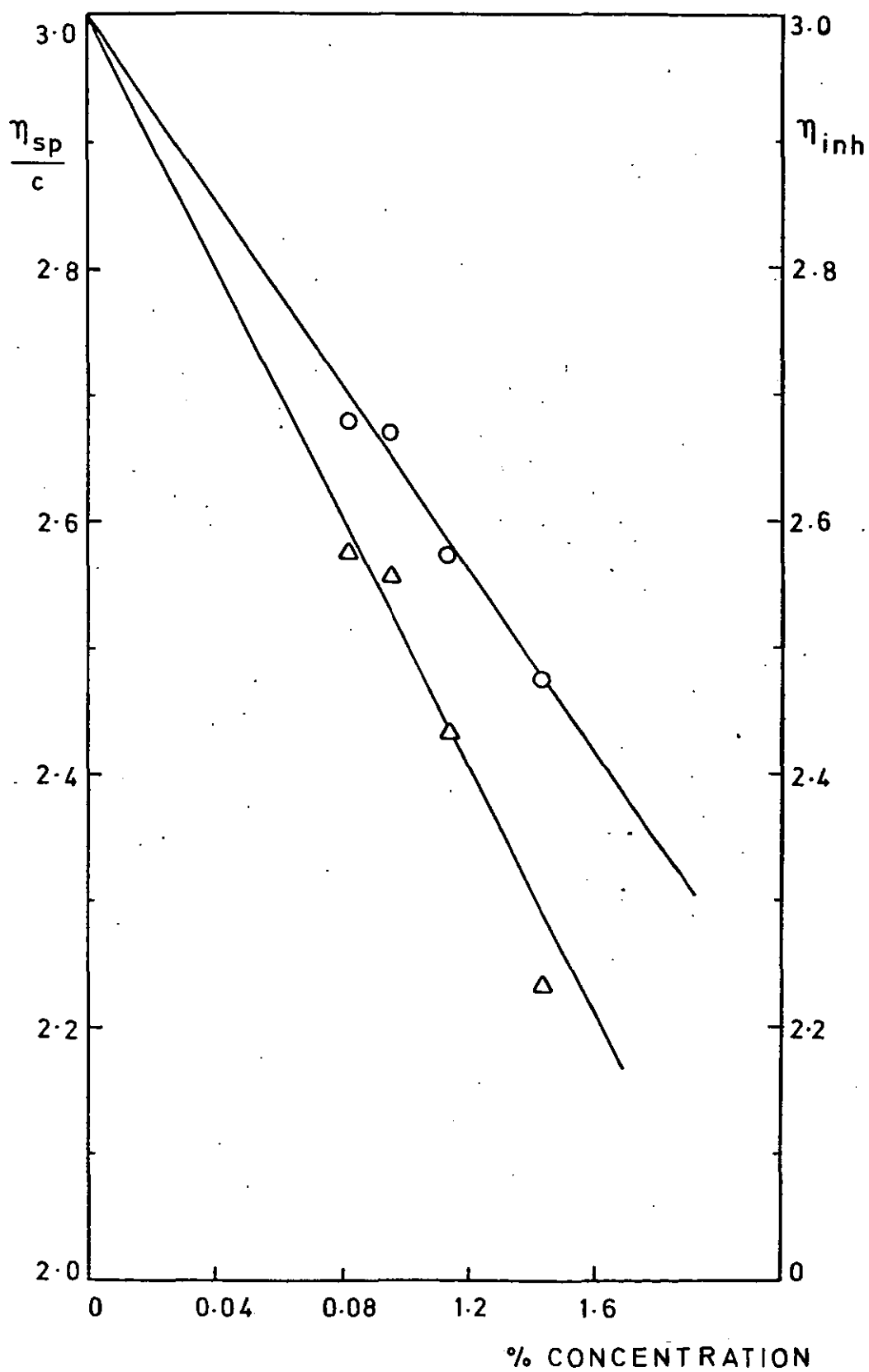
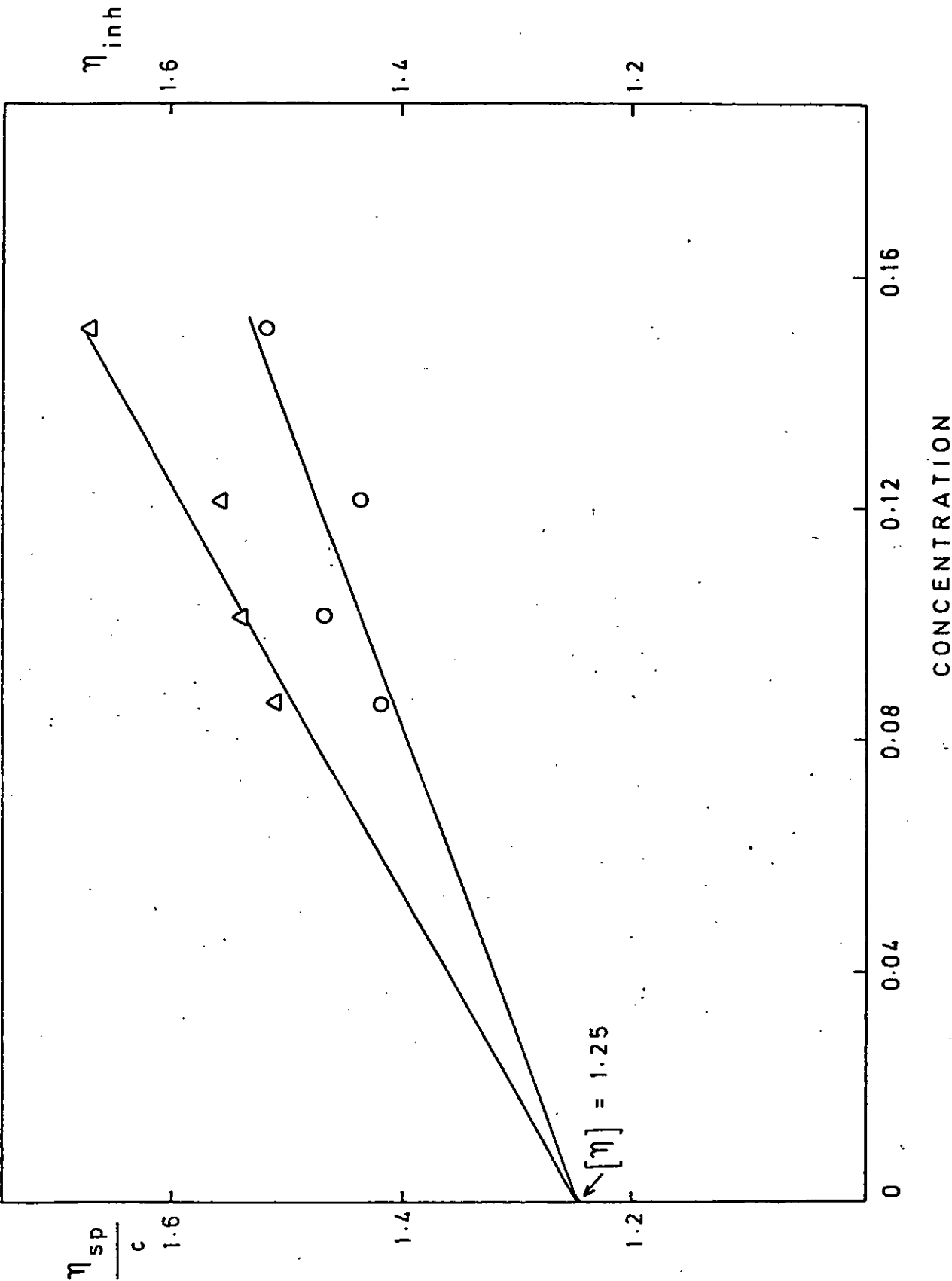


FIGURE 4.5

SOLUTION VISCOSITY OF PA 7 (INTERNAL DILUTION)



the molecular weights were quite reproducible, Figure 4.6. The Huggins constant K' and Kraemer constant β average around 0.59 which is typical of conventional type plots, see Section 2.2.

The large loss of polymeric material shown in Table 4.7 may result in a different molecular weight distribution from that of the as-polymerised product. If it is assumed that no polymer is lost on filtration then values of η_{sp} and η_{inh} for polyacrylamides PAll ($\bar{M}_v = 144,000$) and PA7 ($\bar{M}_v = 46,000$) such as those in Figures 4.4 and 4.5, will not be calculated correctly. This is likely to lead to errors in determining $[\eta]$, so that the value of \bar{M}_v could be incorrect.

The filtration unit for the GPC solutions consisted of a stainless steel mesh which is placed on a filter paper of a glass fibre composition supported by a stainless steel disc having an outlet for the filtered solution to pass through. A Teflon ring acts as a gasket between the filtration unit and the reservoir for the solution which are clamped together very tightly so that filtration can be performed under high pressures. With filter paper (Whatman's GF/C) in this unit, a solution of polyacrylamide PA5 divided into two equal aliquots was filtered. The concentration of the filtrate was monitored gravimetrically. The results are tabulated in Table 4.9. Each filtered solution was placed in a viscometer and the intrinsic viscosity was determined by the external dilution method, see Section 3.2.2. The solution viscosity results are presented in Table 4.10. The results in Table 4.9 demonstrate that the GF/C filter paper retains less polyacrylamide than the Grade A filter paper, see Table 4.7. The retention on the GF/C filter paper is reproducible in terms of polymer loss and solution viscosity, and the values of \bar{M}_v for polymer determined from solutions filtered through the two types of filter paper are similar. It was decided in all this research work to filter all solutions through the GPC unit containing the Whatman's grade GF/C filter paper before attempting any solution characterisation experiments. The polyacrylamide concentration determined gravi-

Table 4.9Polyacrylamide PA5 filtered through Whatman's Grade GF/C filter paper

| PA5 solution | Initial concentration | Final concentration | % loss |
|--------------|-----------------------|---------------------|--------|
| First | 0.418 | 0.356 | 14.85 |
| Second | 0.418 | 0.361 | 13.66 |

Table 4.10Viscosity analysis of PA5 solutions

| PA5 solution | $[\eta]$ | \bar{M}_v | K' | β | $K' + \beta$ |
|-----------------|----------|-------------|-------|---------|--------------|
| First solution | 3.65 | 447,900 | 0.443 | 0.110 | 0.553 |
| Second solution | 3.68 | 453,500 | 0.482 | 0.084 | 0.566 |

Table 4.11Solution viscosity of Polyacrylamide PAll obtained from external dilution

| Solution | $[\eta]$ | \bar{M}_v | K' | β | $K' + \beta$ |
|----------|----------|-------------|-------|---------|--------------|
| PAll | 2.1 | 194,000 | 0.587 | 0.036 | 0.063 |

metrically after filtration was used in calculating results from the characterisation experiments.

4.2.2 Dilution Method

It was postulated that the observations in Figures 4.4 and 4.5 might be explained by not allowing sufficient time for polymer and water to equilibrate when each solution is diluted within the viscometer. The solution viscosity determination of polyacrylamide PAll was repeated with solutions prepared outside the viscometer, see Section 3.2. The results from this external dilution method are shown in Figure 4.6. The data exhibit the conventional behaviour giving the results in Table 4.11. It was also found that the viscosity behaviour hardly changed after storing the solutions for a period of time, see the data in Table 4.14. This suggests that reproducible solution viscosities may be obtained and in all subsequent determinations the external dilution method was employed.

The behaviour in Figures 4.4 and 4.5 has been explained by hydrolysis, chain degradation and solution ageing (29, 116). Sheats and Linke (115) suggested the use of alcohols and glycols as stabilisers. Mark-Houwink equations for calculating \bar{M}_v are not available for polyacrylamides in solvents containing stabilisers. Alternatively, some workers suggest that the effect of hydrolysis on viscosity measurements is suppressed by adding salts, e.g. sodium chloride or sodium nitrate, or by acidifying the solution (29). Mark-Houwink equations are available for these solutions (29). However, the reproducible results in Figure 4.6 and Table 4.10 suggest that the addition of stabilisers to aqueous polyacrylamide solutions is not necessary.

4.2.3 Solution Viscosity of Polyacrylamide in Binary GPC Solvent

GPC separations of polyacrylamide were performed with an eluent consisting of a binary mixture of formamide/water (1:5) on a column of porous

silica having a chemically bonded aminopropyl phase, see Section 4.6.5.

The retention volumes for polymers in this eluent were different from those for the same polymers in pure water. Solution viscosities of a polymer in the two eluents were required in order to determine whether separation was brought about by the polymer adopting a different conformation in the binary mixture of water/formamide (5:1). An alternative explanation is that the interactions of polymer with the exposed active surface are influenced by the presence or absence of formamide in the eluent, thus determining whether separation is solely by a steric exclusion mechanism.

The results are presented in Table 4.12 and plots of viscosity data for polyacrylamide in water and in the binary mixture are shown in Figures 4.7 and 4.8. These results suggest that the hydrodynamic volume of polyacrylamide is similar in the two GPC eluents.

A mixture of water/formamide (5:1) was chosen so that the refractive index of this mixture can be accommodated by the low index prism in the refractometer. Kotera's (112) values of the Mark-Houwink constants for polyacrylamide in formamide were $k = 1.08 \times 10^{-3}$ and $a = 0.54$, equation (2.55). Collinson's (80) values of $k = 68 \times 10^{-5}$ and $a = 0.66$ were for polyacrylamide in water, equation (2.54). Then, the intrinsic viscosity for a polymer of known molecular weight in a mixture of water/formamide (5:1) can be calculated, as shown in Appendix 2, confirming the experimental observations in Table 4.12.

4.2.4 Ageing Effects on Polyacrylamide of Storage

Aqueous polyacrylamide solutions were stored in stoppered flasks and were used when needed in the GPC experiments. On one occasion the polyacrylamide solution PA7 was depleted and a fresh solution of PA7 was prepared from PA7 which had been stored in the dry state in a perspex sample tube. This solution on injection into the SG 120 GPC column using water/formamide as eluent produced a different chromatogram compared to the initial injection

Table 4.12

Comparison of intrinsic viscosities of polyacrylamide in water and water/formamide

| Polymer Sample | $[\eta]_{\text{H}_2\text{O}}$ | $[\eta]_{\text{H}_2\text{O}/\text{HCONH}_2}$ | Molecular weight _(H₂O) | $K'_{(\text{H}_2\text{O})}$ | $\beta_{(\text{H}_2\text{O})}$ | $K' + \beta_{(\text{H}_2\text{O})}$ |
|----------------|-------------------------------|--|--|-----------------------------|--------------------------------|-------------------------------------|
| PA43 | 4.7 | 4.9 | 657,000 | 0.48 | 0.09 | 0.57 |
| PA44 | 3.7 | 4.2 | 456,200 | 0.54 | 0.078 | 0.618 |
| PA45 | 3.8 | 4.2 | 476,100 | 0.418 | 0.114 | 0.532 |
| PA46 | 4.3 | 4.1 | 574,200 | 0.460 | 0.084 | 0.544 |
| PA56 | 3.15 | 3.25 | 358,300 | 0.490 | 0.062 | 0.552 |

Table 4.13

Effect of storage time on the molecular weight of polyacrylamide stored in the dry state

| Polymers | Initial Molecular Weight | Final Molecular Weight | Time interval |
|----------|--------------------------|------------------------|---------------|
| 29 | 159,000 | 341,200 | 10 months |
| 7 | 88,000 | 158,660 | 21 months |
| 9 | 152,000 | 216,650 | 10 months |
| 42 | 307,900 | 615,000 | 8 months |
| 5 | 316,000 | 668,000 | 21 months |

FIGURE 4.6

SOLUTION VISCOSITY OF PA 11 (EXTERNAL DILUTION)

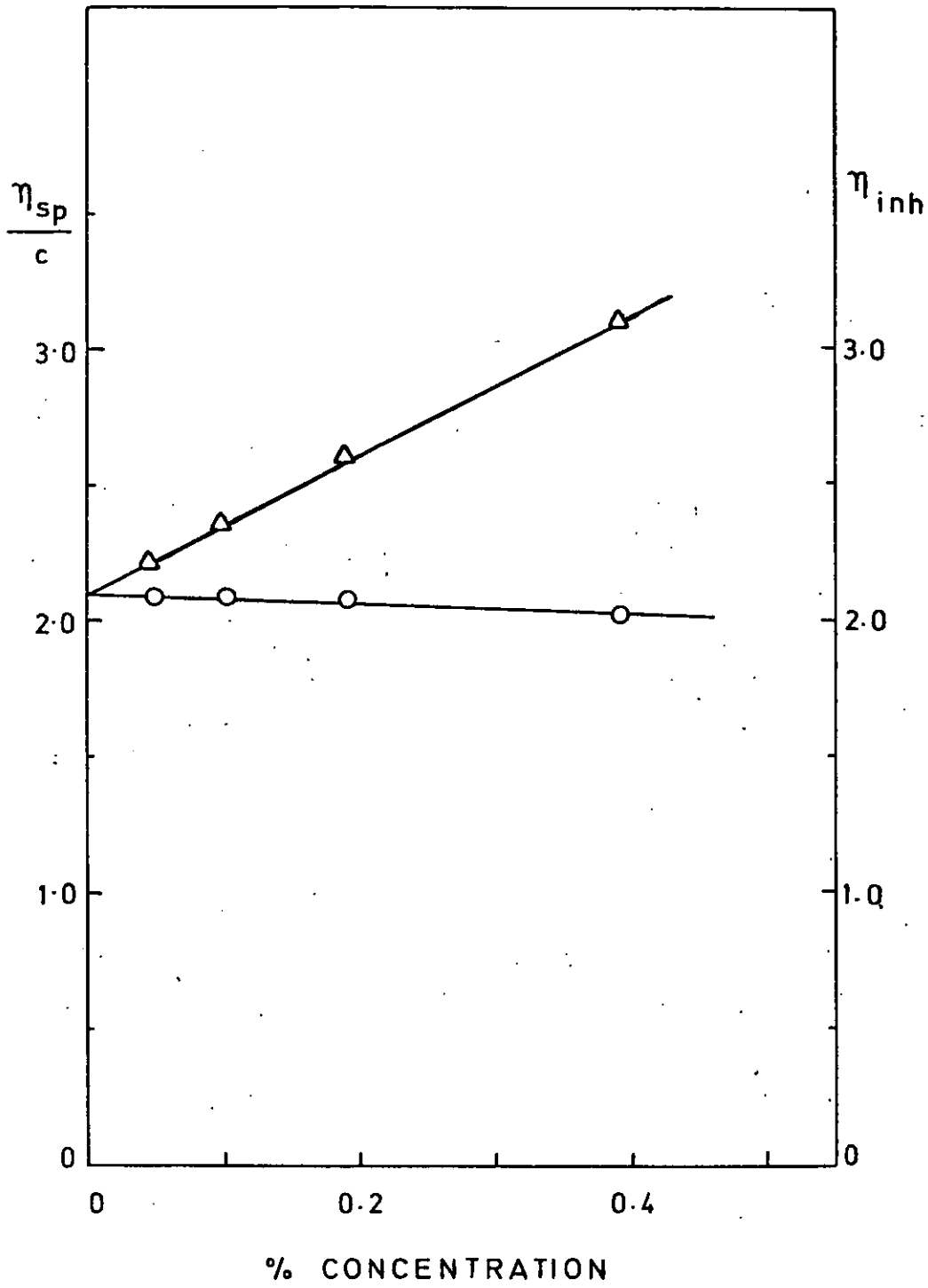


FIGURE 4.7

SOLUTION VISCOSITY OF PA43 IN WATER

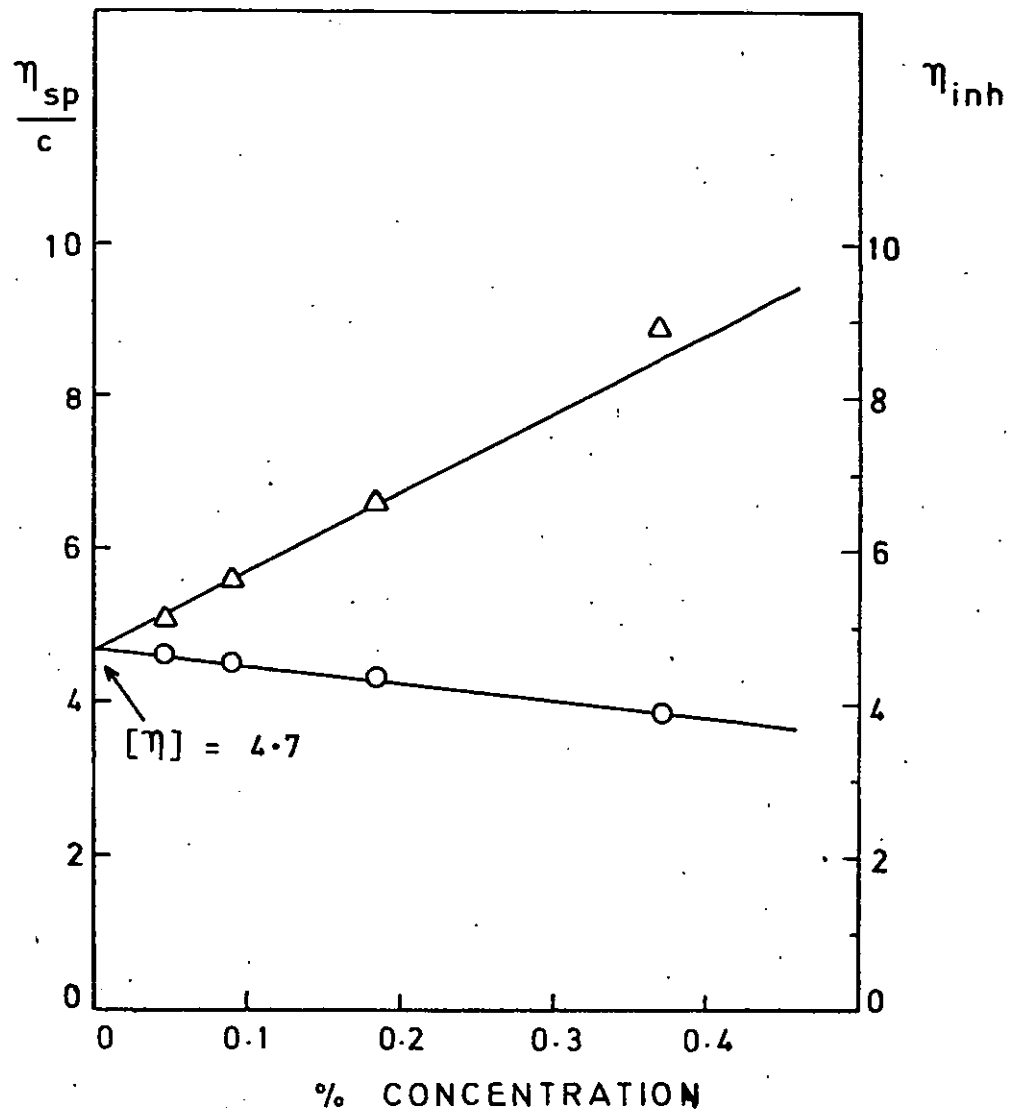
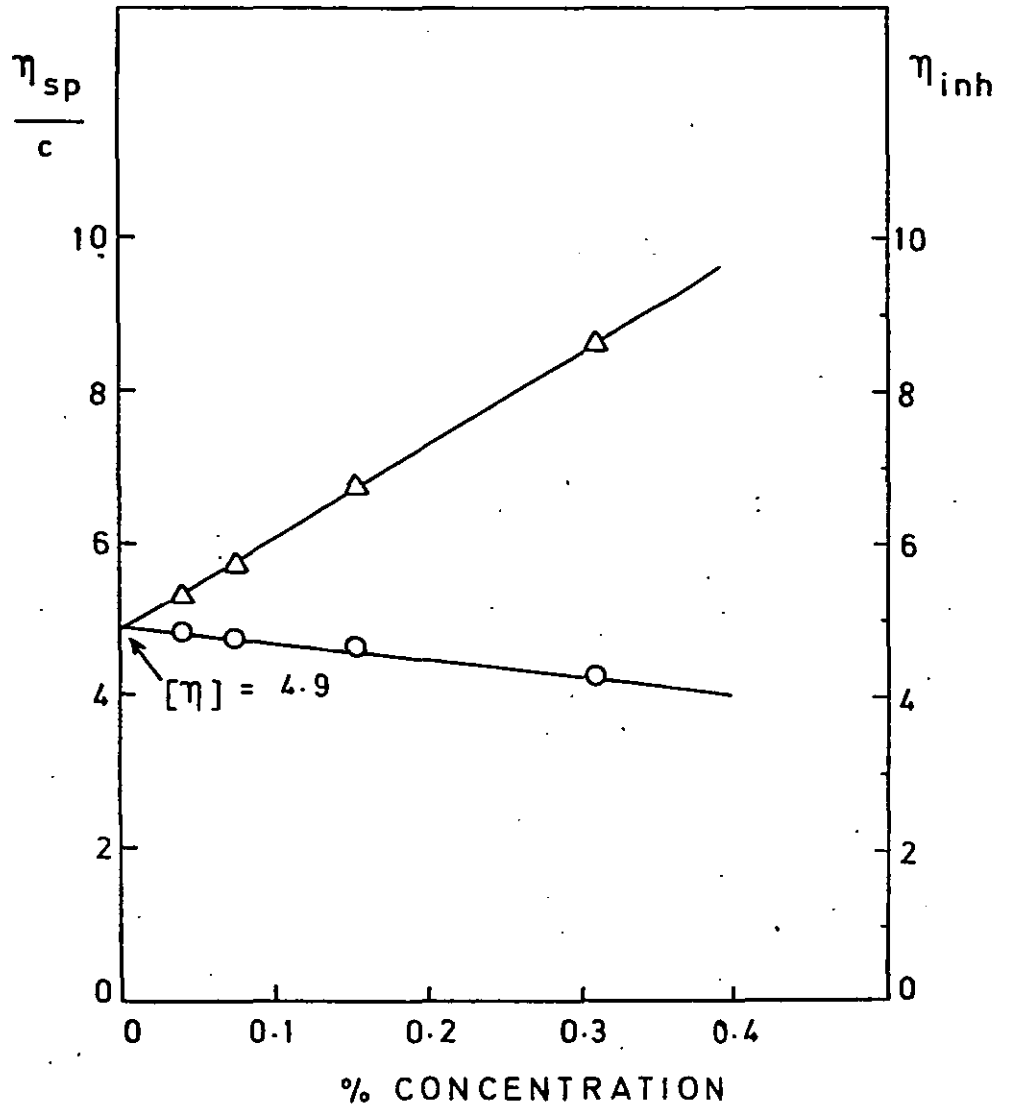


FIGURE 4.8

SOLUTION VISCOSITY OF PA43 IN FORMAMIDE/WATER (1:5)



of the original PA7 solution, see Figure 4.9. The chromatogram obtained of polyacrylamide PA7 from dry storage indicated that because the polymer was excluded from the gel the molecular weight had increased. To check this observation a viscosity determination of polyacrylamide PA7 (dry storage) was performed and twice the original molecular weight was obtained. A random selection of polymers stored in the dry state was chosen for further viscosity determinations in order to confirm this increase in molecular weight with storage time. These results are given in Table 4.13 and the viscosity data are shown in Figures 4.10 to 4.13. It was decided to perform similar experiments on polymers which had been stored in solution and the results are shown in Table 4.14. The results obtained from this experiment suggest that the molecular weight of the polymer stored in solution does not change as a function of time. It is not easy to postulate feasible explanations for these observations. In view of the reproducibility of the viscosity experiments as shown by the results in Tables 4.8, 4.10 and 4.14, it would appear that the data in Table 4.13 cannot be explained by a physical entanglement effect. Therefore, it is possible that the increase in molecular weight is due to intermolecular chemical reactions, possibly via the hydroxyl or sulphate end groups. This might be favoured by the dry state in which the polymer chains are in close proximity. However, the polyacrylamide chains are not mobile at ambient temperature, so that the reactive sites would have to be close together on precipitation and drying of the polymer. The presence of residual water giving regions which are plasticised could aid such reactions. Alternatively, the dry product could contain residual initiator which decomposes to release radicals which ultimately attack chains and lead to chain coupling. The possibility that trapped "living" long chain radicals in the solution polymerisation could persist until the dry state would appear to be remote. All of these possibilities may be activated photochemically.

FIGURE 4.9

CHROMATOGRAMS OF PA7 (INITIAL) AND PA7 (ON STANDING IN THE DRY STATE)

ELUTION ON SG120 (AMINO PROPYL) USING FORMAMIDE/WATER (1:5)

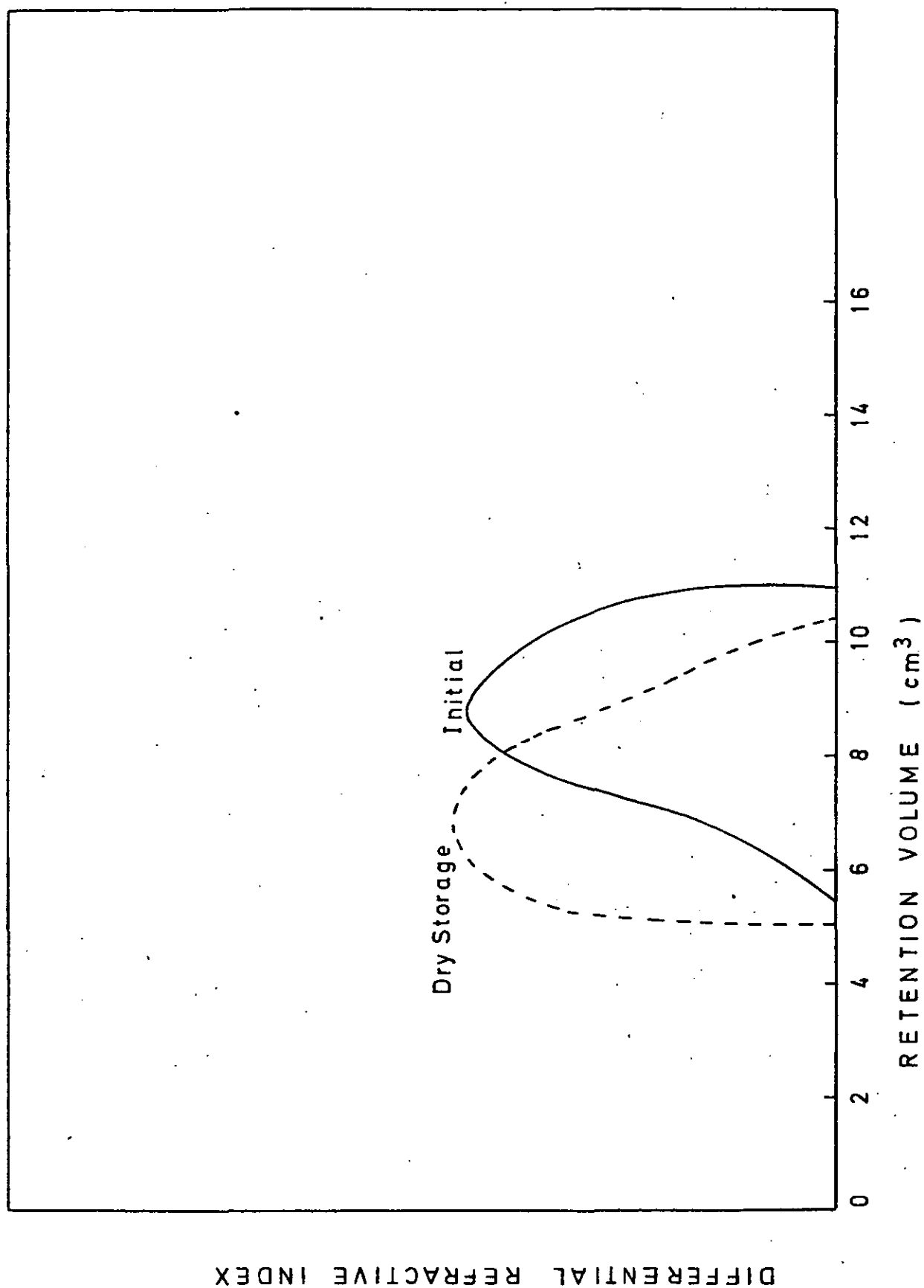


FIGURE 4.10

EFFECT OF MOLECULAR WEIGHT OF PA42
WITH TIME ON STANDING IN THE DRY STATE

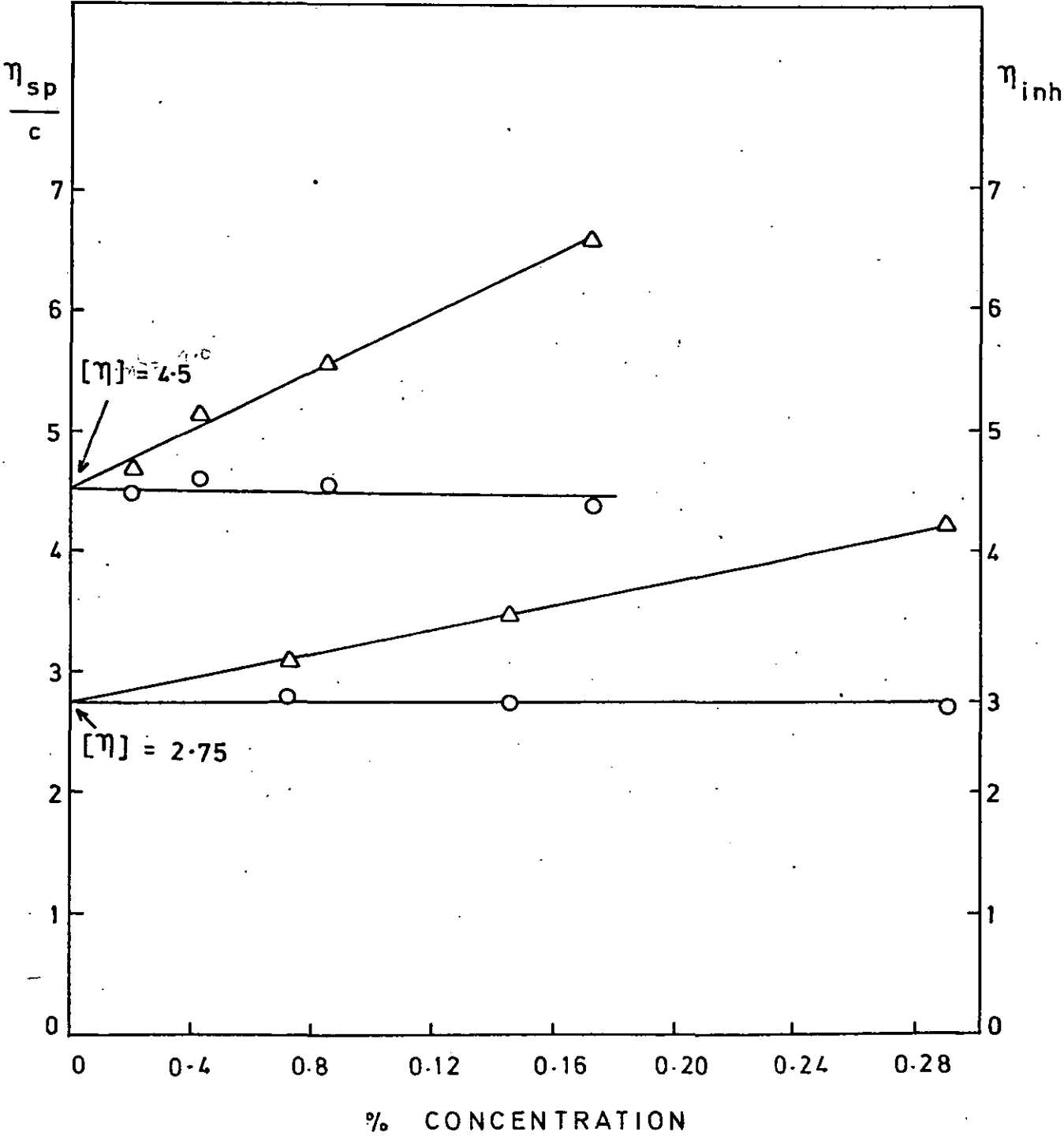


FIGURE 4.11

EFFECT OF MOLECULAR WEIGHT OF PA29
WITH TIME ON STANDING IN THE DRY STATE

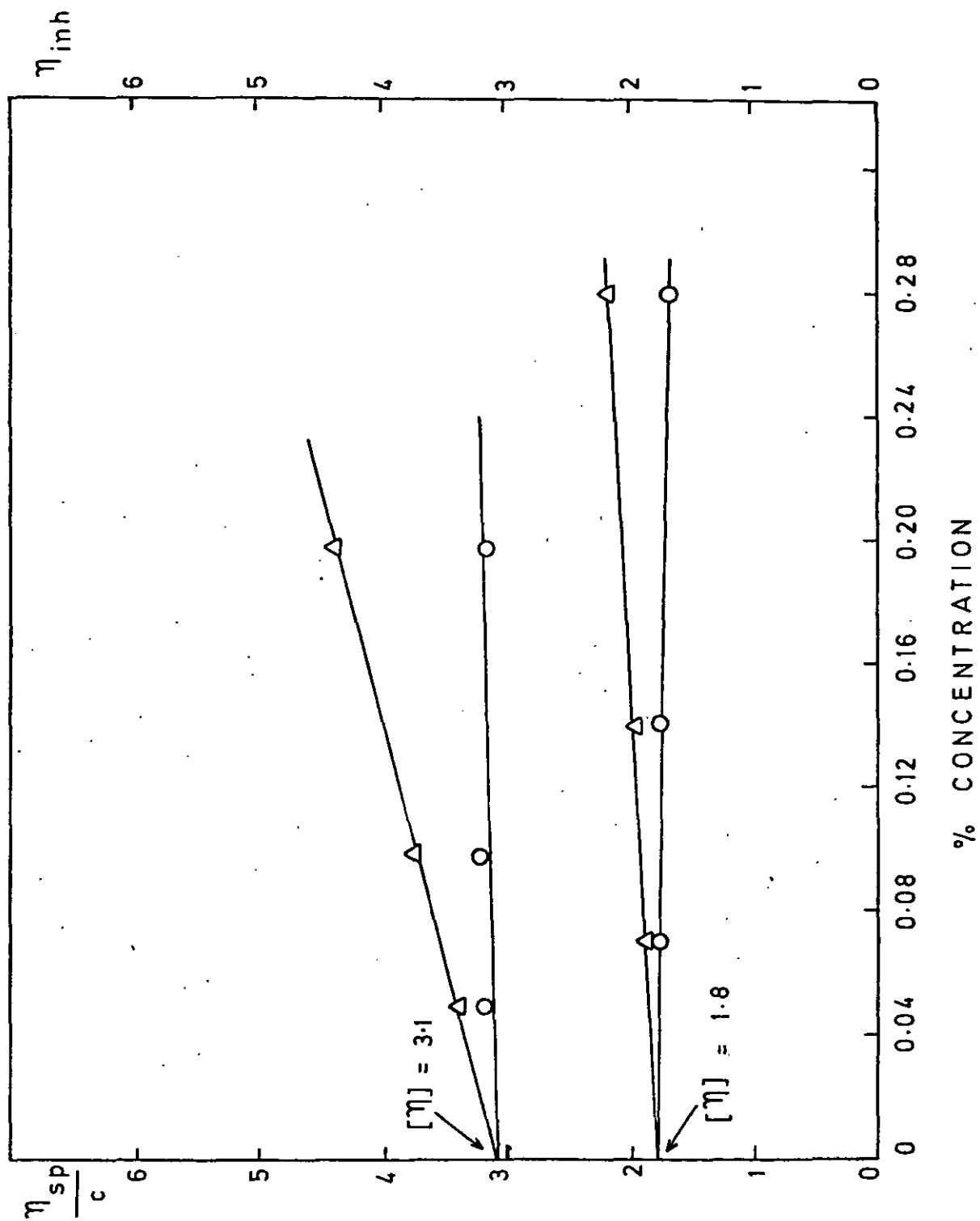


FIGURE 4.12

EFFECT OF MOLECULAR WEIGHT OF PA57 (TRI-PRECIPITATED)
WITH TIME ON STANDING IN DRY STATE

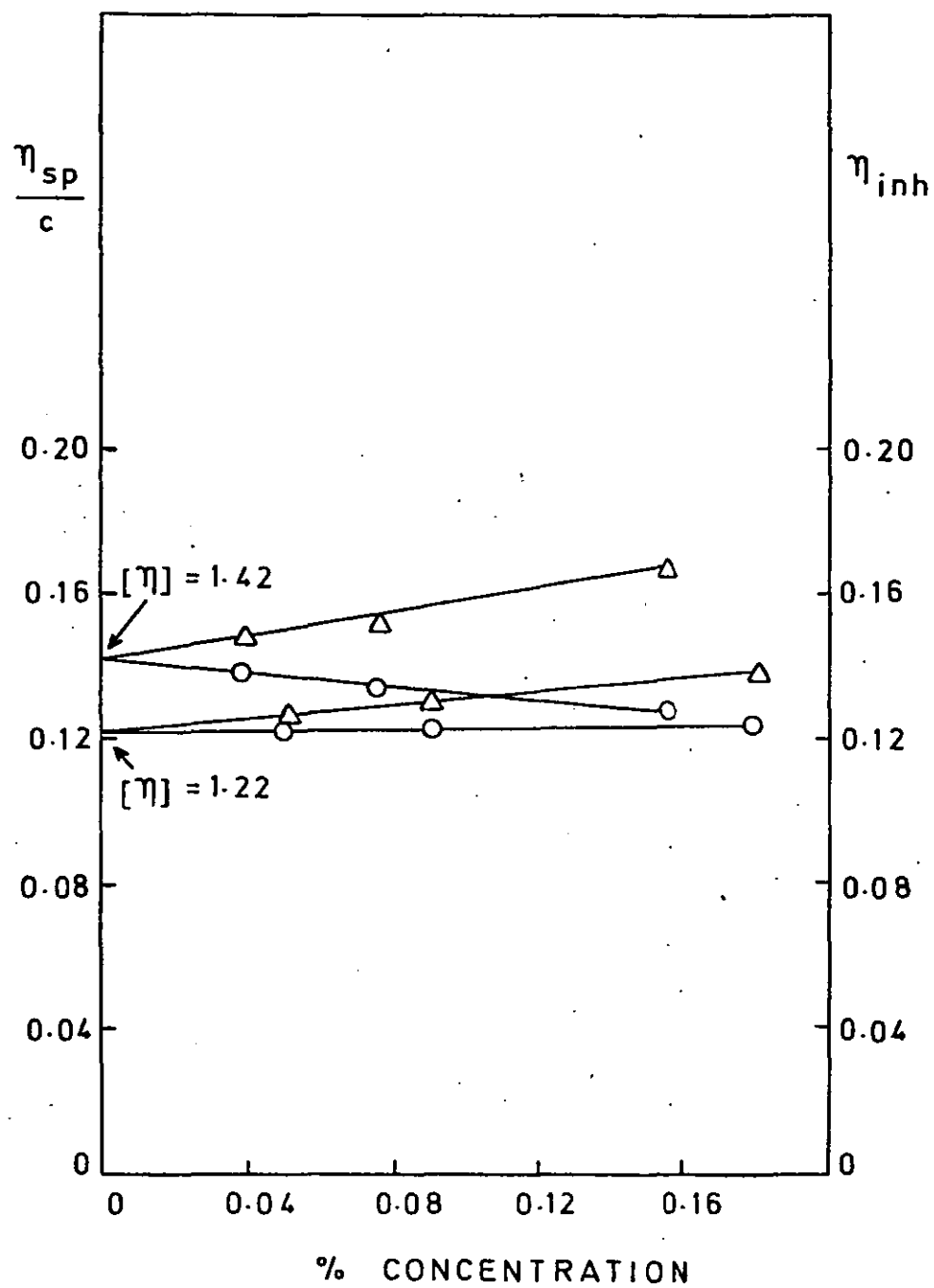


FIGURE 4.13

EFFECT OF MOLECULAR WEIGHT OF PA 9
WITH TIME ON STANDING IN THE DRY STATE

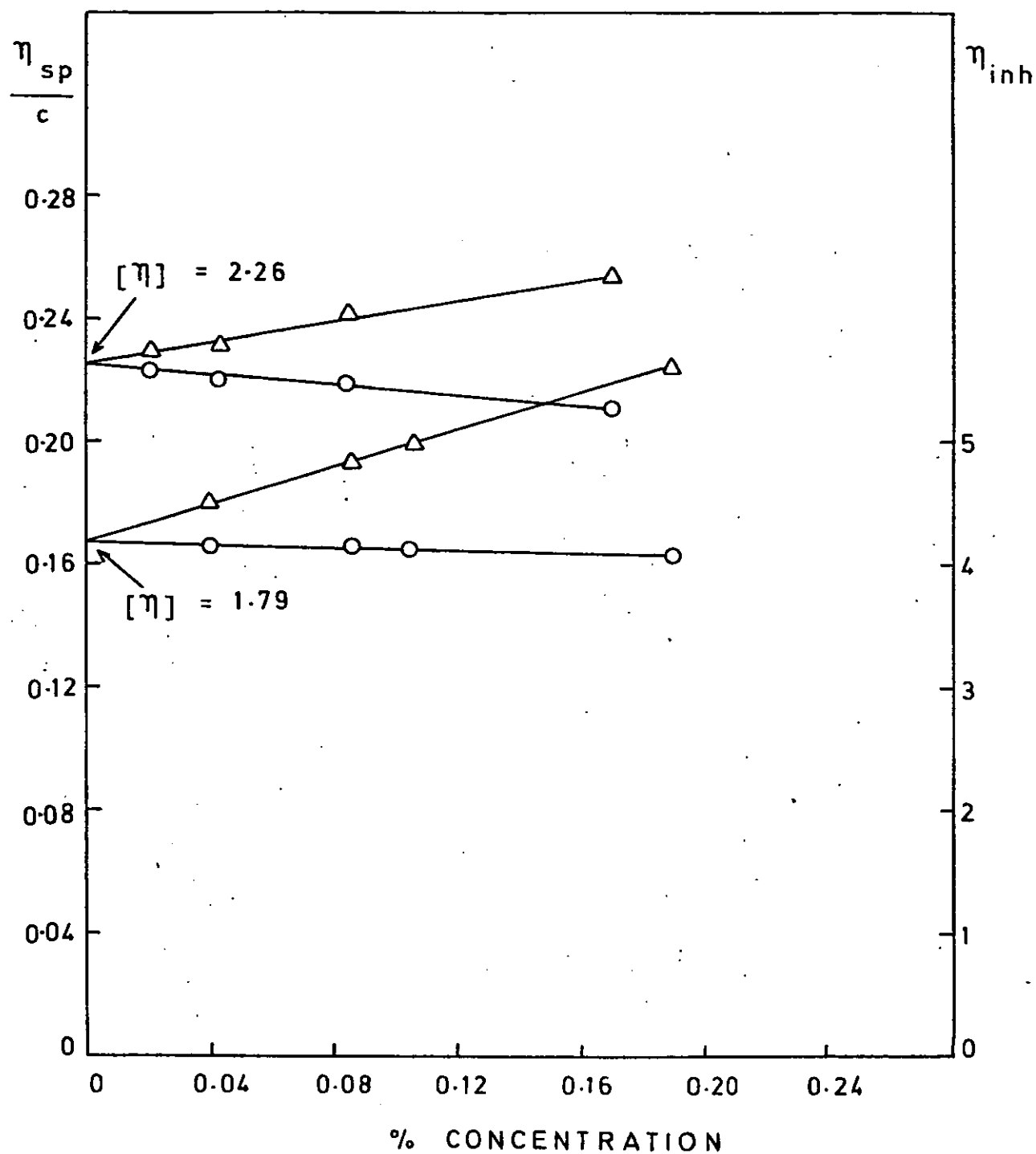


Table 4.14

Effect of storage time on the molecular weight of polyacrylamide
stored in aqueous solution

| Polymers | Initial Molecular Weight | Final Molecular Weight | Time (months) |
|----------|--------------------------|------------------------|---------------|
| 29 | 159,000 | 159,000 | 10 |
| 51 | 135,750 | 135,750 | 2.5 |
| 9 | 217,000 | 213,750 | 4 |
| 49 | 109,000 | 109,500 | 1 |

In order to try and eliminate the possibilities of residual initiator, monomer or "long-lived" radicals being involved in the change in molecular weight during dry storage of polyacrylamide, polyacrylamide PA57 was re-precipitated three times by dissolution in water and precipitation in excess methanol in order to minimise any contaminants. This polymer was stored in the dried state and the molecular weight was measured before and after storage. The results are shown in Table 4.15. After 8 weeks there was little further increase in molecular weight.

4.3 Membrane Osmometry

In Section 3.3, membrane osmometry of polyacrylamide was described. Experiments with solvents such as distilled water or buffer solutions of sodium chloride or sodium nitrate did not produce stable readings with type B19 (Hewlett Packard) membranes. Experiments were performed with formamide as solvent but both aqueous membranes (B19) and non-aqueous membranes (0-8) disintegrated. It was found that the B19 membrane did not deteriorate in a binary mixture of formamide and water (1:3). In Figure 2.3 osmotic pressure data for polyacrylamide PA43 solutions in this binary mixture were plotted according to equation (69). Straight plots similar to the linear behaviour in Figure 2.3 were obtained for other polyacrylamides as shown by the examples in Figures 4.14 → 4.16. In Table 4.16 the results obtained from membrane osmometry and viscometry and the polydispersity ratio (\bar{M}_w/\bar{M}_n) are given. The slope of the osmotic pressure curve is also included.

Although the osmotic pressure data in Figures 2.3 and 4.15 → 4.17 compare favourably with results for polymers in organic media such as polystyrene in toluene, the reliability for aqueous systems is less satisfactory. This is attributed to the diffusion of air into the system. If the binary solvent mixture is not thoroughly degassed, unstable osmotic pressure readings are produced. If the mixture is degassed correctly, stable readings are obtained, but after a period of stability there is a

Table 4.15

Molecular weight of polyacrylamide PA57 tri-precipitated
and stored in the dry state

| Storage time (weeks) | Molecular weight |
|----------------------|------------------|
| 0 | 85,100 |
| 5 | 107,150 |
| 8 | 158,000 |

detectable drift of readings with time. The results documented in Table 4.16 were obtained immediately when the eluent was degassed and the osmometer was set up. However, in some experiments the measurements for one polymer at a series of concentrations required one day's work during which air could diffuse into the system. This possible drift will determine the accuracy of the results for the polyacrylamides in Table 4.16 because the osmotic pressure is about 1-2 cm for polymer concentrations around 1%. Consequently, the values for \bar{M}_n are less reliable than the data for \bar{M}_v . However, the values for \bar{M}_v/\bar{M}_n in Table 4.16 are in the range ($\bar{M}_w/\bar{M}_n = 1.5-2.0$) predicted, see Section 2.3, for a low conversion polymerisation unaffected by side reactions.

There is little work reported in the literature on osmotic pressure measurements of synthetic polymers in aqueous media. However, the results of Coll (176) confirm that osmotic pressure measurements of aqueous solutions are not straight forward. He determined \bar{M}_n for two surfactants, Tergitol 15-59 (Union Carbide) and Neodol 25-9 (Shell Chemical Co.) using water as the solvent. He showed that after four hours the osmotic pressure was constant after decreasing initially. He also showed that the osmotic pressure of Aerosol OT (d 2-ethylhexyl sodiumsulfosuccinate) increased with time and the slope decreased with time. This led him to believe that two possibilities could have arisen. Firstly, the solute was permeating through the membrane and secondly, sorption of the solute on the membrane was taking place. He proved the first was not happening.

4.4 Fractional Precipitation

Since the position of the molecular weight calibration in GPC is dependent on polymer structure, it was necessary to prepare fractions of polyacrylamide. The technique of fractional precipitation was chosen for the fractionation experiments as described in Section 2.5. The highest molecular weight fraction is produced first followed by fractions having

FIGURE 4.14

MEMBRANE OSMOMETRY OF PA44

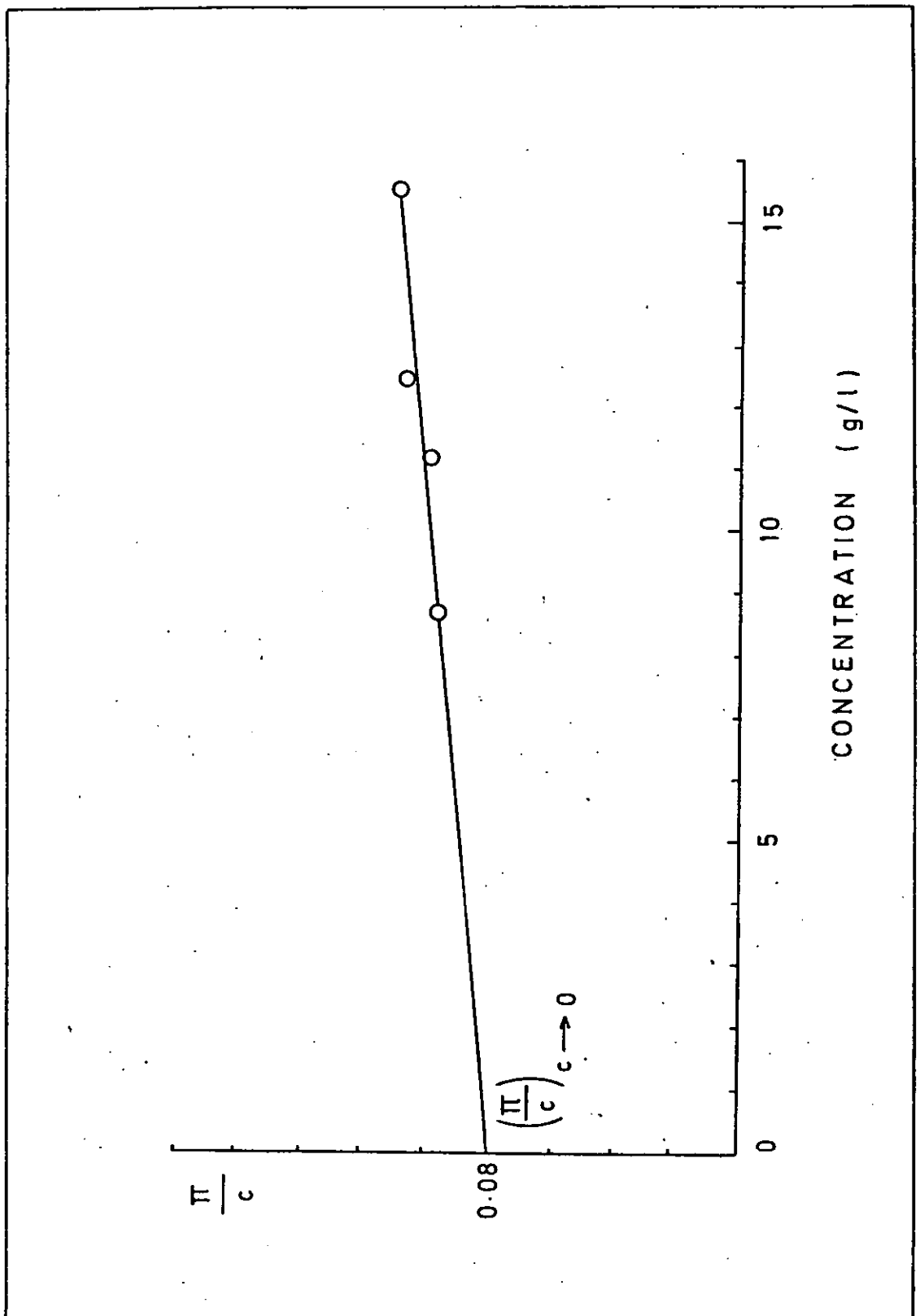


FIGURE 4.15

MEMBRANE OSMOMETRY OF PA45

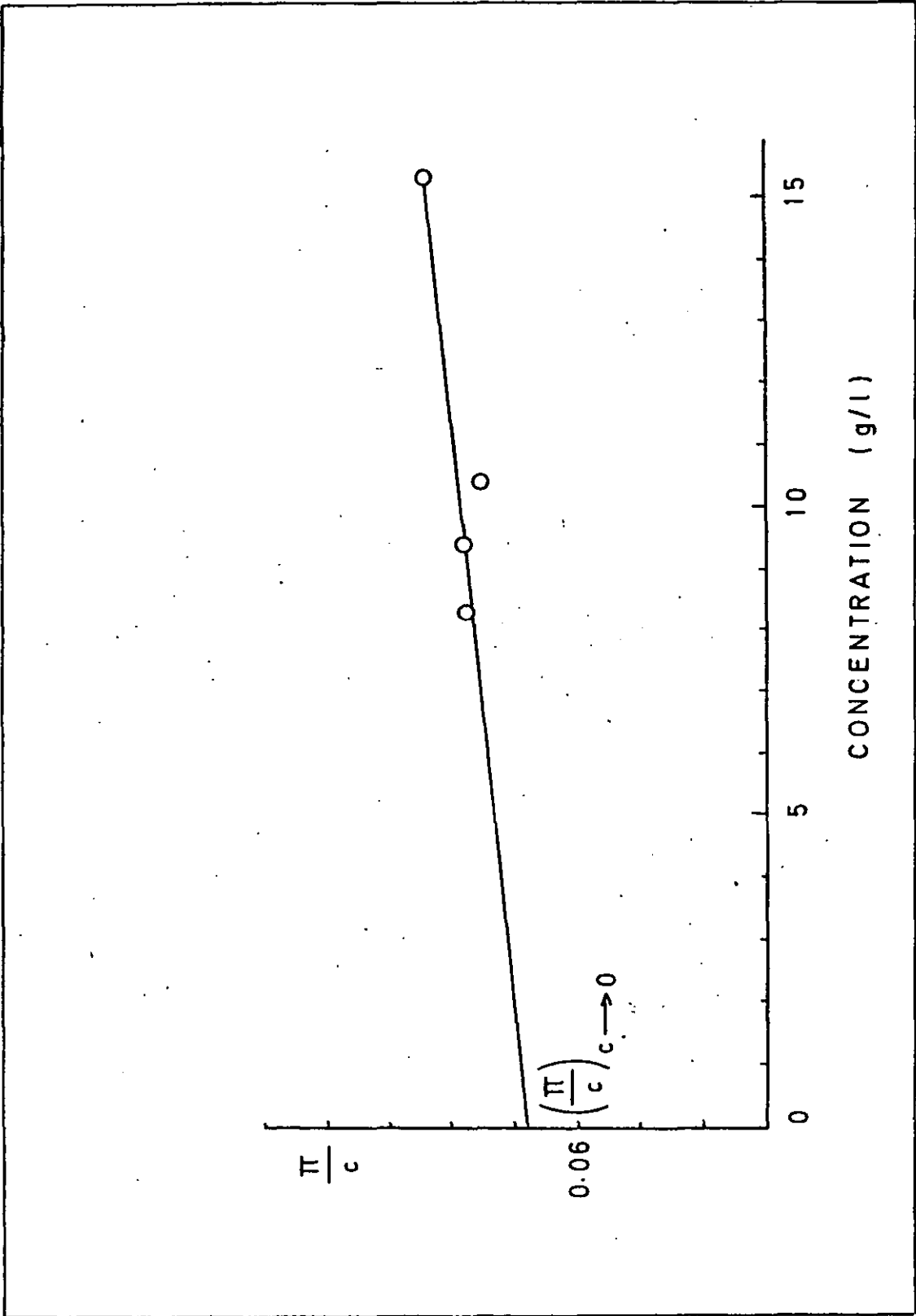


FIGURE 4.16

MEMBRANE OSMOMETRY OF PA46

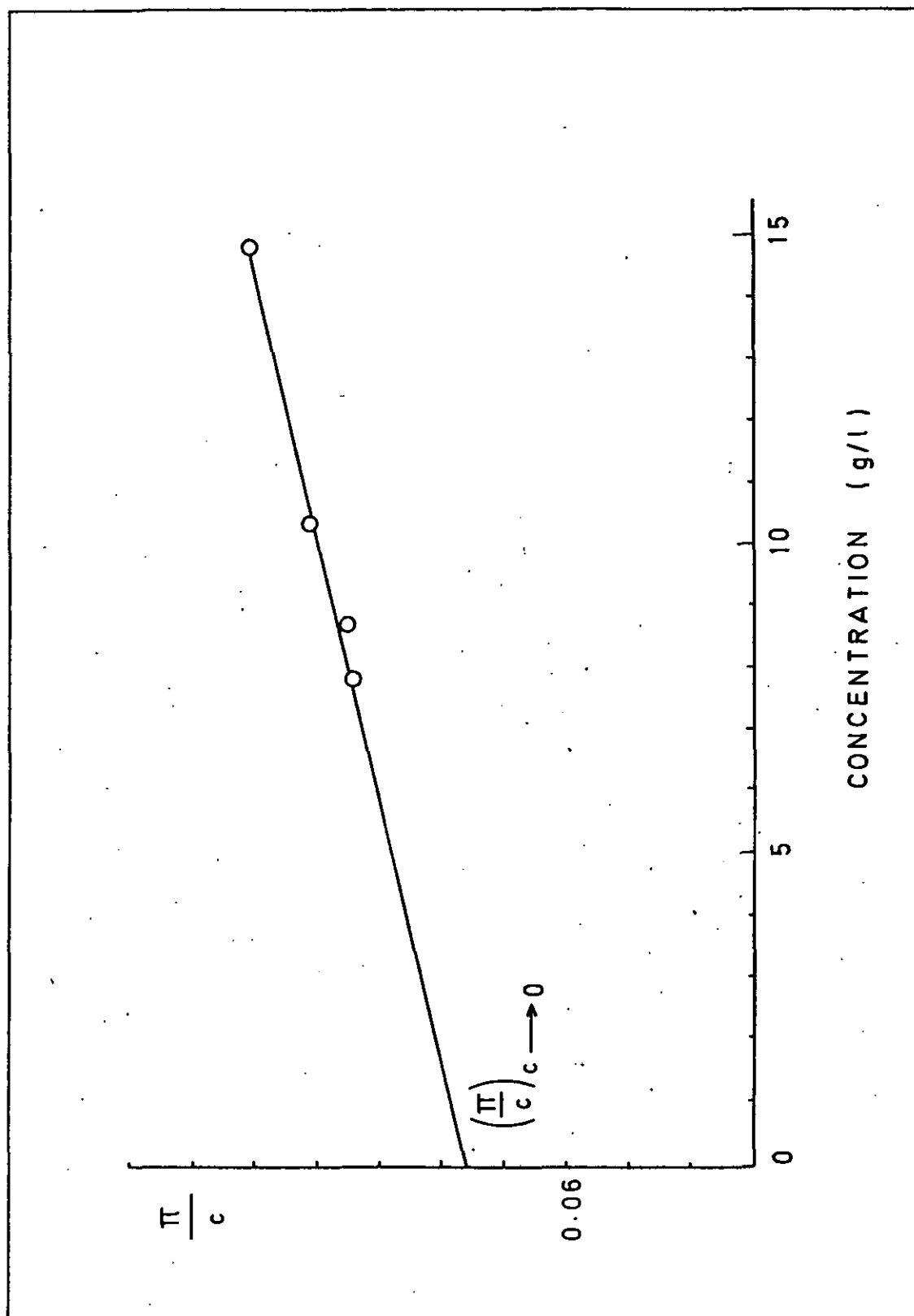


FIGURE 4.17

% POLYMER VERSUS VOLUME OF METHANOL

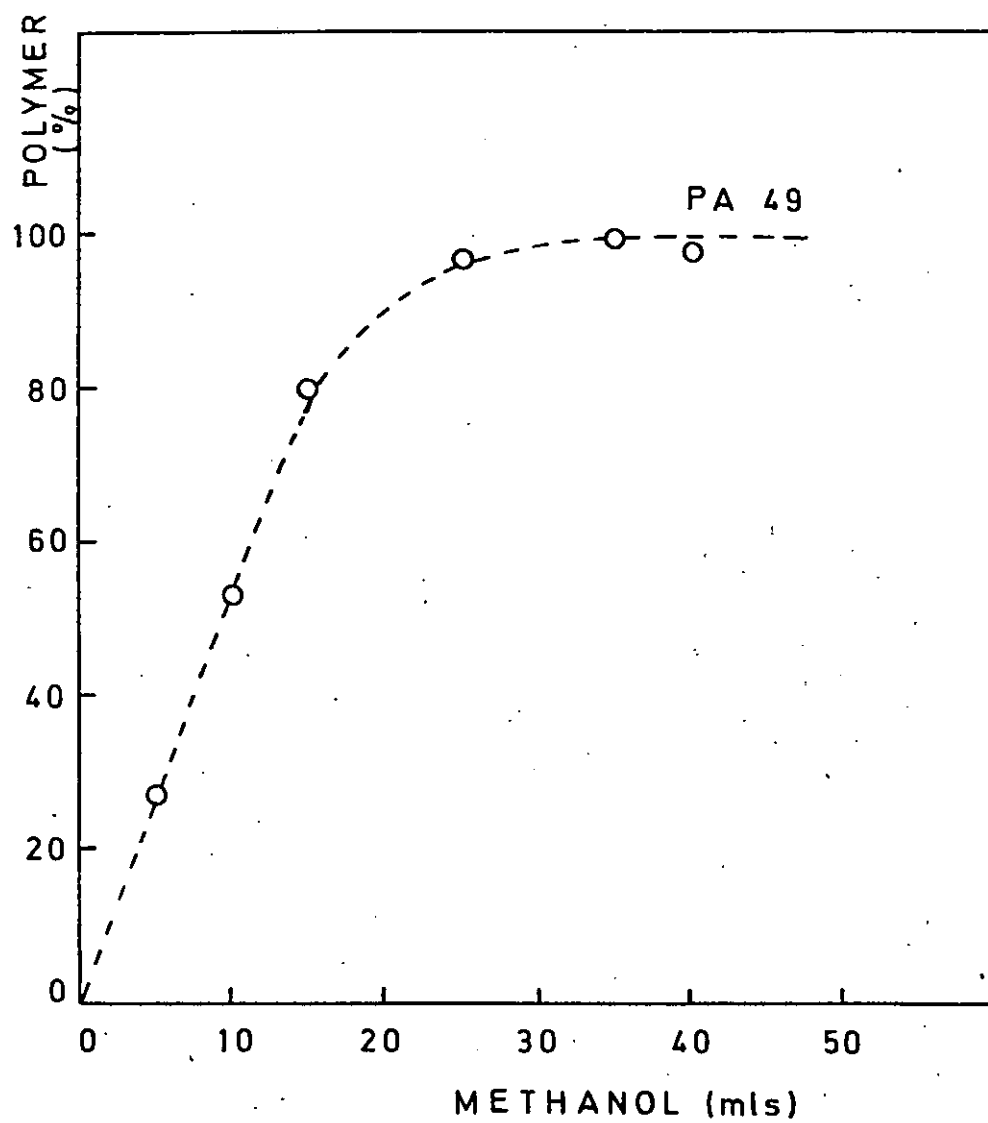


Table 4.16

Osmotic pressure data and polydispersity

| Polymer | \bar{M}_n | \bar{M}_v | \bar{M}_v/\bar{M}_n | Slope of osmotic pressure curve |
|---------|-------------|-------------|-----------------------|---------------------------------|
| 41 | 404,200 | 534,200 | 1.32 | 0.008 |
| 43 | 420,000 | 657,000 | 1.57 | 0.007 |
| 44 | 304,000 | 457,000 | 1.50 | 0.002 |
| 45 | 312,000 | 476,000 | 1.53 | 0.002 |
| 46 | 265,000 | 574,000 | 2.17 | 0.005 |
| 58 | 228,600 | 316,000 | 1.38 | 0.002 |

progressively decreasing molecular weight.

Before proceeding with the fractionation, it was necessary to establish the precipitation behaviour of polyacrylamide with methanol as non-solvent. The results in Table 4.17 show that five times the volume of methanol to that of the initial aqueous polymer solution is needed in order to precipitate almost all the polymer from solution. A plot of the data in Table 4.17 is shown in Figure 4.17. As each fraction is precipitated out the concentration of the polymer in the supernatant would decrease allowing the use of less methanol. However, in precipitating all the polymer from solution in the fractional precipitation experiment, the threshold value of five times the volume of polymer solution was exceeded.

4.4.1 Fractionation using heating and cooling cycles

The standard fractional precipitation procedure is to add non-solvent at constant temperature, e.g. methanol at 25°C, in order to precipitate the first fraction and then to raise the temperature, say to 40°C, in order to dissolve the precipitate. Subsequent cooling down to 25°C allows the precipitate to form under equilibrium conditions at constant temperature over a long period of time, e.g. overnight. After the removal of the precipitate, the whole procedure is repeated for each subsequent fraction. Such a fractionation was performed with an aqueous solution (1 dm³) of polyacrylamide PA47 (0.9% w/v) having $\bar{M}_v = 430,000$ and methanol as non-solvent. Several difficulties were encountered with this procedure. First, a fraction having formed on addition of methanol did not reprecipitate after heating and cooling. If this occurred, the procedure was repeated until a fraction formed on cooling. Second, although 98.8% of the polymer was recovered, the order of fractions with respect to molecular weight was not always in the correct sequence.

4.4.2 Fractionation omitting heating and cooling cycles

It was therefore decided to perform a fractional precipitation experi-

Table 4.17Precipitation of a 1% PA49 aqueous solution using methanol

| Tube | Volume of PA49 (mls) | Volume of MeOH (mls) | Weight of polymer (gms) | % recovery |
|------|-------------------------|-------------------------|----------------------------|------------|
| 1 | 5 | 5 | 0.016 | 26.79 |
| 2 | 5 | 10 | 0.031 | 52.73 |
| 3 | 5 | 15 | 0.047 | 76.86 |
| 4 | 5 | 25 | 0.057 | 97.08 |
| 5 | 5 | 35 | 0.058 | 99.49 |
| 6 | 5 | 40 | 0.057 | 97.94 |

ment with the heating and cooling cycles omitted. The fractionation of polyacrylamide was performed by placing 95 cm³ of an aqueous solution (0.922 w/v, PA49) in the fractionation flask in a thermostatted water bath at 25°C. The required volume of methanol to precipitate the first fraction, determined from Figure 4.17, was added slowly with stirring. The supernatant was removed the following morning and the precipitate was dried in a vacuum oven at 50°C for 24 hours. Further fractions were isolated by repeating the procedure with further additions of methanol. The final fraction was obtained by evaporating the liquids in the fractionation flask. 98% of the polymer was recovered in fractions. The molecular weights of the fractions were determined by solution viscometry. The results are tabulated in Table 4.18 with viscosity curves in Figures 4.18 and 4.19.

Having obtained fractions of molecular weight ranging from 35,000 to 151,000, it was decided to synthesise polyacrylamide PA58 with the objective of preparing fractions with molecular weights above 200,000. The viscosity and osmometry plots for PA58 are given in Table 4.18 and Figure 4.20. The three fractions obtained gave similar curves to PA49 fractions.

4.5 Aqueous GPC

In this project a GPC technique was being developed to analyse the aqueous polymer, polyacrylamide. The chromatographic packing for the GPC separation of polyacrylamide in aqueous media was chosen to be silica. Investigations leading to the modification of the surface of the silica packing by physically or chemically bonding suitable phases are documented in order to show that the GPC separation of polyacrylamide occurs by steric exclusion with minimal interference by adsorption. The choice of eluent, single, binary or ternary, will also influence the GPC behaviour.

The following terms that are used are defined as follows:

- (a) Uncoated silica - silica used as received from the manufacturer (i.e. untreated).

Table 4.18Fractions from polyacrylamides PA49 and PA58

| Fraction | \bar{M}_v |
|----------|-------------|
| PA49/1 | 151,000 |
| PA49/2 | 95,000 |
| PA49/3 | 35,100 |
| PA58/1 | 811,000 |
| PA58/2 | 534,000 |
| PA58/3 | 18,800 |

FIGURE 4.18

SOLUTION VISCOSITY OF PA 49 UN-FRACTIONATED

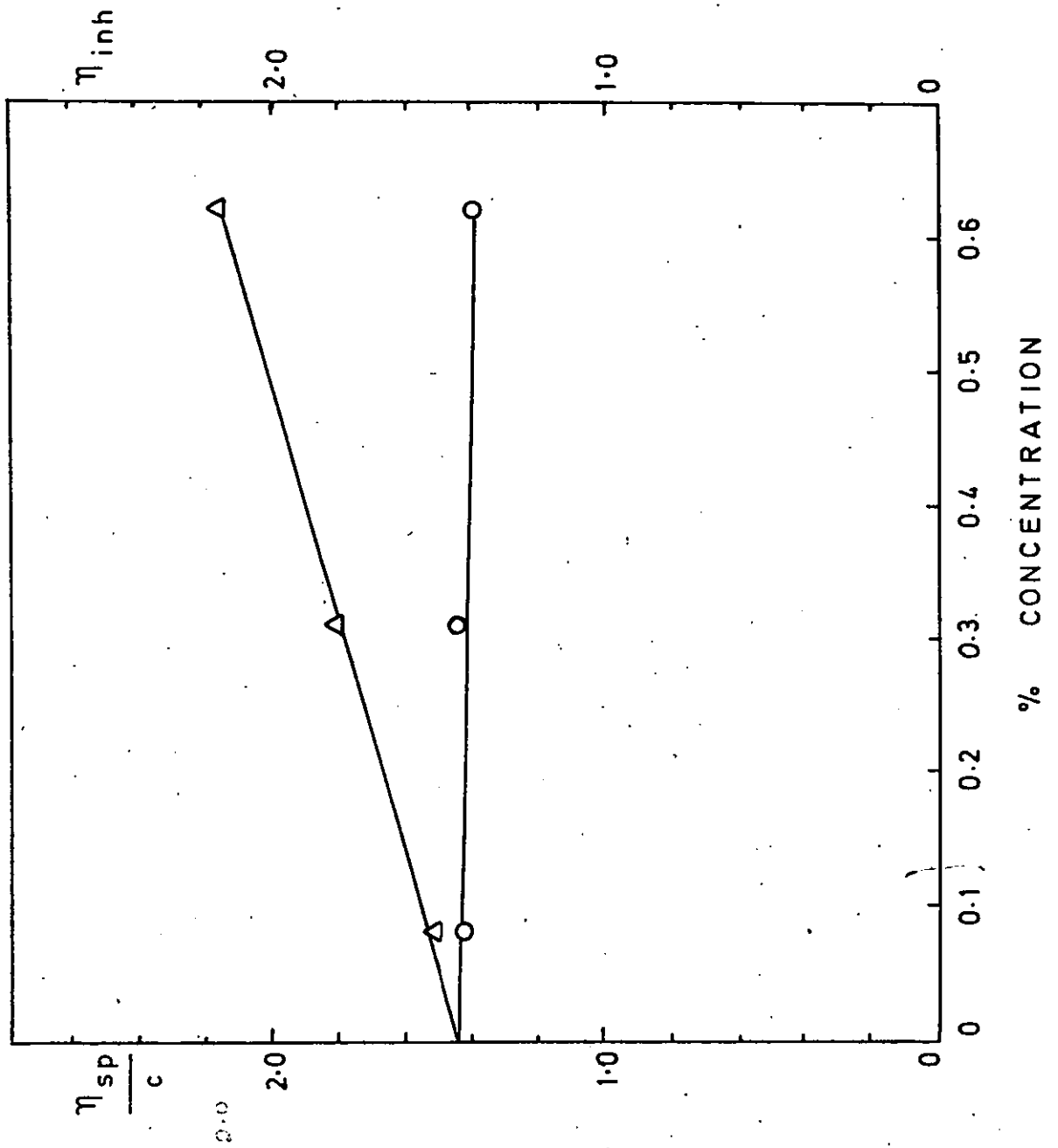
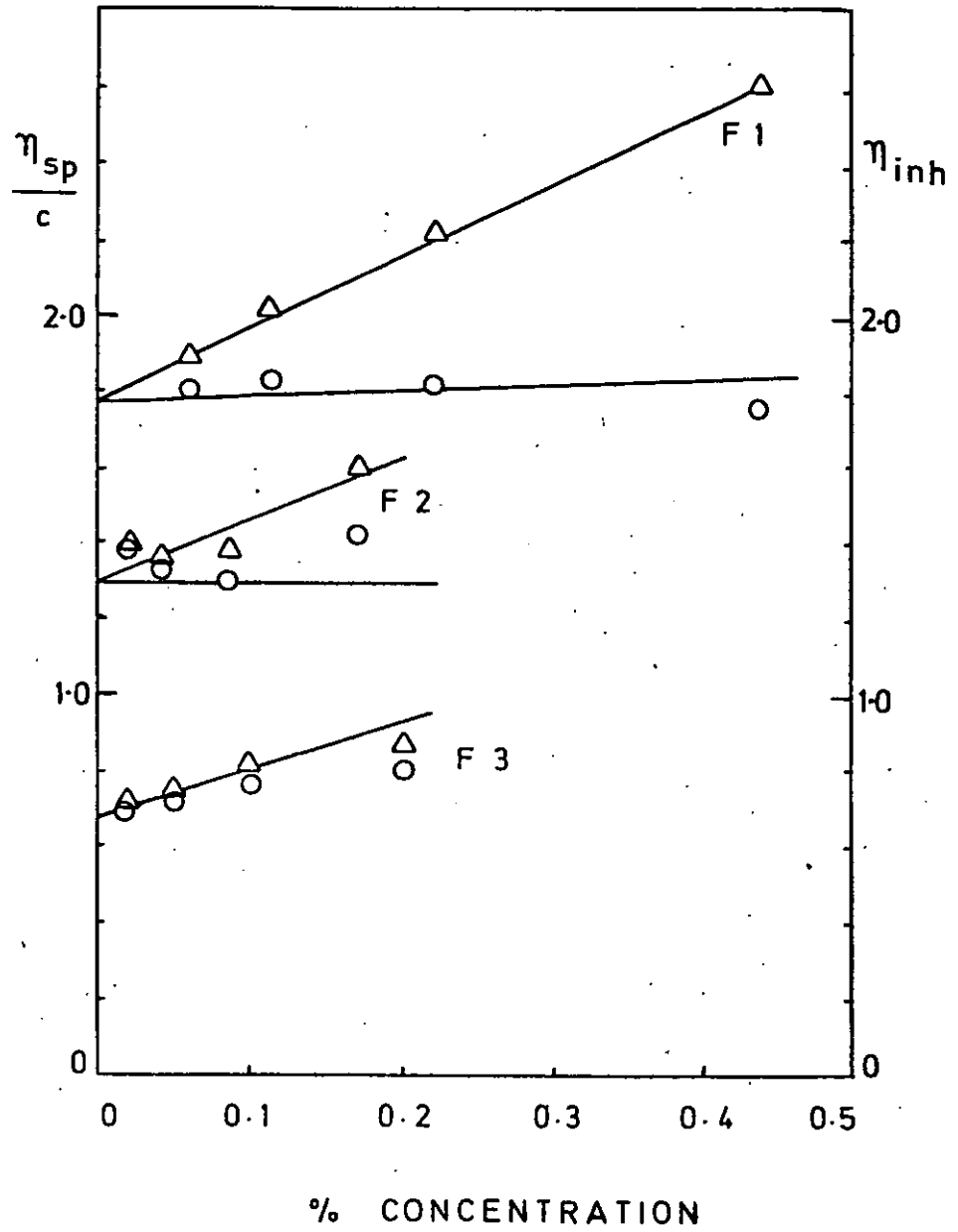
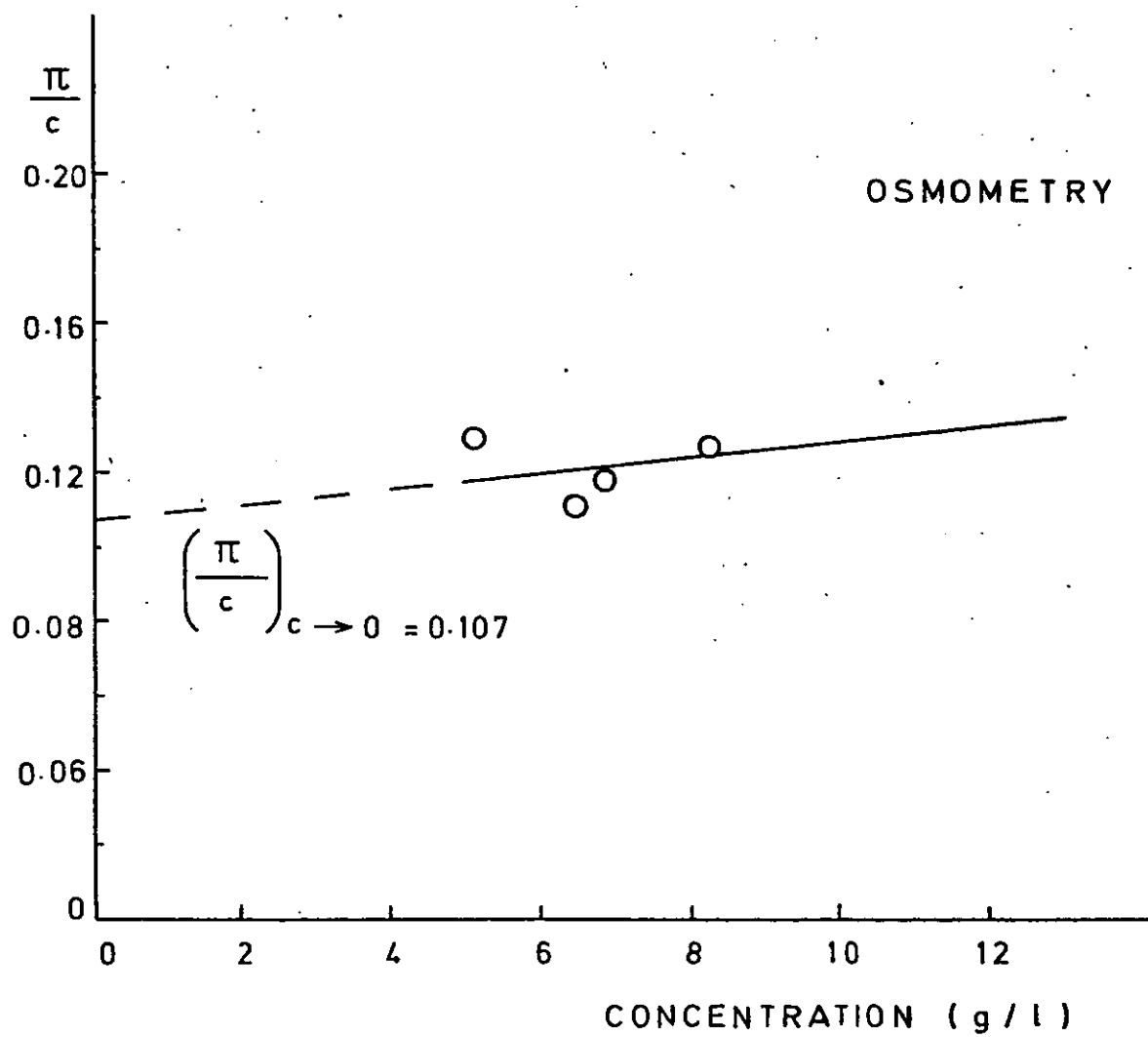
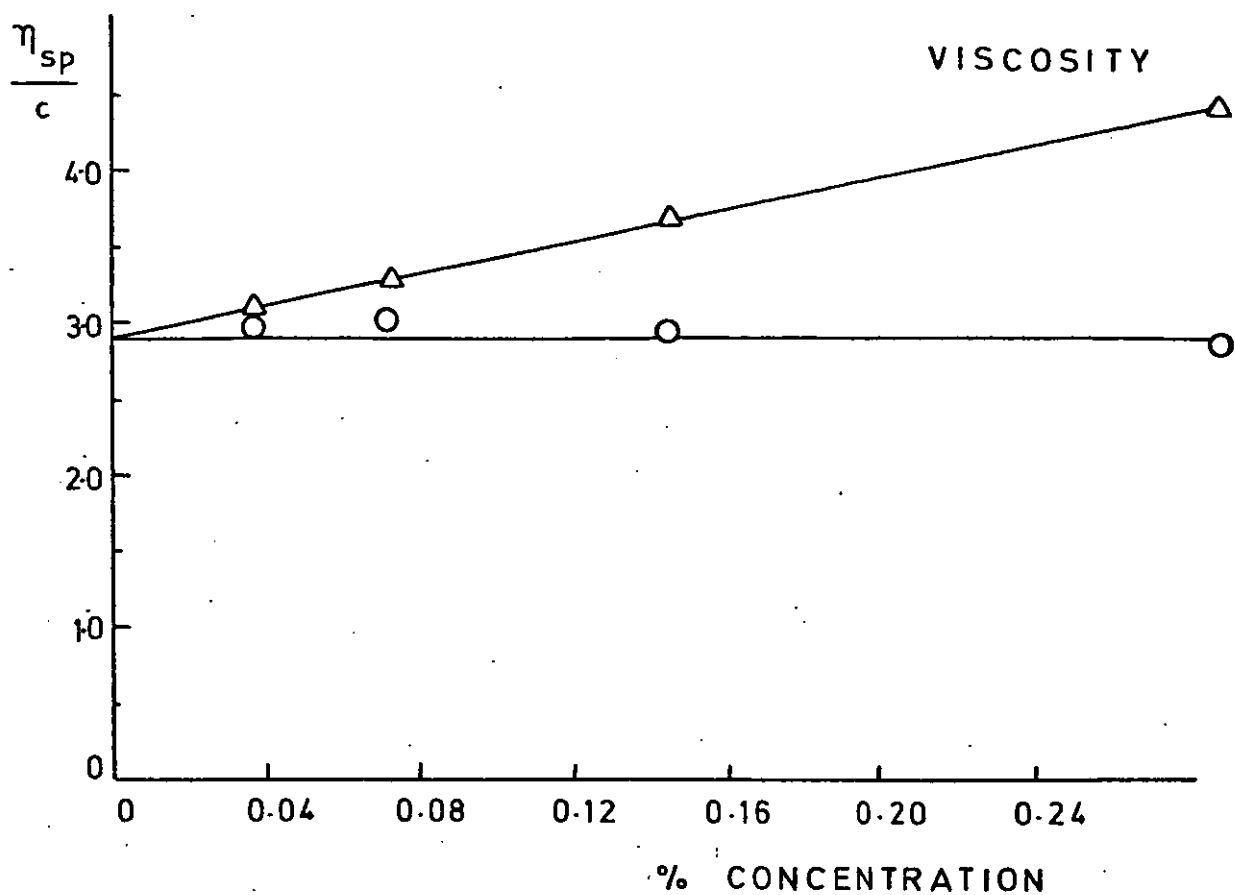


FIGURE 4.19

SOLUTION VISCOSITIES OF PA 49 FRACTIONS





- (b) Coated silica - silica having a physically bonded phase onto the surface of the packing in order to reduce polyacrylamide adsorption.
- (c) Decoated silica - silica after the removal of the physically adsorbed phase with concentrated nitric acid.
- (d) Bonded silica - silica having a chemically bonded phase onto the surface of the packing in order to reduce polyacrylamide adsorption.

4.5.1 Calibration of refractometer

A solution of PAll was filtered through a Whatman's GF/C filter paper. Different concentrations of PAll were injected directly into the refractometer and a calibration curve of refractometer response versus polyacrylamide concentration was determined. A linear relation not passing through the origin was obtained as shown in Figure 4.21. A similar calibration curve was obtained with polyacrylamide PA8.

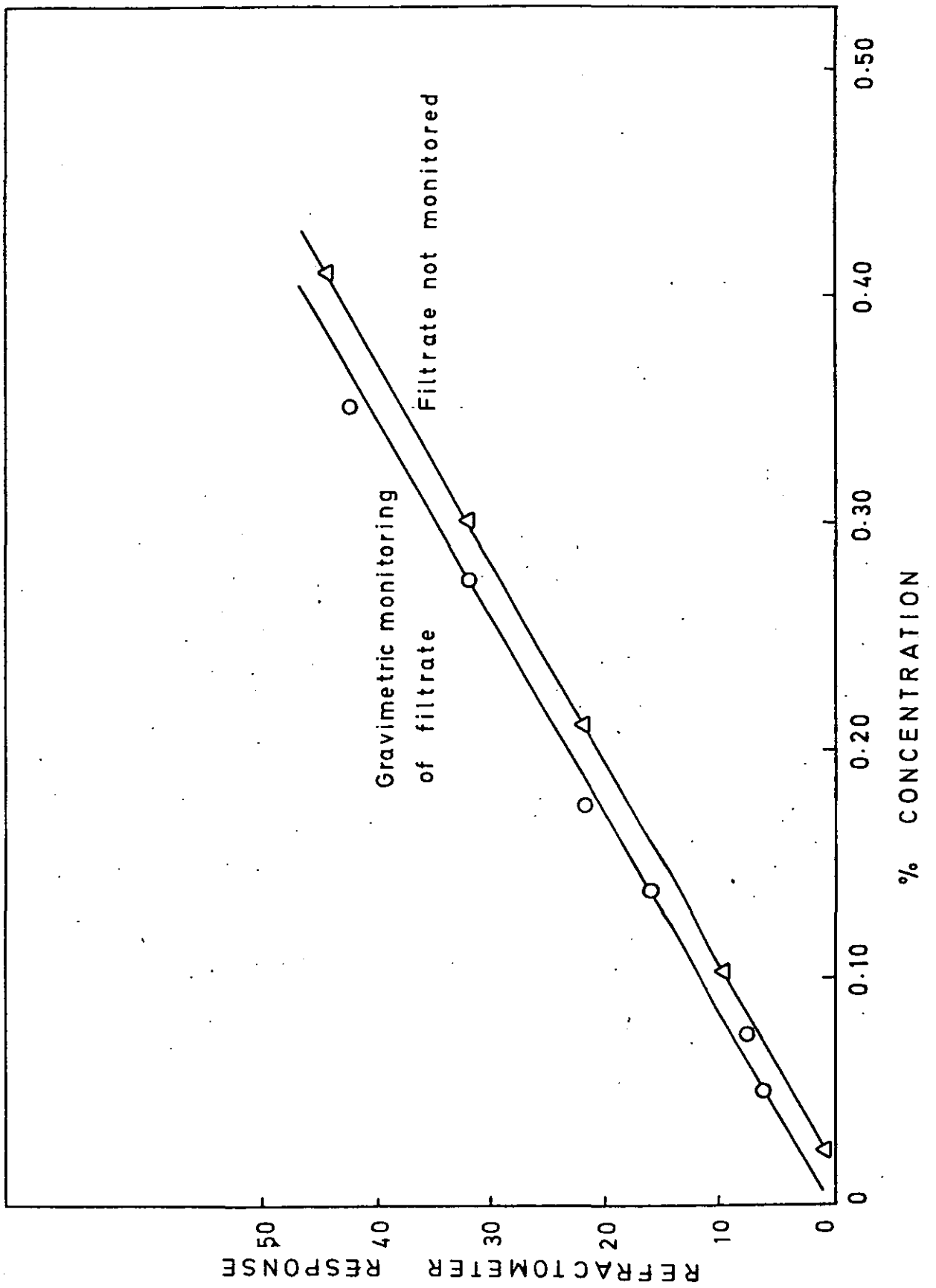
On monitoring the concentration of the filtrate gravimetrically, it was found that the polymer concentration was about 15% less than the initial concentration. When the true concentrations were used in Figure 4.21 a straight line graph passing through the origin was obtained. Polyacrylamide concentrations in the range 0.2 to 0.5% (w/v) were used in the GPC injections in order to obtain reasonable peaks with the refractometer detector on maximum sensitivity.

4.5.2 Preparative GPC

In Chapter 3.4.1, work was described on the establishment of a preparative GPC system. The total volume of the preparative GPC column containing the chromatographic packing is equal to 171 cc. About one-third of this volume, i.e. 57.1 cc, represents the void volume. The experimental procedure is described in Chapter 3.4.1. Fractions (20 ml aliquots) were

FIGURE 4.21

CALIBRATION OF REFRACTOMETER



collected from the column, and each solution was injected in turn into the refractometer. To establish an initial baseline, water was injected. The results are shown in Figure 4.22. Calibration of the refractometer response, illustrated in Figure 4.21, permitted the conversion of the results in Figure 4.22 into a chromatogram of sample weight versus retention volume.

The Bio-Glas support used in this experiment was coated with PEO 800 using the solution technique. An aqueous solution of polyacrylamide PA8 (5 ml of PA8, 0.296%, $\bar{M}_v = 208,000$) was injected into the column. After the appearance of 30 ml of eluent fractions were collected at 20 ml intervals and monitored directly into the refractometer detector using a linear pen recorder operating at 10 mV full scale deflection. A peak retention volume of 130 ml suggested that the polymer did not elute at the void volume. At the same time some form of adsorption may take place on unreacted active sites of the Bio-Glas support. The chromatogram bed support was made of a porous glass sinter which can cause some adsorption problems, thus Bio-Glas had to be coated with PEO 800 in order to reduce active sites, see Section 2.4.5. Elution of the polyacrylamide solute started from fraction 5 till fraction 8, corresponding to a spread of 60 ml for the molecular weight distribution of the polymer.

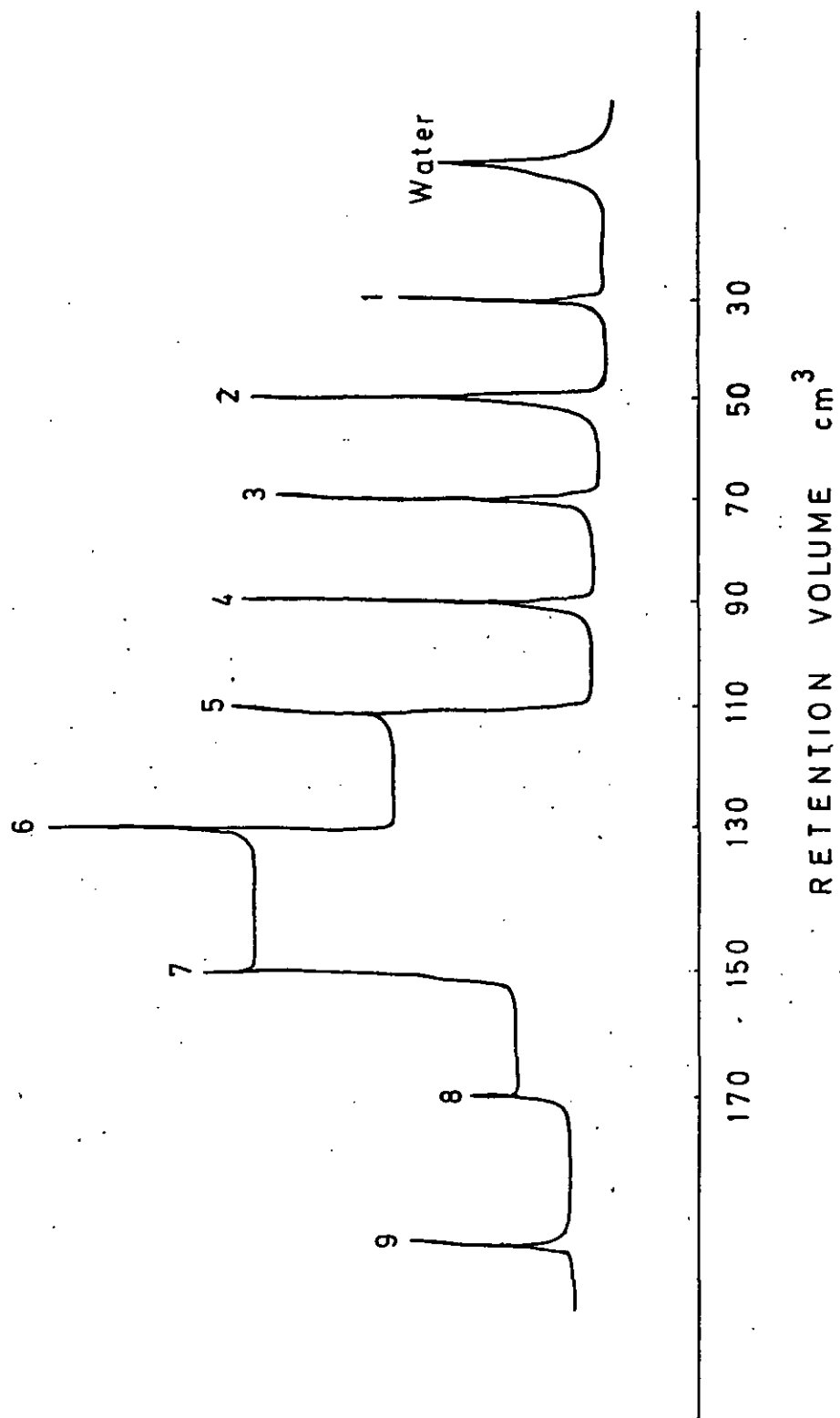
Apart from the possible fragmentation of the inorganic packing giving a blocked sinter, problems were encountered with leakage of eluent and packing in the end-fitting at the bottom of the column. In view of the experimental problems, it was decided to abandon the preparative technique and to develop a small-scale analytical arrangement. The result in Figure 4.22 does demonstrate that polyacrylamide may be fractionated on an inorganic packing.

4.5.3 Uncoated silica

Porasil E1500 dry packed into a stainless steel column (two feet long) was flushed with degassed distilled water. Anomalous results were obtained

FIGURE 4.22

REFRACTOMETER RESPONSE FOR FRACTIONS FROM PREPARATIVE GPC



from injections of polyacrylamide solutions as shown in Table 4.19.

From these results the low molecular weight solutes gave a reproducible peak retention volume of 23.5 ml. The retention volumes of polyacrylamides PA21 and PA5 are greater than the retention volume of the low molecular weight solutes, with the retention volumes of PA8 irreproducible in peak retention volume. From the above results (Figure 4.23) the abnormally high retention volumes of the polyacrylamides are indicative of reversible adsorption taking place. This adsorption reflects the degree of hydrogen bonding between the solute and the packing as illustrated schematically in Figure 4.24. Variable chromatograms of PA8 were obtained on repeated injections which indicated that some polymer may interact permanently with the porous packing or that polymer deposited on the packing in one injection is displaced and eluted in subsequent injections.

Acetamide and iodoacetamide have the same functional group as polyacrylamide, so that adsorption onto the packing may take place with these monomeric solutes. However, because of size differences, the number of amide groups in a polymer chain would be greater, thus enhancing a higher degree of adsorption and consequently a higher retention volume.

Hamielec (16) in his work reported the use of an electrolyte, a potassium bromide (0.15% w/v) in aqueous solution. A solution of this concentration was prepared and flushed through a column (two feet long) containing uncoated Porasil E1500 which was dry packed. The results are shown in Table 4.20, and suggest that reversible adsorption may have taken place between the solute and the packing in Hamielec's work. Since the chromatogram in Figure 4.25 is similar to the behaviour in Figure 4.23 it would appear that the GPC separations of polyacrylamide are unaffected by the presence of potassium bromide in water. This suggests that the polyacrylamides are non-ionic. Ionic groups could result from hydrolysis of the amide groups. The GPC behaviour of polyelectrolytes in DMF has been shown to

Table 4.19Polyacrylamide injections on uncoated Porasil E1500

| Solute | % concentration | Molecular weight | V _R (ml) |
|---------------|-----------------|------------------|---------------------|
| Ethanol | 1.0 | 46 | 23.5 |
| Acetamide | 1.0 | 59 | 23.5 |
| Iodoacetamide | 1.0 | 185 | 23.5 |
| PA21 | 0.24 | 159,900 | 33.05 |
| PA5 | 0.28 | 668,000 | 41.04 |
| PA8 | 0.62 | 208,000 | 27.3 |
| PA8 | 0.62 | 208,000 | 22.44 |

Table 4.20Polyacrylamide injections using 0.15% w/v KBr as eluent

| Solute | % concentration | Molecular weight | V _R (ml) |
|-----------|-----------------|------------------|---------------------|
| Ethanol | 2.0 | 46 | 23.5 |
| Acetamide | 2.0 | 59 | 23.5 |
| PA21 | 0.30 | 159,900 | 26.7 |
| PA21 | 0.30 | 159,960 | 32.4 |

FIGURE 4.23

UNCOATED PORASIL E 1500 WITH WATER

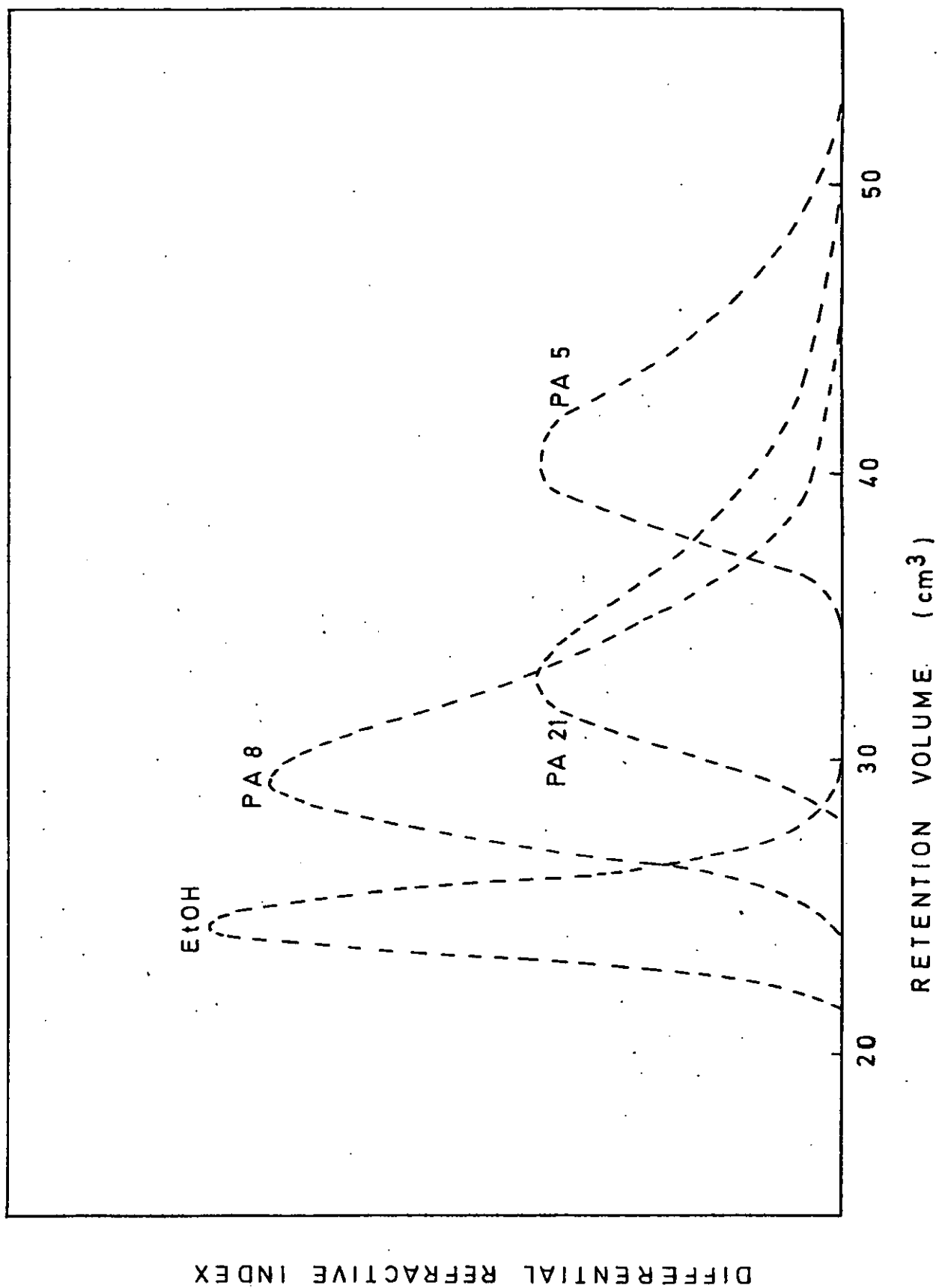


FIGURE 4.24

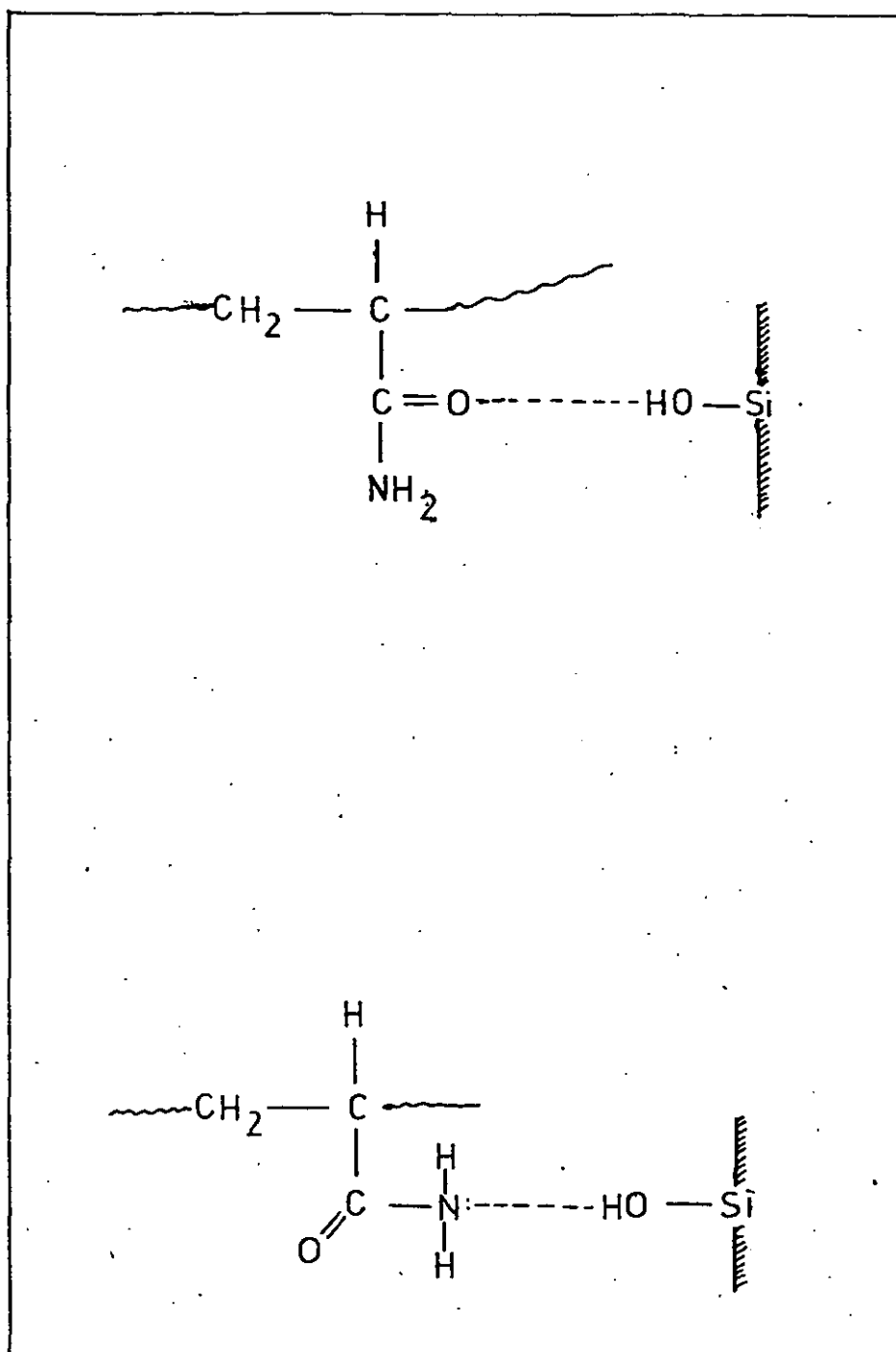
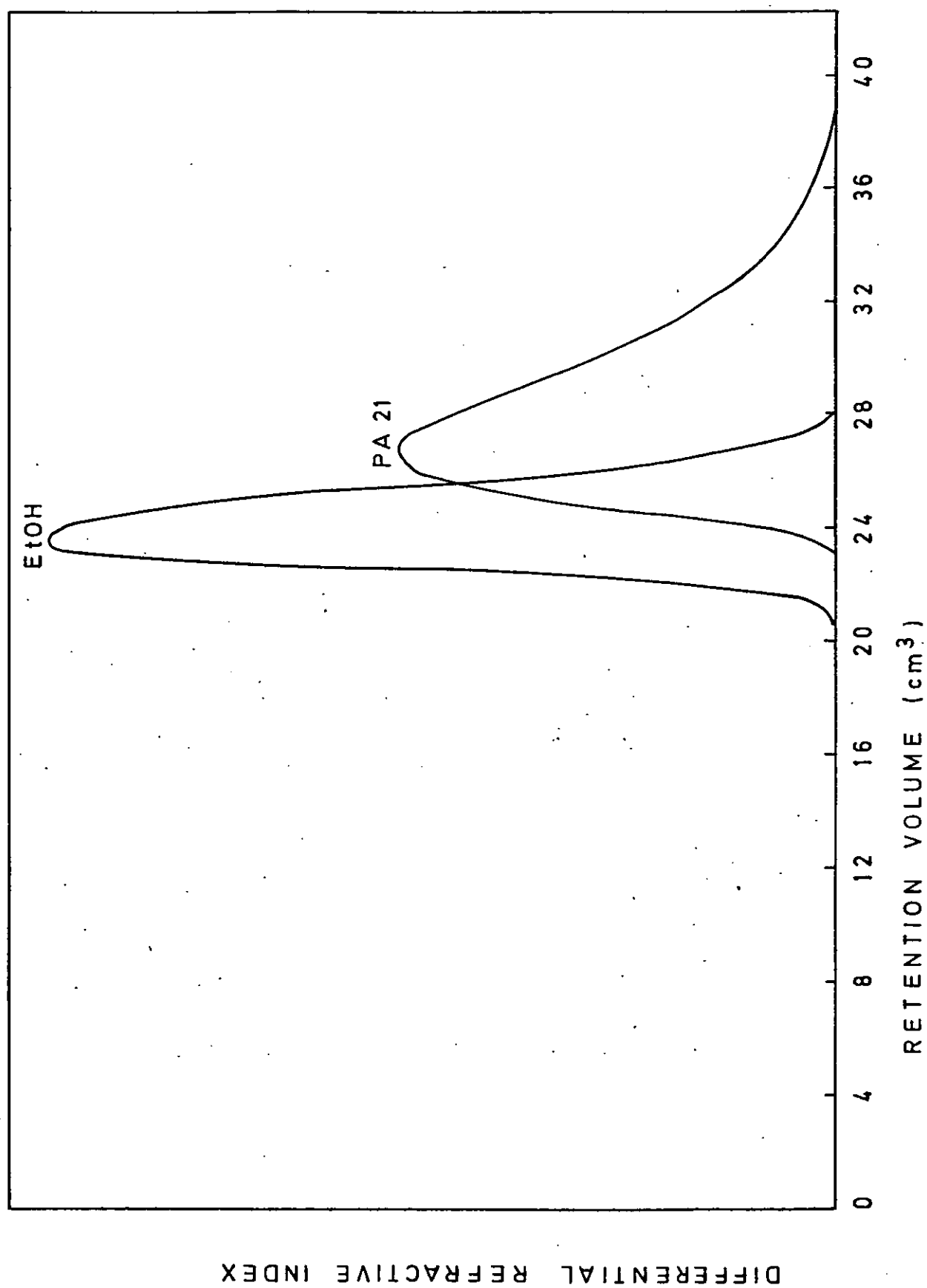
TYPES OF HYDROGEN BONDING BETWEEN POLYACRYLAMIDE
AND ACIDIC SITES OF SILICA

FIGURE 4.25

UNCOATED PORASIL E 1500 WITH 0.15% POTASSIUM BROMIDE SOLUTION



change on adding lithium bromide, which was explained by Cha (177) by a polyelectrolyte screening effect reducing the size of the polyelectrolyte chain. Dubin (178) has also observed that lithium bromide influenced the chromatogram position of poly(N-vinylacetamide) separating on silanised porous glass with dimethylformamide as eluent. With this polymer the lithium bromide addition appeared to increase the size of the polymer since the chromatogram of poly(N-vinylacetamide) shifted towards the void volume of the column. An alternative explanation is that the electrolyte neutralised sites on the surface of the glass which were not deactivated by the silanisation treatment. Then, the polymer is not retarded by polymer-surface interactions. However, it would appear that the presence of an inorganic salt offers no advantages for the separation of polyacrylamide in water with uncoated silica.

4.5.4 Coated silica

Howard and McConnell (179) studied the adsorption of polyethylene oxide on Aerosil silica. Their results showed that polyethylene oxide adsorbed from water adopted a nearly flat conformation but moderate looping occurred on adsorption from organic liquids. Also, polyethylene oxides of low molecular weight lie closer to the surface of the silica than polyethylene oxides of high molecular weight.

Viruses (180) and plant gums (181) have been successfully separated using Bio-Glas without pretreatment. Hawk et al. (170) and Hiatt et al. (169) treated CPG (commercially available porous glass) with polyethylene glycol or polyethylene oxide in order to block off the active sites by hydrogen bonding, so that proteins, viruses, carbohydrates and hydrophilic synthetic polymers can be separated. It was therefore thought that polyacrylamide could be separated in this way.

Coated silicas prepared either by solution or suction (as described in Section 3.4.3.2) were dry packed into a stainless steel column (two feet

long) and flushed through using degassed distilled water as eluent. The GPC results for Porasil EL500 coated with PEO 800 are given in Tables 4.21 and 4.22 and the chromatograms are shown in Figures 4.26 and 4.27. The significant difference between these results and the chromatograms for the uncoated silicas, see Figures 4.23 and 4.25, is that the chromatograms lie between the void volume and the totally permeating volume. This suggests a permeation separation dominated by steric exclusion with minimum polyacrylamide adsorption onto the packing. The retention volume V_R in Table 4.21 corresponds to the maximum peak height on the chromatogram which occurs at the void volume owing to the large concentration of excluded high molecular weight chains in the polyacrylamide samples. Therefore, the peaks at $V_R = 12.0 \text{ cm}^3$ for polyacrylamide PA12 and PA30 in Figure 4.26 are not representative of the molecular weight distribution.

Similar results were observed for Porasil EL500 coated with PEO 6000. The data are shown in Table 4.23 and plotted in Figure 4.28. On the other hand Porasil EL500 coated with PEO 20,000 gave the chromatograms in Figure 4.29 for two of the polyacrylamides in Table 4.24. In Figure 4.29, there are no polymeric species eluting after a retention volume of 15 cm^3 , suggesting that no polyacrylamide is permeating the silica packing. This may be explained by the blockage of the pores by the higher molecular weight (20,000) of the polyethylene oxide. Clearly, this effect is much less severe for PEO 6000 and PEO 800, since the position of the chromatograms between retention volumes of 12 and 24.5 cm^3 suggests permeation of the silica by polyacrylamide chains. The blockage effect will become more important as the pore size decreases, so that the PEO should be as short as possible whilst retaining complete coverage of the active sites on the pore surface. In Table 4.25 and Figure 4.30, results are presented for Porasil DL000 coated with PEO 200. The position of the chromatograms is consistent with a permeation mechanism as observed in Figures 4.26 to 4.28.

Table 4.21Porasil E1500 coated with PEO 800 (solution technique)

| Solute | % concentration | Molecular weight | V _R (ml) |
|-----------|-----------------|------------------|---------------------|
| Ethanol | 2.0 | 46 | 23.5 |
| Acetamide | 2.0 | 59 | 23.5 |
| PA30 | 0.375 | 333,000 | 12.0 |
| PA30 | 0.375 | 333,000 | 12.0 |
| PA12 | 0.522 | 47,000 | 12.0 |
| PA9 | 0.156 | 152,000 | 12.0 |

Table 4.22Porasil E1500 coated with PEO 800 (suction technique)

| Solute | % concentration | Molecular weight | V _R (ml) |
|---------------|-----------------|------------------|---------------------|
| Ethanol | 2.0 | 46 | 23.5 |
| Acetamide | 2.0 | 59 | 23.5 |
| Iodoacetamide | 2.0 | 185 | 23.5 |
| PA12 | 0.522 | 47,000 | 11.0 |
| PA30 | 0.375 | 333,000 | 11.0 |
| PA30 | 0.375 | 333,000 | 12.0 |
| PA8 | 0.62 | 208,000 | 11.5 |
| PA9 | 0.156 | 152,000 | 11.5 |

Table 4.23Porasil E1500 coated with PEO 6000 (solution technique)

| Solute | % concentration | Molecular weight | V _R (ml) |
|---------------|-----------------|------------------|---------------------|
| Ethanol | 2.0 | 46 | 23.5 |
| Acetamide | 2.0 | 59 | 23.5 |
| Iodoacetamide | 2.0 | 185 | 23.5 |
| PA21 | 0.479 | 159,900 | 13.0 |
| PA30 | 0.375 | 330,000 | 13.0 |
| PA5 | 0.28 | 668,000 | 13.0 |

Table 4.24Porasil E1500 coated with PEO 20,000 (solution technique)

| Solute | % concentration | Molecular weight | V _R (ml) |
|---------------|-----------------|------------------|---------------------|
| Ethanol | 2.0 | 46 | 23.5 |
| Acetamide | 2.0 | 59 | 23.5 |
| Iodoacetamide | 2.0 | 185 | 23.5 |
| PA21 | 0.479 | 159,900 | 11.5 |
| PA5 | 0.28 | 668,000 | 12.0 |
| PA11 | 0.477 | 194,000 | 11.5 |
| PA30 | 0.375 | 333,000 | 11.5 |
| PA9 | 0.484 | 152,000 | 11.0 |
| PA6 | 0.588 | 112,900 | 12.0 |
| PA12 | 0.498 | 47,000 | 11.5 |

Table 4.25Porasil D1000 coated with PEO 200 (solution technique)

| Solute | % concentration | Molecular weight | V _R (ml) |
|-----------|-----------------|------------------|---------------------|
| Ethanol | 2.0 | 46 | 24.5 |
| Acetamide | 2.0 | 59 | 24.5 |
| PA7 | 0.302 | 40,000 | 12.0 |
| PA30 | 0.375 | 333,000 | 12.5 |
| PA12 | 0.522 | 47,000 | 13.0 |
| PA21 | 0.479 | 159,900 | 13.0 |
| PA13 | 0.145 | 41,000 | 12.5 |

FIGURE 4.26

PORASIL E 1500 COATED WITH PEO 800 (SOLUTION) USED WITH WATER

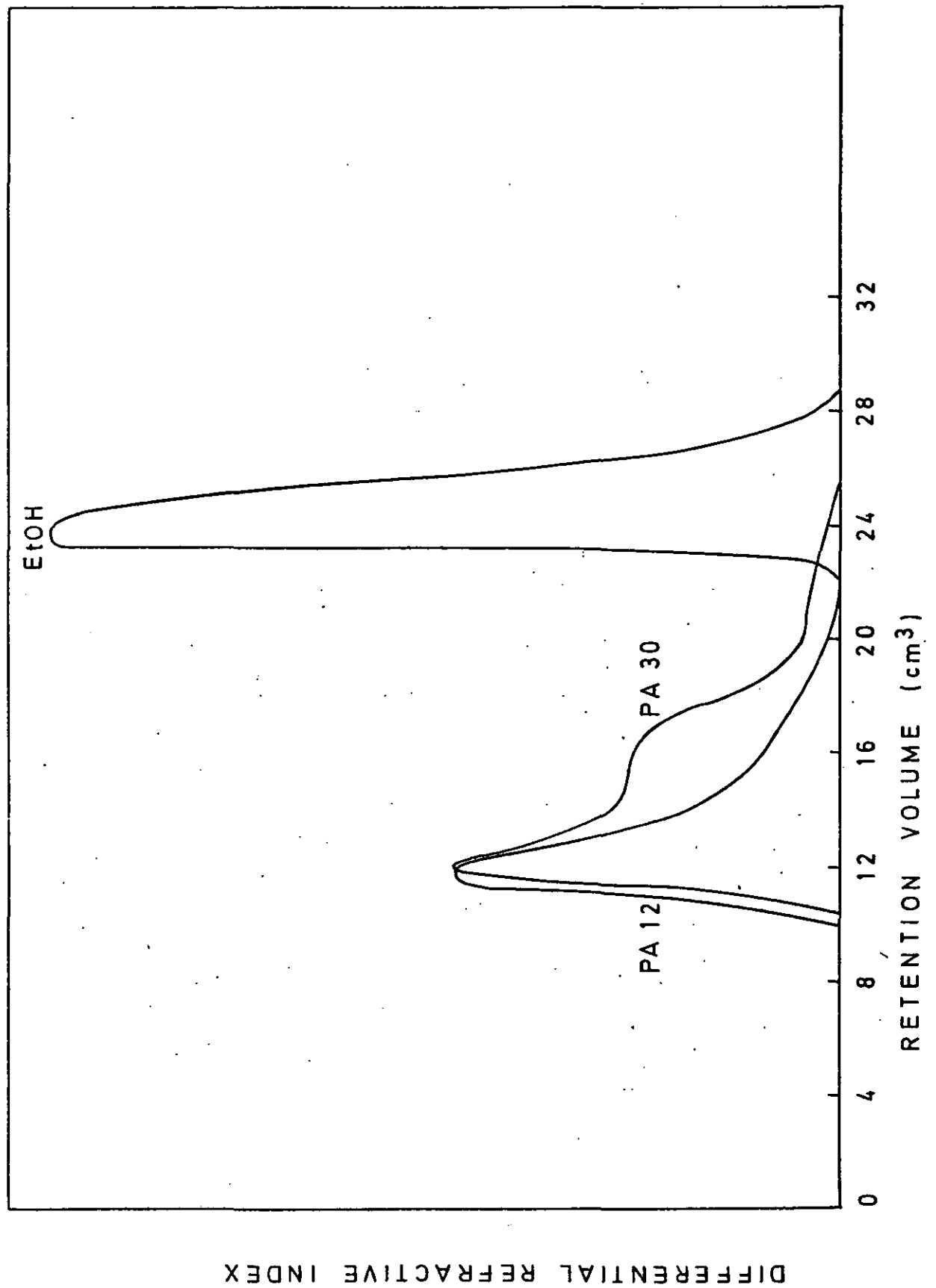


FIGURE 4.27

POPASIL E 1500 COATED WITH PEO 800 (SUCTION) USED WITH WATER

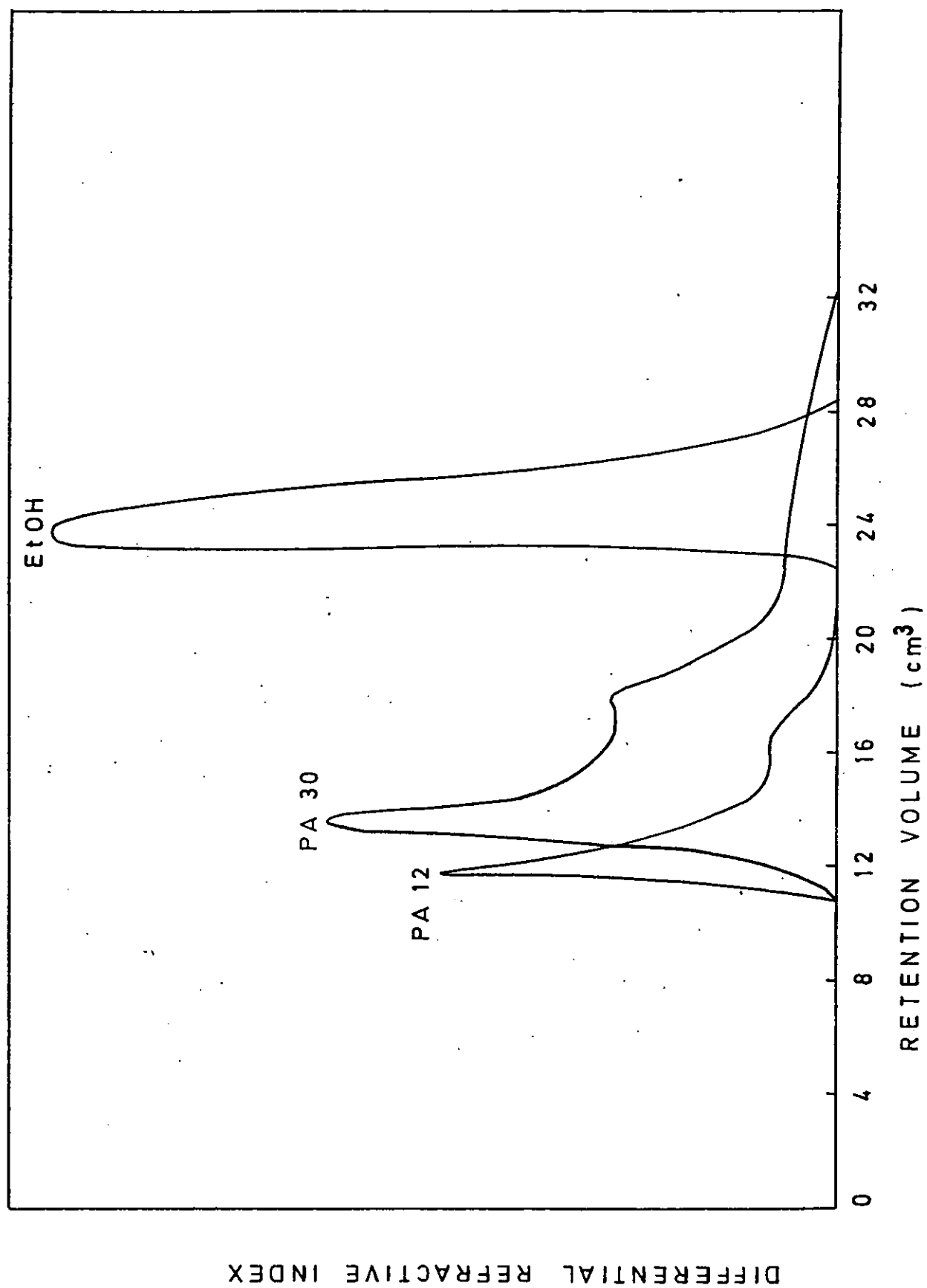


FIGURE 4.28

PORASIL E 1500 COATED WITH PEO 6000 (SOLUTION) USED WITH WATER

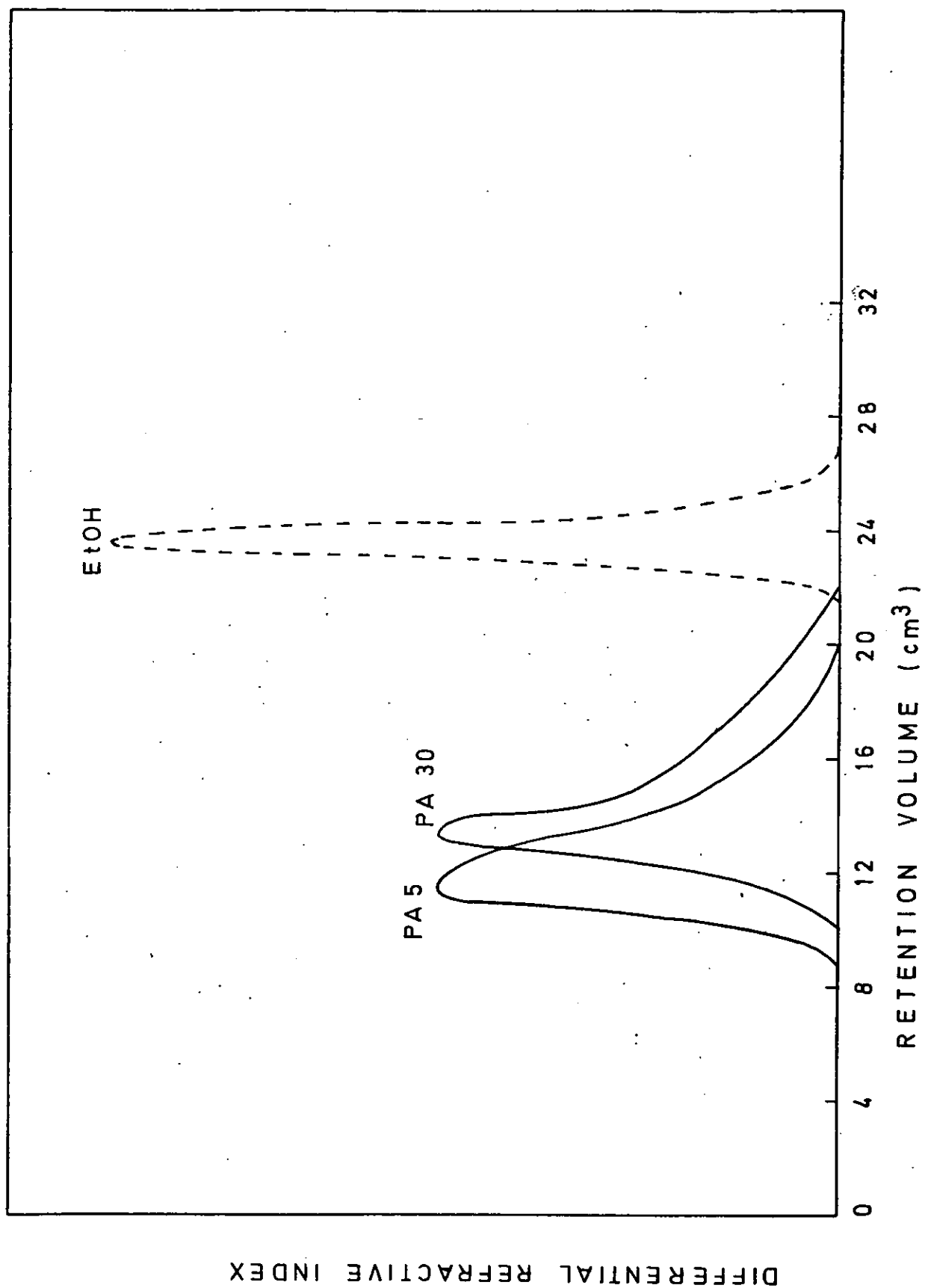


FIGURE 4.29

PORASIL E 1500 COATED WITH PEO 20,000 (SOLUTION) USED WITH WATER

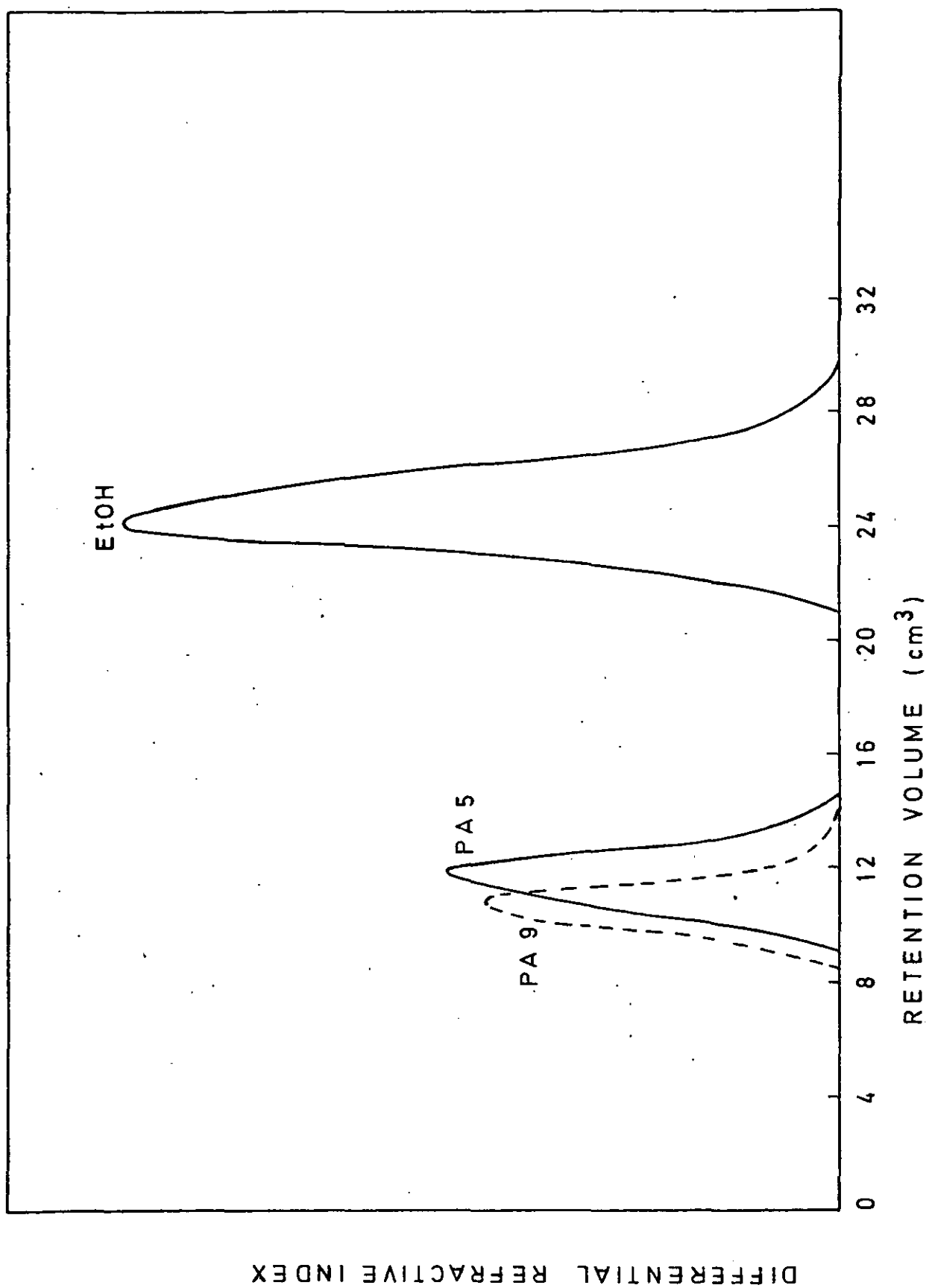
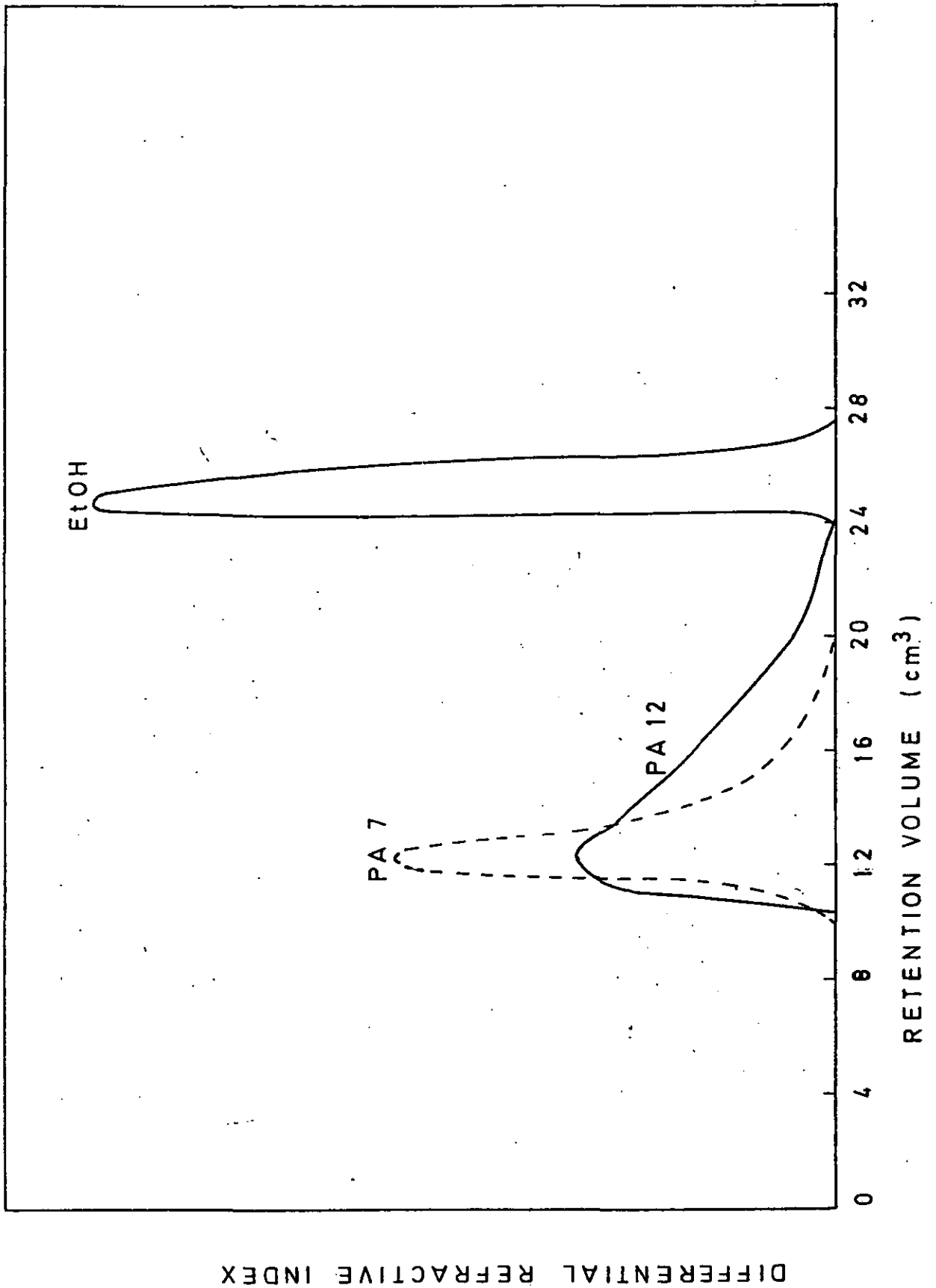


Figure 4.30

PORASIL D 1000 COATED WITH PEO 200 USED WITH WATER



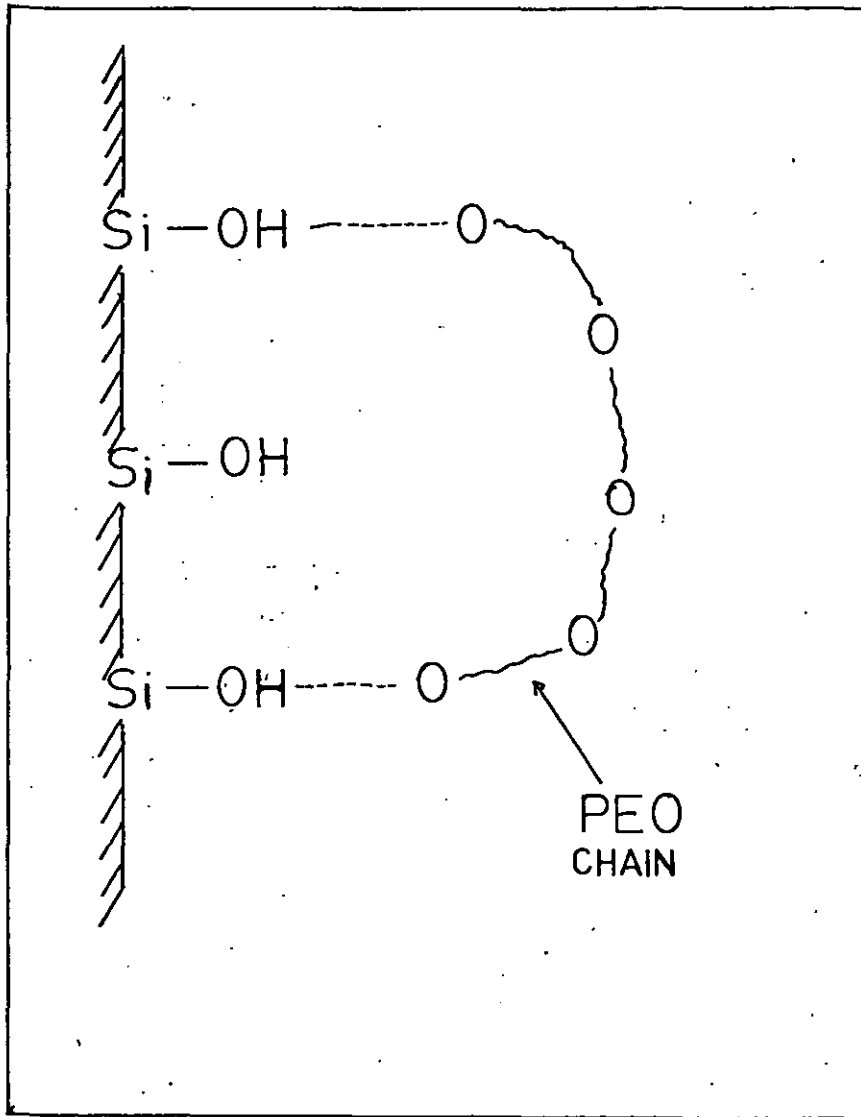
The flat conformation of polyethylene oxide on silica can be schematically represented as shown in Figure 4.31. In order to achieve good adhesion, each chain must anchor on the silica surface at several points, so that the chain must have a minimum length, and the results in Table 4.23 suggest that a minimum molecular weight of 200 may be acceptable. As the molecular weight is raised, the loop length between anchor points in Figure 4.31 will tend to increase, thus reducing the effective pore diameter. As depicted in Figure 4.31 it is possible that not all of the active sites on the silica surface are removed on physically coating the surface with an adsorbed phase. Therefore, it is possible for reversible adsorption to occur on these uncoated sites even with the polyethylene oxide present.

On comparing the chromatograms of Porasil E1500 coated with PEO 800 by solution and suction technique (Figures 4.26, 4.27), there are the same basic chromatogram shape but small variations occurred at the low molecular weight tail of the chromatogram obtained from the suction technique. It is possible that in the initial injections, polyacrylamide may interact permanently with uncoated spots on the packing surface until complete coverage is obtained. Uncoated spots would lead to solute retardation. For packings coated by the solution technique, experiments were performed to assess the permanence of the coating. This is shown in Figure 4.21 in which an injection of a known concentration of polyacrylamide was performed.

Polyacrylamide solution (filtered) was injected into a column. The peak was monitored by a refractometer and recorded on a 10 mV full scale deflection chart recorder. The volume of eluent collected with the solute was recorded so that the concentration of the solute could be calculated. The refractometer signal was compared at the observed concentration of the solute on the calibration curve. This result compared quite favourably with the injected polymer concentration into the column indicating that there was no form of irreversible adsorption of the polyacrylamide on the PEO 800 coated Porasil E1500 support.

FIGURE 4.31

CONFORMATION OF POLYETHYLENEOXIDE
AT THE SILICA/LIQUID INTERPHASE



Bio-Glas 1500 particles are irregular shaped with a similar size to Porasil particles, i.e. 37-75 μm . These particles were coated with PEO 6000 using the solution technique. The packing was dried in a vacuum oven at 50°C for 24 hours. The packing was dry packed into a stainless steel column (two feet long) and was flushed through with degassed distilled water. The results are tabulated in Table 4.26. The chromatograms obtained for Bio-Glas 1500 coated with PEO 6000 were similar to those in Figure 4.28 for Porasil El500 coated with the same PEO. However, one of the interesting features that was observed was the increase in pore volume for Bio-Glas 1500 compared to Porasil El500 on injecting the monomeric solute, ethanol. The same type of instrumentation and experimental procedure were utilised for both packings. Similar increases in void volume were noted for Bio-Glas on the injection of polyacrylamide solutes. Porasil El500 and Bio-Glas 1500 have the same pore sizes, i.e. 1500 Å. Also, both supports have the same particle size distribution, i.e. 37-75 μm . It therefore means that the pore volume of Bio-Glas 1500 is greater than the pore volume of Porasil El500 because of a different manufacturing process assuming that the fraction of surface hydroxyls on both types of packing are the same. It is concluded that as far as adsorption characteristics are concerned porous glass has no particular advantages over Porasil silica.

Persiani et al. (182) claimed that CPG columns coated with polyethylene oxide minimised adsorption effects but were chemically unstable. This was supported experimentally by the authors who removed the slight negative charge of the CPG surface in aqueous media using PEO 20,000 as the adsorbed phase. Their column worked well for a while for the separation of lysozyme. After fifteen runs they observed changes in their calibration curve and column deterioration after twenty runs. In the elution of polyacrylamide on the Porasil El500 column coated with PEO 20,000, no form of separation based on steric exclusion was obtained. However, after 31 runs there was no change in peak structure of the polyacrylamide peak nor was there any

Table 4.26Bio-Glas 1500 coated with PEO 6000 (solution technique)

| Solute | % concentration | Molecular weight | V _R (ml) |
|---------------|-----------------|------------------|---------------------|
| Ethanol | 2.0 | 46 | 30.0 |
| Acetamide | 2.0 | 59 | 30.0 |
| Iodoacetamide | 2.0 | 185 | 30.0 |
| PA11 | 0.477 | 194,000 | 18.0 |
| PA8 | 0.62 | 208,000 | 18.0 |
| PA9 | 0.156 | 152,000 | 18.0 |
| PA5 | 0.28 | 668,000 | 18.5 |
| PA21 | 0.479 | 159,900 | 18.5 |

shift to higher retention volumes indicating partial stripping of the polyethylene oxide from the surface of the support.

Persiani et al. (182) recommended the use of glyceryl CPG (bonded silica) which is compatible with aqueous and organic eluents. They injected polyvinyl alcohol (PVA) using distilled water as eluent, and they successfully separated PVA observing changes in the shape of chromatograms with the molecular weight distribution. However no calibration curve of PVA showing the relationship of log molecular weight and peak retention volume was reported.

Bombaugh et al. (183) performed similar experiments using polyvinyl alcohol on deactivated Porasil. Polyvinyl alcohols prepared by bulk, solution and suspension polymerisation were injected and their molecular weight distributions were compared. No calibration curve for the polyvinyl alcohol was disclosed, so it is not possible to deduce whether the separations are dominated solely by steric exclusion or whether some adsorption occurs.

Since the coating procedure based on poly(ethylene glycol) was not completely successful, an alternative method was attempted. Porasil F2000 was coated with a 0.333% aqueous solution of Aerosol OT using the solution technique. Aerosol OT (sodium di-2-ethylhexylsulphosuccinate) is a surfactant which is quoted to be relatively stable against hydrolysis and ionizes completely in solution. Saleeb (184) studied the adsorption of Aerosol OT on carbon which has a non-polar surface and found that a physically adsorbed monolayer of Aerosol OT was formed. However, on polar solids adsorption reached a bimolecular level. The first layer is adsorbed with the surfactant polar head groups directed towards the polar sites on the surface while the second layer is held by interchain cohesion.

The silica was dried in a vacuum oven for 24 hours at a temperature of 50°C. The dried coated silica was then dry packed into a stainless steel column (two feet long). The column was then flushed with degassed distilled

water which was used as eluent. The results are given in Table 4.27 and it was found that the polyacrylamide chromatograms were irreproducible both in shape and in retention volumes. Also, the low molecular weight tail of the polyacrylamide curve exceeded the tail end of the ethanol curve, see Figure 4.32. This is indicative of a small degree of adsorption.

In Figure 4.32 the first injection of PAll yielded a chromatogram showing no form of reversible adsorption. However, on the second injection of the same polymer the low molecular weight tail exceeded the chromatogram for the ethanol. This suggested that there could be possible slow leaching of the coating from the packing, thereby revealing some exposed active sites to the eluting polyacrylamide.

From these results and the results for the poly(ethylene glycol) coated Porasil columns, the hydrogen bonding between Aerosol OT and the active hydroxyls on the silica packing would appear to be weaker than that for the poly(ethylene glycol) coated silica. However, extensive work on the Aerosol OT coated silica was not performed because successful separations of polyacrylamide were unlikely.

4.5.5 Decoated silica

Porasil El500 which was coated with PEO 20,000 was decoated using hot concentrated nitric acid by the technique reported for removing PEO from Bio-Glas (10). After the Porasil had been decoated by this technique, it was washed several times with distilled water and then dried in a vacuum oven for 24 hours at a temperature of 50°C. The gel was then dry packed in to a stainless steel column (two feet long) and was flushed with degassed distilled water. The results are tabulated in Tables 4.28 and 4.29. From the results in Tables 4.28 and 4.29 and the chromatograms in Figures 4.33 to 4.35, it would appear that the separation behaviour is closer to coated silica than to uncoated silica. The chromatograms lie between the void volume and the totally permeating volume, suggesting a permeated separation

Table 4.27Porasil F2000 coated with Aerosol OT (solution technique)

| Solute | % concentration | Molecular weight | V _R (ml) |
|-----------|-----------------|------------------|---------------------|
| Ethanol | 1.0 | 46 | 22.5 |
| Acetamide | 1.0 | 59 | 22.5 |
| PA11 | 0.144 | 194,000 | 11.0 |
| PA9 | 0.156 | 152,000 | 14.0 |
| PA11 | 0.144 | 194,000 | 15.0 |
| PA9 | 0.156 | 152,000 | 12.5 |

Table 4.28Porasil E1500 (decoated)

| Solute | % concentration | Molecular weight | V _R (ml) |
|---------------|-----------------|------------------|---------------------|
| Ethanol | 2.0 | 46 | 23.5 |
| Iodoacetamide | 2.0 | 185 | 23.5 |
| Acetamide | 2.0 | 59 | 23.5 |
| PA11 | 0.144 | 194,000 | 13.0 |
| PA12 | 0.522 | 47,000 | 12.0 |
| PA21 | 0.479 | 159,900 | 13.0 |
| PA30 | 0.375 | 333,000 | 13.0 |
| PA24 | 0.83 | 822,000 | 12.5 |
| PA8 | 0.62 | 208,000 | 12.5 |
| PA22 | 0.23 | 3,000,000 | 13.0 |
| PA13 | 0.145 | 41,000 | 13.0 |
| PA29 | 0.091 | 159,000 | 13.0 |

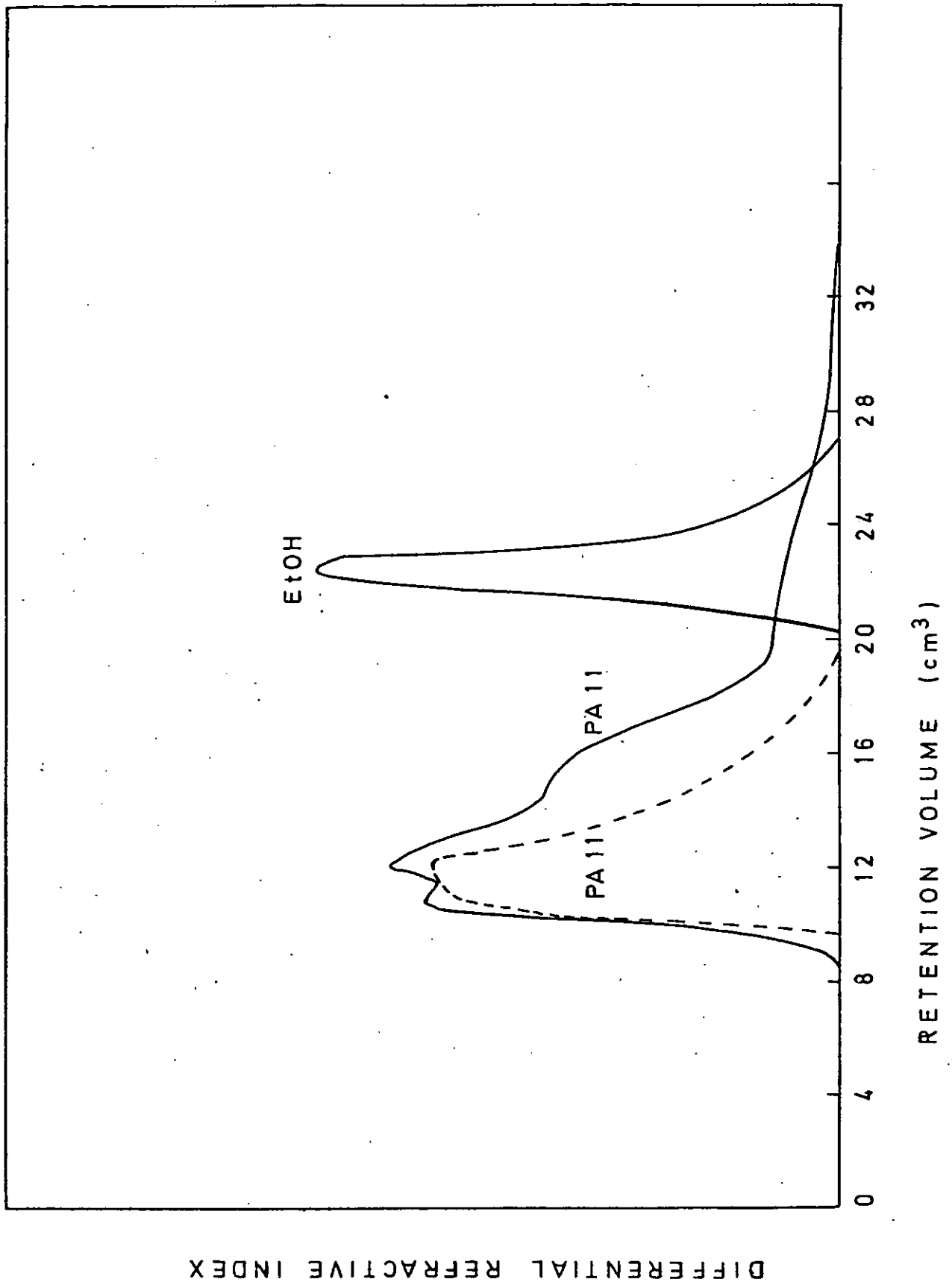
Table 4.29Porasil E1500 (decoated)

| Solute | % concentration | Molecular weight | V _R (ml) |
|-----------|-----------------|------------------|---------------------|
| PA49 | 0.313 | 109,500 | 12.5 |
| PA49(F3)* | 0.203 | 35,100 | 12.5 |
| PA49(F2)* | 0.169 | 95,000 | 12.5 |
| PA49(F1)* | 0.435 | 151,000 | 12.0 |
| PA5 | 0.153 | 402,250 | 12.5 |
| PA56 | 0.270 | 420,300 | 12.5 |

* F - fraction of polymer obtained from fractional precipitation

FIGURE 4.32

PORASIL F 2000 COATED WITH AEROSOL O.T. (SOLUTION)
USED WITH WATER



PORASIL E 1500 DE-COATED WITH CONCENTRATED NITRIC ACID (S.G. 1.42)

USED WITH WATER

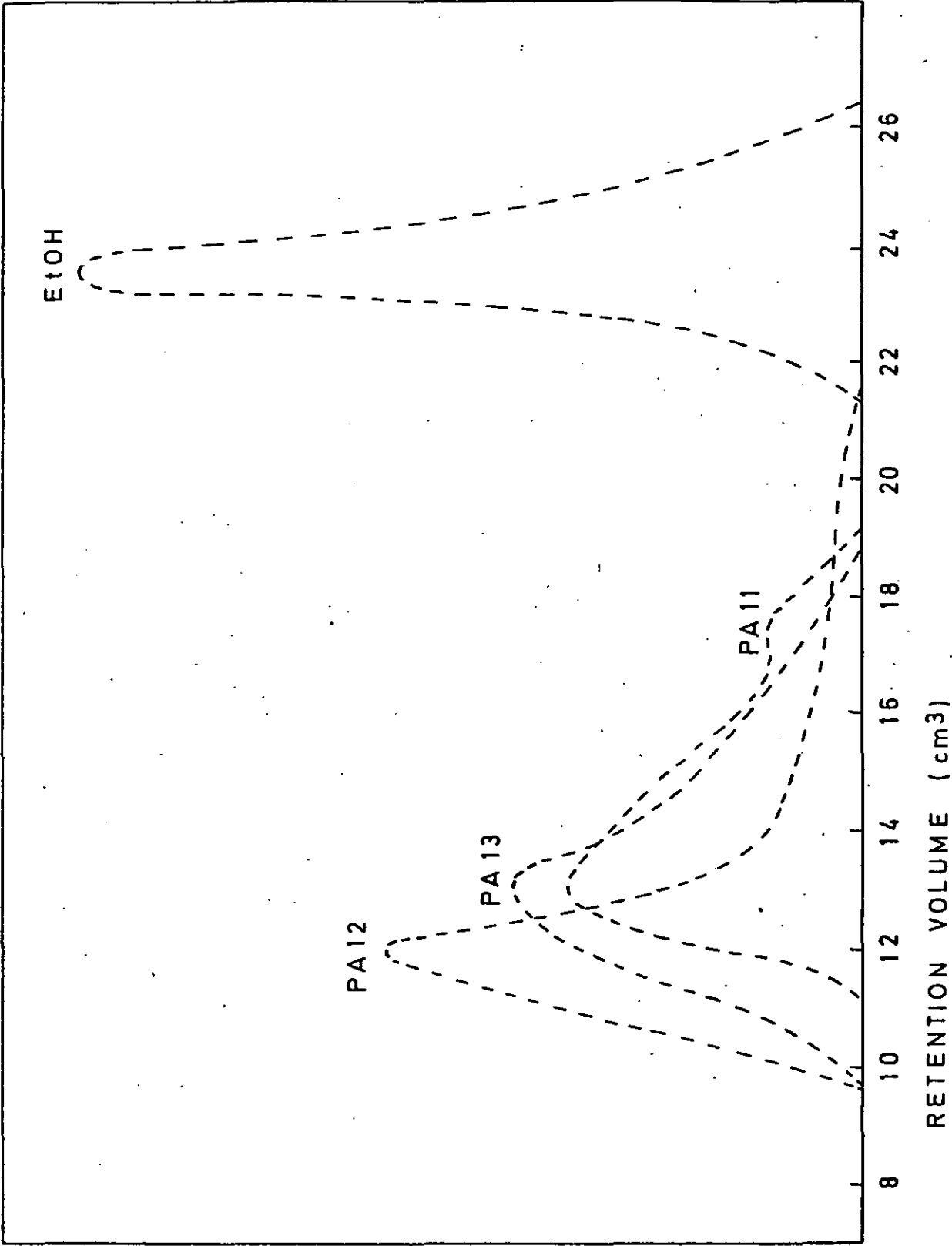


FIGURE 4.34

PORASIL E1500 DE-COATED WITH CONCENTRATED NITRIC ACID (S.G. 1.42)

USED WITH WATER

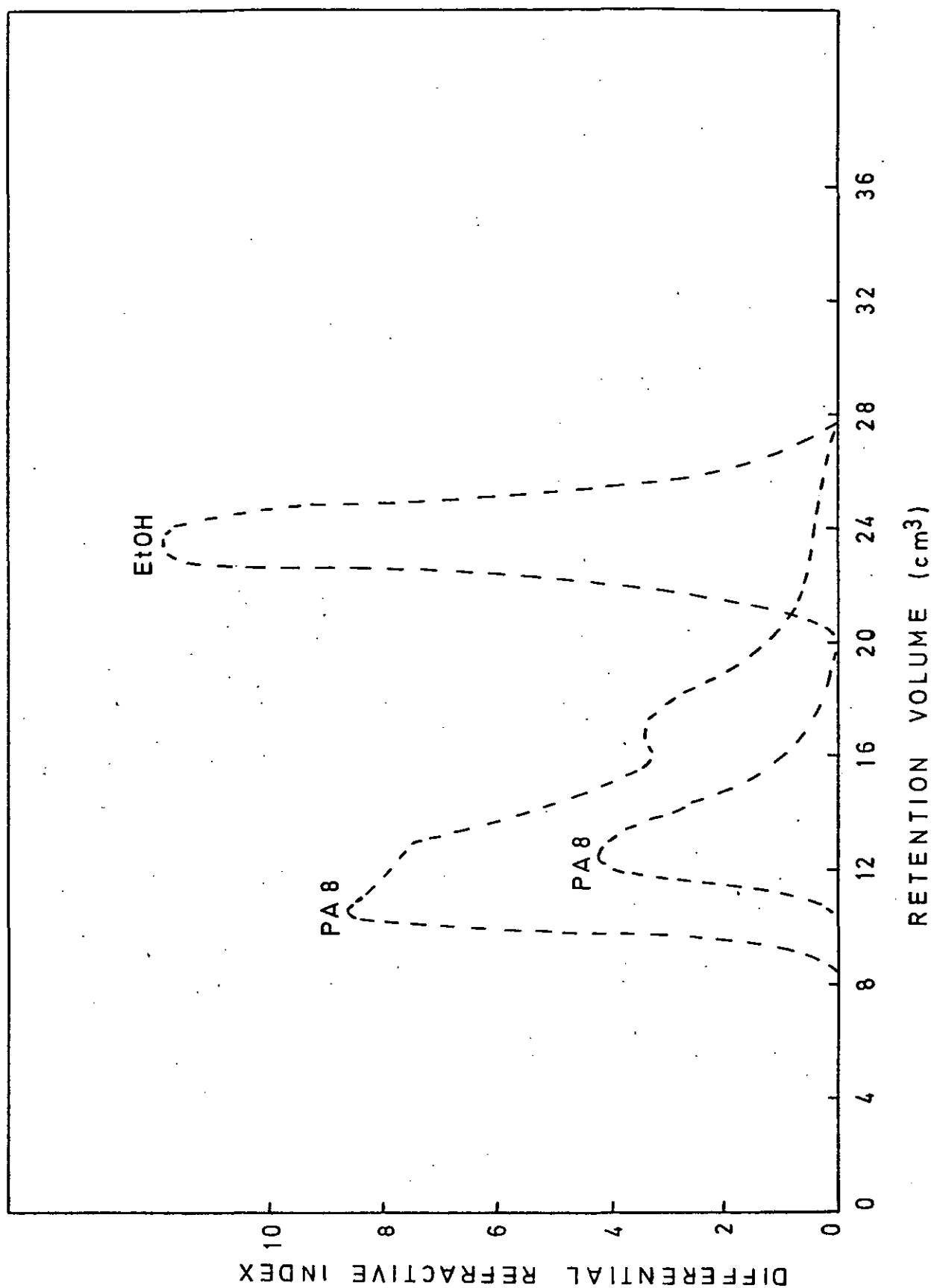
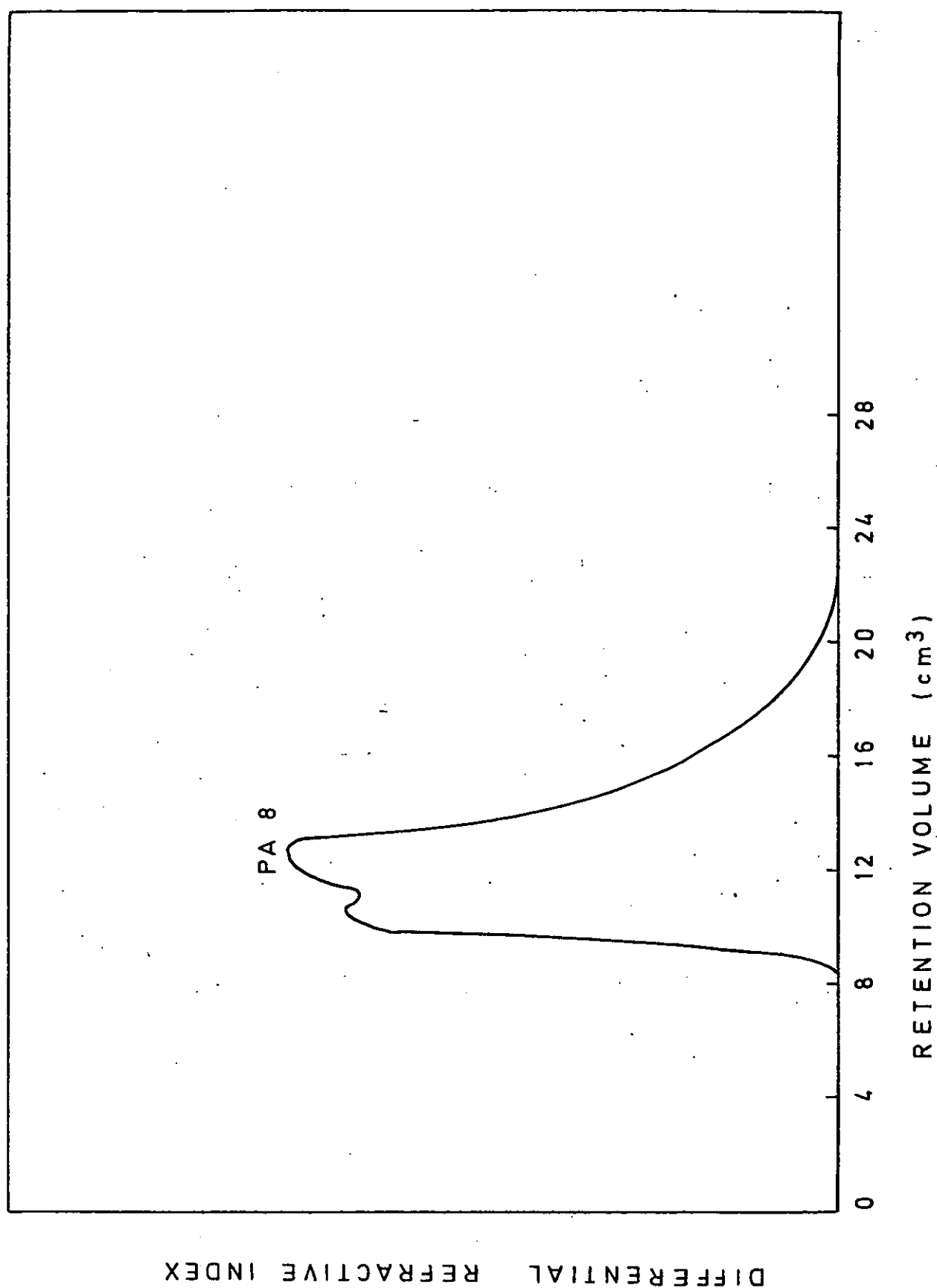


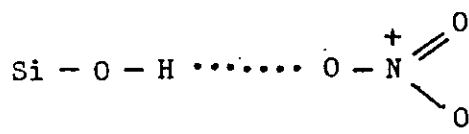
FIGURE 4.35

PORASIL E 1500 DE-COATED WITH CONCENTRATED NITRIC ACID (S.G. 1.42)

USED WITH WATER



mechanism. However, the polyacrylamide peaks were irreproducible in shape as shown in Figures 4.34 and 4.35. The peak at $V_R = 12 \text{ cm}^3$ again suggests very high molecular chains which are excluded from the porous packing. The irreproducible chromatograms indicate that the surface of the silica has been modified such that the original silica has not been regenerated because retention volumes would have been greater for polyacrylamides than for ethanol. It is possible that partial stripping of the PEO could have occurred, leaving some exposed active sites on the surface of the support, so that reversible adsorption may occur. Also, full stripping of the PEO from the surface of the support could have taken place simultaneously, resulting in some of the active sites hydrogen bonding to the nitrate group of the nitric acid, such as:



A fresh sample of Porasil E1500, i.e. uncoated, was washed with hot concentrated nitric acid. The packing will not be classed as decoated, although no polyethylene oxide had been present at the silica surface. The purpose of this experiment was to establish whether the silica surface was modified by the nitric acid. The results are shown in Table 4.30. The peak retention volumes were not reproducible (see Figure 4.36). There was a maximum of 3 cm^3 between the peaks for the two polymer injections, although PA5 and PA56 had a similar molecular weight. However, irreproducibility was not on the same scale as with uncoated Porasil. From these results it would appear that the surface of the silica was modified such that some of the hydroxyl groups (active sites) of the support hydrogen bonds to the nitrate groups of the nitric acid, thereby creating an environment close to that of polyacrylamide. Consequently, polyacrylamide elutes between the void volume and the totally permeating volume, suggesting a permeation mechanism with similar separation behaviour to that observed for

Table 4.30

| Solute | % concentration | Molecular weight | V _R (ml) |
|-----------|-----------------|------------------|---------------------|
| Ethanol | 1.0 | 46 | 23.5 |
| Acetamide | 1.0 | 59 | 23.5 |
| PA5 | 0.153 | 450,000 | 12.0 |
| PA56 | 0.270 | 420,300 | 15.0 |

coated silica. After six runs and after the injection of PA56 with a similar molecular weight to PA5, a different peak shape and peak retention volume as in Figure 4.36, was obtained which suggests that some of the nitrate groups were leaching out leaving the exposed hydroxyls to cause reversible adsorption once more. It is possible to speculate that after numerous runs conditions resulting in extensive reversible adsorption would emerge, as obtained with the uncoated support in earlier experiments, see Figures 4.23 and 4.25.

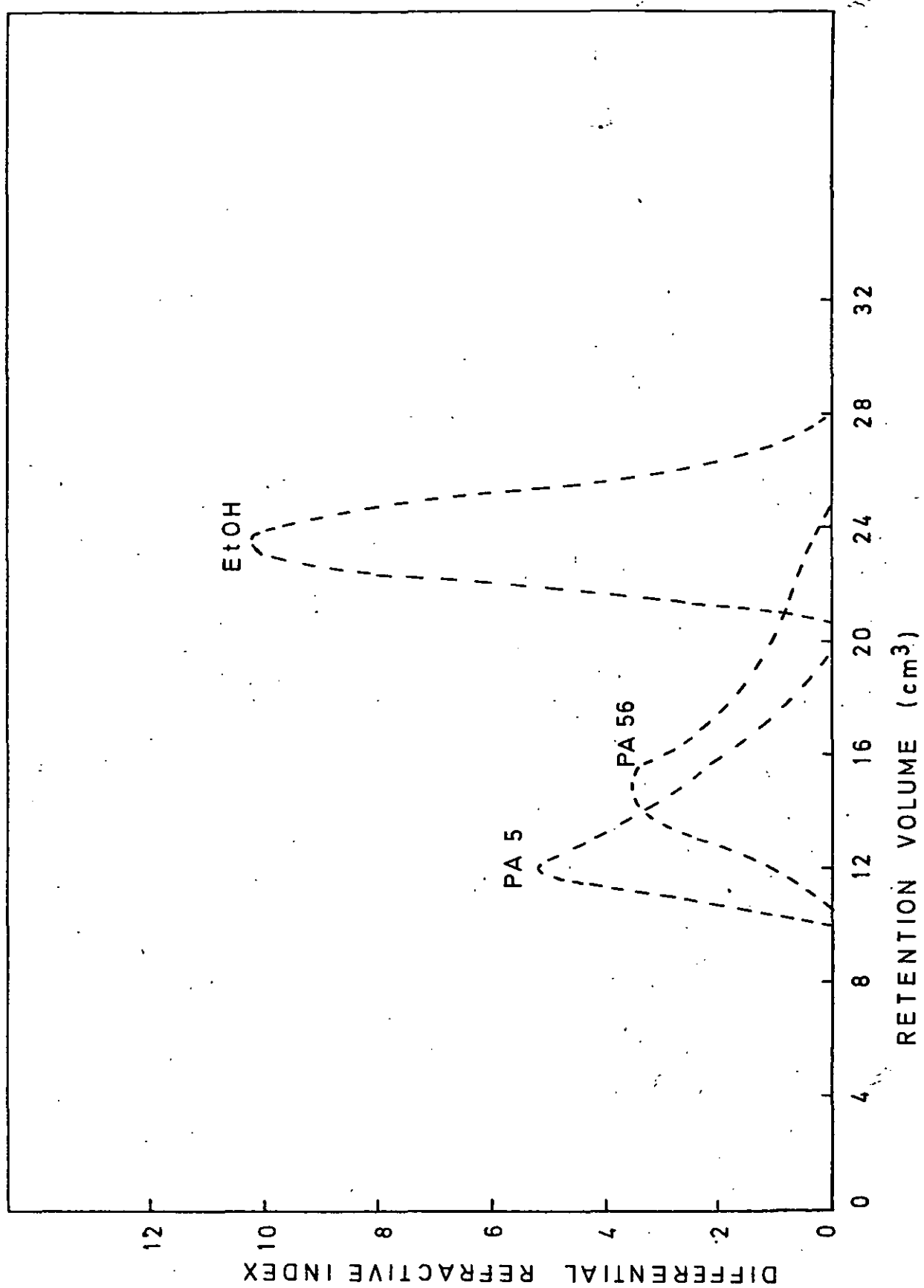
In the case of the PEO coated silica washed with hot concentrated nitric acid, the retention volumes were constant after 36 runs. This is indicative of the fact that the PEO on the silica support is playing some intrinsic part when reacted with the hot concentrated nitric acid and washed with distilled water.

Griot and Kitchener (185) showed that silica heated to about 600°C still had "isolated silanol groups" which provided the best adsorption sites for polyacrylamide. However, Tadros (186) observed that polyvinyl alcohol (PVA) does not adsorb at pH 7 on silica. He suggested therefore that the loss of adsorption with rise in pH is due to a reduction of the number of silanol groups available for hydrogen bonding. If a silica whether it is uncoated or coated with PEO is washed with nitric acid it is feasible that the number of available hydroxyl groups would be enhanced, especially with subsequent washings with distilled water. This should enhance the adsorption of polyacrylamide. However, the opposite effect seems to occur which suggests that some form of nitration takes place on the surface of the silica. It is possible that the PEO is not completely stripped off from the surface of the silica in nitric acid resulting in Porasil coated with PEO and washed in nitric acid, giving more reproducible behaviour than Porasil (uncoated) washed in nitric acid. Rubio and Kitchener (187) stated that ethers are known to form oxonium salts and hydrogen-bonded complexes with strong acids. It is possible that the improvement of the decoated and

FIGURE 4.36

PORASIL E 1500 TREATED WITH CONCENTRATED NITRIC ACID (SG 1.42)

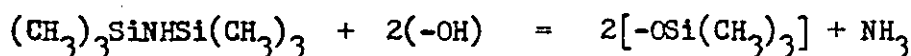
USED WITH WATER



and coated packings over the uncoated packings is due to some type of physically bonded surface phase. Since this phase may not be stable over a long period of time, such packings are not suitable for routine separations of polyacrylamide.

4.5.6 Bonded silica

Hsing and Zettlemoyer (188) and Perret and Purnell (189) studied the reactions of hexamethyldisilazane (HMDS) and silica and their isotherms with HMDS $(\text{CH}_3)_3\text{SiNHSi}(\text{CH}_3)_3$. The reaction of the hydroxyl groups on the silica surface represented by $-\text{OH}$ is



Hsing (188) showed from near infra-red studies that the ammonia evolved is held very strongly by the exposed surface hydroxyls of the packing. The energy taken to remove the ammonia (at 170°C and at 10^{-6} torr) is equal to that to remove physically adsorbed water from the packing. Silica treated with the above named silane compound is referred to as a silanised packing. This type of packing is used in GPC to separate solutes principally using an organic eluent. Thus, Dubin (178) examined the behaviour of polar polymers with silanised packings. It was thought at the time that an attempt should be made to study if the silanised porous silica support was an effective means of separating polyacrylamides by a steric exclusion mechanism.

Porasil E1500 was silanised with hexamethyldisilazane (HMDS) at Harwell. The support was dry packed into a stainless steel column (two feet long). The column was then flushed through with degassed distilled water as eluent. The results are tabulated in Table 4.31.

The bonding of HMDS onto silica has been described by Ouano et al. (190). On using a silanising agent it is assumed that the most active sites on the surface of the porous silica would be removed by the chemical

Table 4.31Porasil E1500 bonded with hexamethyldisilazane

| Solute | % concentration | Molecular weight | V _R (ml) |
|-----------|-----------------|------------------|---------------------|
| Ethanol | 2.0 | 46 | 13.5 |
| Acetamide | 2.0 | 59 | 13.5 |
| PA12 | 0.522 | 47,000 | 13.5 |
| PA8 | 0.62 | 208,000 | 13.5 |
| PA9 | 0.156 | 152,000 | 13.5 |

bonding of the methyl silyl derivative on the packing. The elution of ethanol, PA12, PA8 and PA9 occurred at the same retention volume, i.e. the void volume of the packing (13.5 ml), see Figure 4.37. This suggested that the pores of the gel were filled with air, and consequently ethanol and acetamide were not totally permeating because the eluent did not wet the hydrophobic surface in the pores. Therefore, if a suitable wetting agent can be used which is miscible with water, then the eluent water can follow the pathway of the wetting agent into the pores of the gel. Therefore, a mixture of tetrahydrofuran and water was used as eluent. Although chromatograms were obtained for ethanol and acetamide, see the values of V_R in Table 4.32, no chromatograms were obtained for polyacrylamide samples.

The overall conclusion is that the silanization treatment did not block all the adsorption sites and that some of the trimethylsilyl groups were only temporarily bonded and were removed during the washing steps, or that a combination of both possibilities occurred.

4.5.7 Studies of Eluents on Uncoated Silica

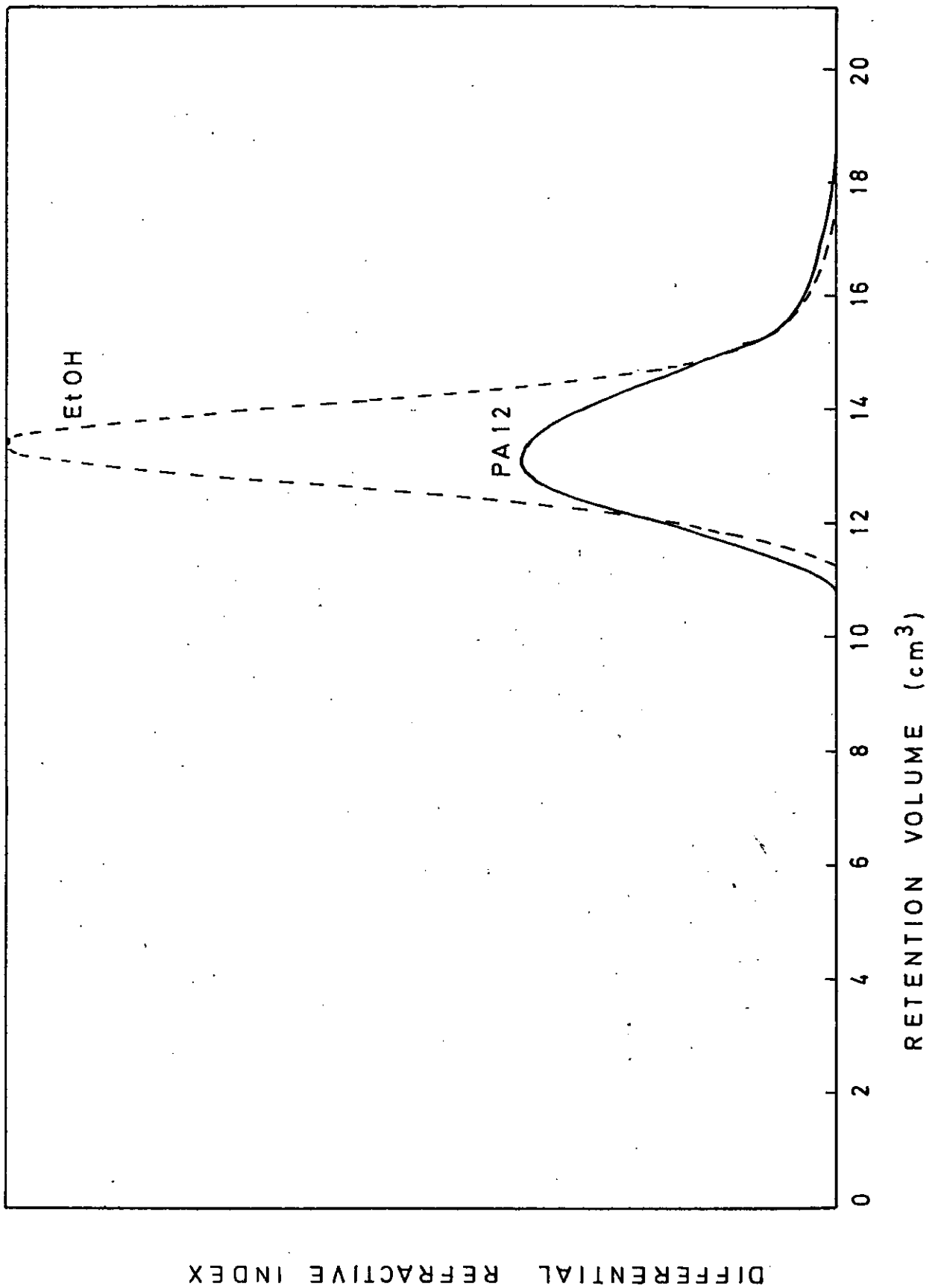
The GPC results for uncoated silica suggest interaction of the polyacrylamide with the silica surface leading to retardation in the stationary phase. The experiments with coated silica suggest that this adsorption mechanism may be minimised by blocking adsorption sites. From studies of polymer adsorption and the solid-liquid interface in a static system (191), the choice of liquid has a marked effect on the extent of polymer adsorption. First, if the liquid is preferentially adsorbed on the active sites, then no polymer is adsorbed. A good GPC example of this effect is the separation of poly(vinyl pyridine) on crosslinked polystyrene gels. The polymer is completely retained in the column with chloroform as solvent but separates by steric exclusion with dimethylacetamide as solvent. Secondly, if the liquid has a similar affinity to that of the polymer for the surface sites, then the extent of adsorption increases as polymer-solvent interaction

Table 4.32Porasil E1500 bonded with hexamethyldisilazane

| Solute | % concentration | Molecular weight | V _R (ml) |
|-----------|-----------------|------------------|---------------------|
| Ethanol | 2.0 | 46 | 23.5 |
| Acetamide | 2.0 | 59 | 23.5 |
| PA12 | 0.522 | 47,000 | - |
| PA9 | 0.62 | 208,000 | - |

FIGURE 4.37

PORASIL E 1500 (SILANIZED) USED WITH WATER



decreases. GPC results following this trend have been reported by Otocka and Hellman (199).

Although treatment of a packing with HMDS or other silyl compounds will remove acidic silanol groups, not all acidic sites such as Lewis acid sites will be deactivated. Consequently, the eluent or an additive in the eluent must be chosen to interact preferentially with the silica. Evidently, very basic compounds must be preferred. In the section (4.5.6) on bonded silica it was suggested that ammonia was tightly held by the active sites of the packing. Therefore, it appeared feasible to use a dilute aqueous solution of ammonia as eluent. The bonding between the active hydroxyl groups of the support to the ammonia is supposed to be held by tight physical bonding



Ammonia is a smaller size molecule compared to molecules such as polyethylene oxide and Aerosol OT. Consequently, active hydroxyls which are sterically shielded from surfactant molecules can be reached by much smaller molecules such as ammonia.

The packing (Porasil) was dry packed into a stainless steel column (two feet long) which was flushed with 1% 880 ammonia in aqueous solution. The results for Porasils D, E and F are summarised in Tables 4.33 to 4.35 and typical chromatograms are presented in Figures 4.38 to 4.40. The chromatograms obtained were reproducible in retention volumes although small changes in chromatogram shapes were noted on repeated injection of polyacrylamide solutes. The behaviour in Figures 4.38, 4.39 and 4.40 is similar to the results obtained for the coated and decoated silicas with the polyacrylamide chromatograms lying between the void volume and the total permeating volume in the column. This suggest that reproducible behaviour is possible by choosing a component such as ammonia in the eluent to reduce the degree of polyacrylamide adsorption on Porasil. As before,

Table 4.33Porasil DL000 (uncoated) with 1% 880 ammonia

| Solute | % concentration | Molecular weight | V _R (ml) |
|-----------|-----------------|------------------|---------------------|
| Ethanol | 2.0 | 46 | 24.5 |
| Acetamide | 2.0 | 59 | 24.5 |
| PA30 | 0.354 | 333,000 | 14.0 |
| PA10 | 0.202 | 291,660 | 14.5 |
| PA11 | 0.213 | 194,000 | 14.5 |
| PA4 | 0.313 | 516,500 | 14.5 |
| PA13 | 0.444 | 40,700 | 14.0 |

Table 4.34Porasil EL500 (uncoated) with 1% 880 ammonia

| Solute | % concentration | Molecular weight | V _R (ml) |
|-----------|-----------------|------------------|---------------------|
| Ethanol | 2.0 | 46 | 23.5 |
| Acetamide | 2.0 | 59 | 23.5 |
| PA11 | 0.189 | 194,000 | 15.0 |
| PA10 | 0.301 | 291,660 | 15.0 |
| PA4 | 0.253 | 516,500 | 14.5 |
| PA43 | 0.371 | 194,000 | 15.0 |
| PA30 | 0.352 | 333,000 | 15.0 |
| PA13 | 0.183 | 40,700 | 14.5 |

Table 4.35

Porasil F (uncoated) with 1% 880 ammonia

| Solute | % concentration | Molecular weight | V _R (ml) |
|---------------|-----------------|------------------|---------------------|
| Ethanol | 2.0 | 46 | 24.0 |
| Acetamide | 2.0 | 59 | 24.0 |
| Iodoacetamide | 2.0 | 185 | 24.0 |
| PA13 | 0.499 | 41,000 | 20.0 |
| PA30 | 0.375 | 333,000 | 20.0 |
| PA4 | 0.32 | 517,000 | 20.0 |
| PA43 | 0.371 | 657,000 | 20.0 |
| PA11 | 0.144 | 47,000 | 20.0 |
| PA10 | 0.172 | 292,000 | 20.0 |

FIGURE 4.38

UN-COATED PORASIL D 1000 USED WITH 1% 0.880 AMMONIA

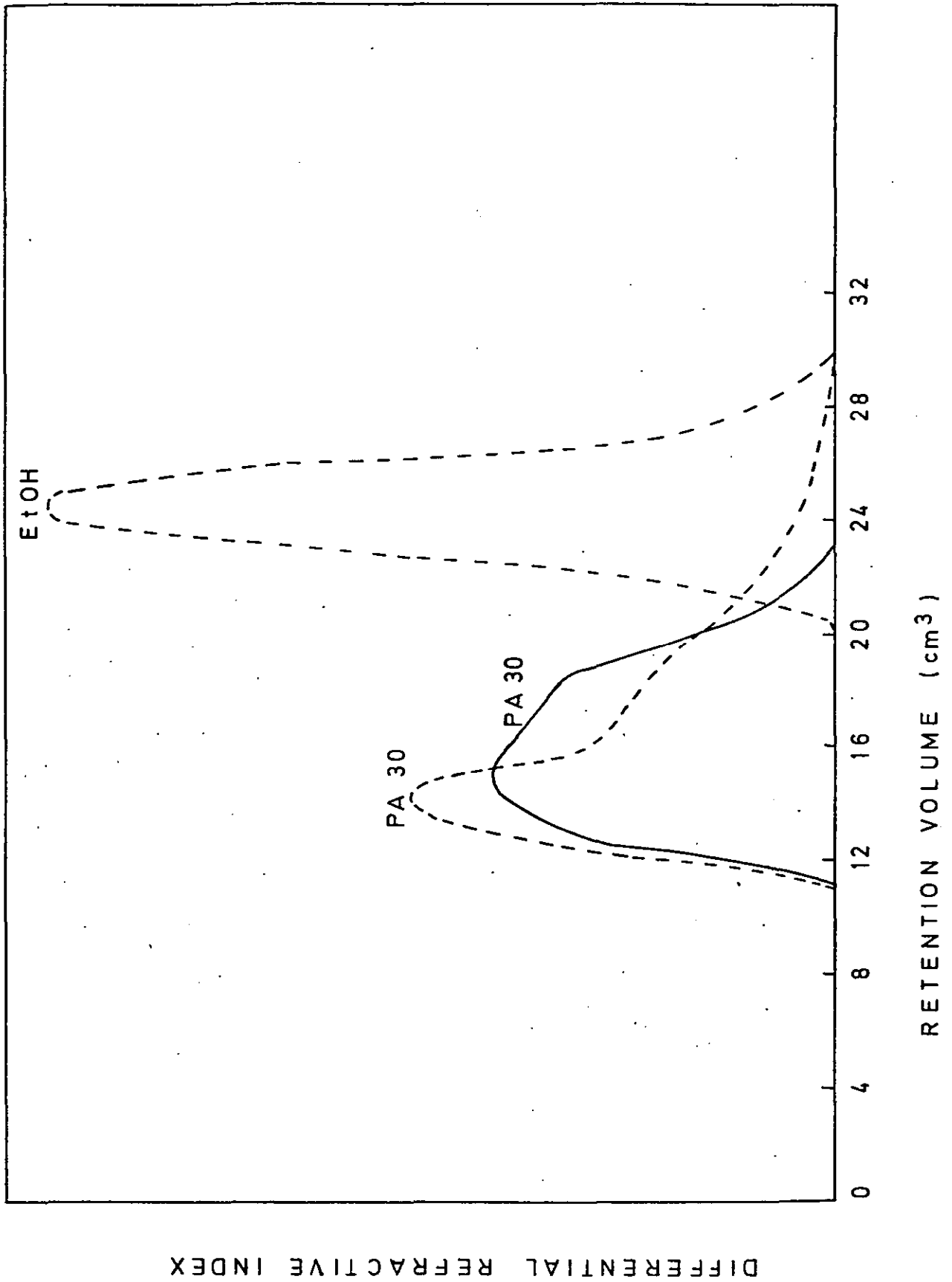


FIGURE 4.39

UN-COATED PORASIL E 1500 USED WITH 1% 0.880 AMMONIA

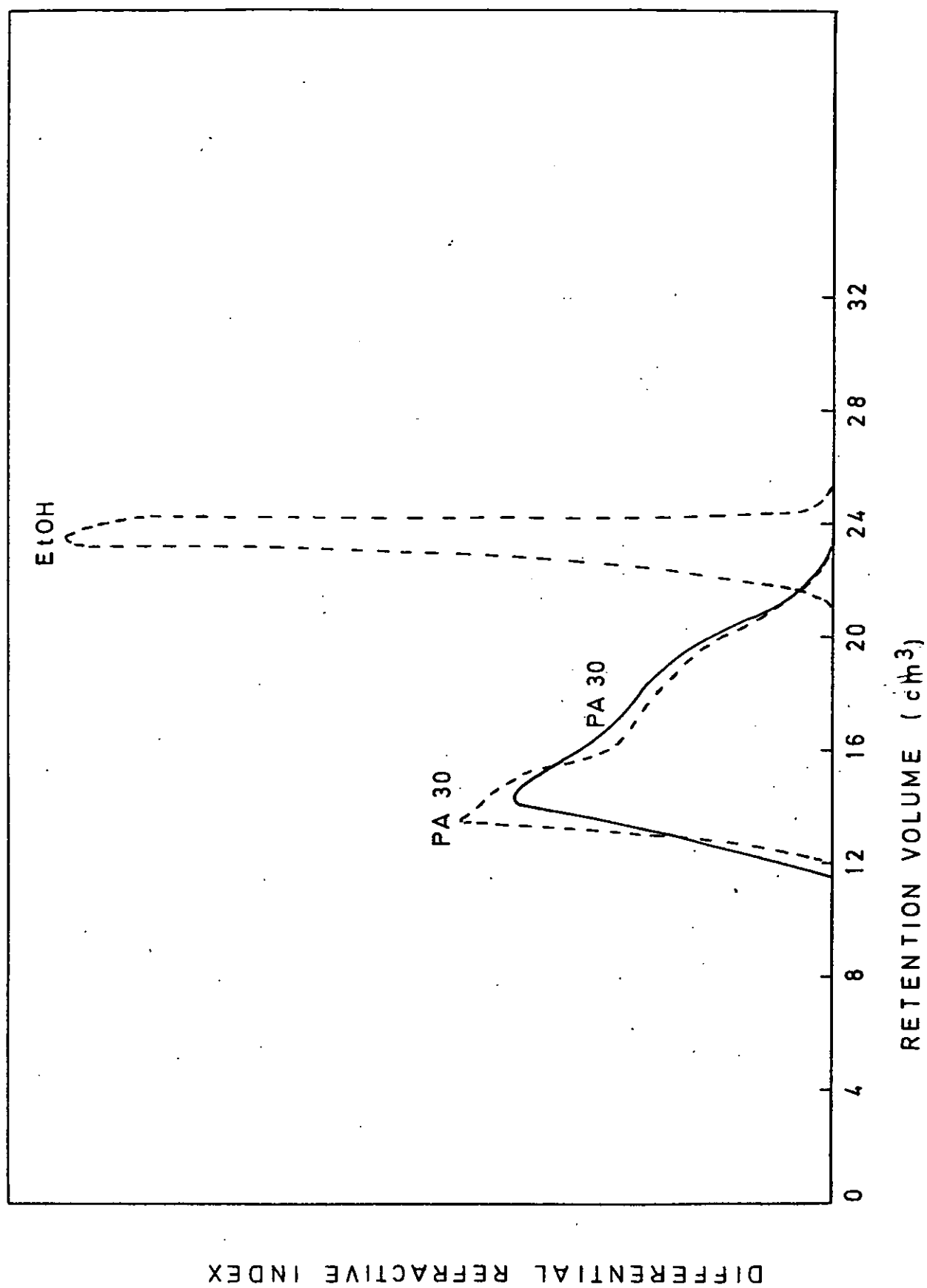
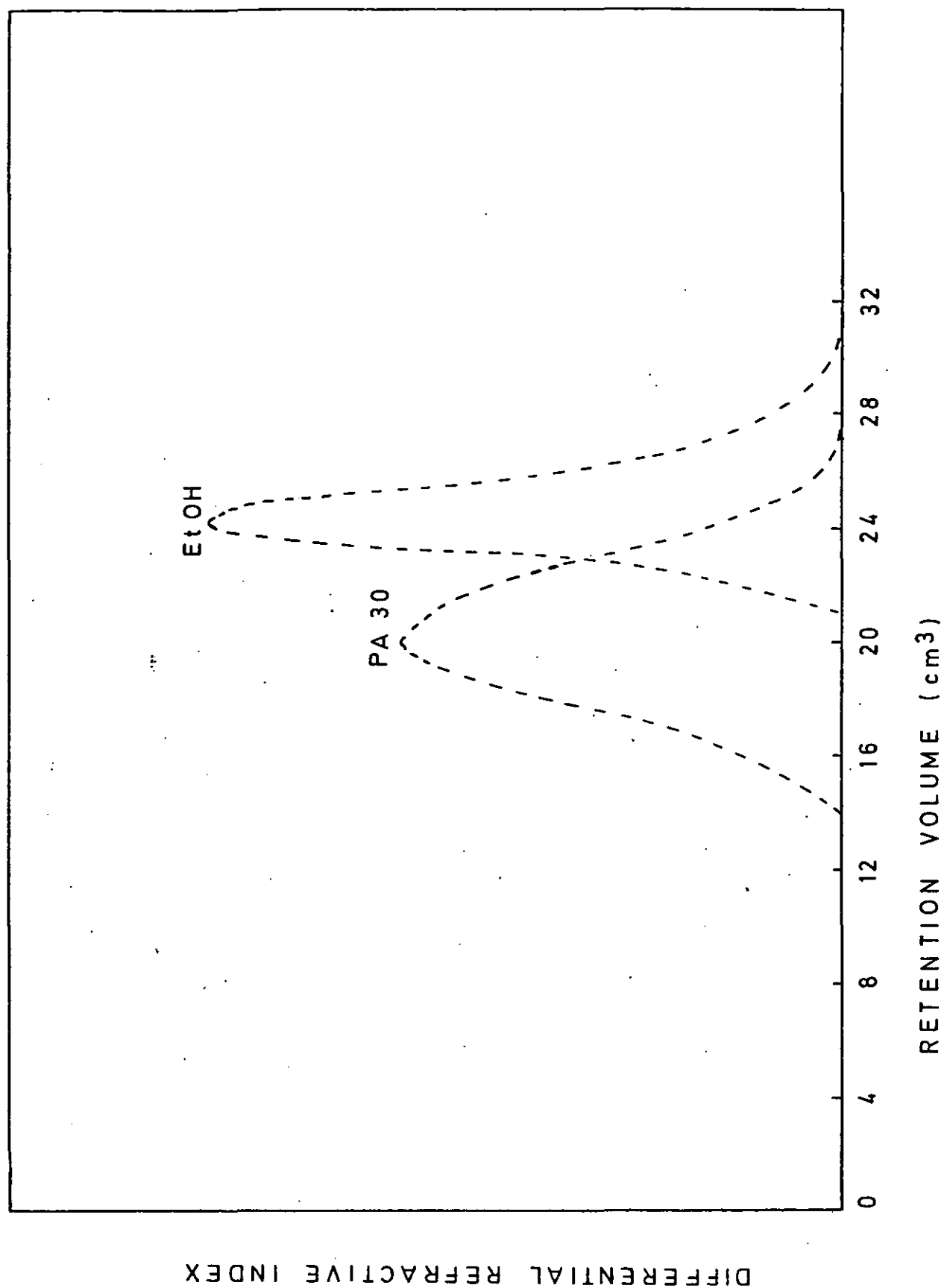


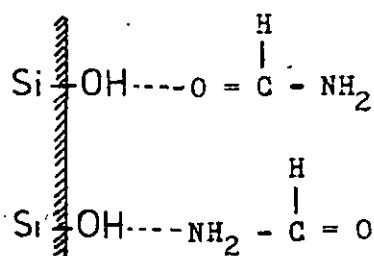
FIGURE 4.40

UN-COATED PORASIL F 2000 USED WITH 1% 0.880 AMMONIA



the value of V_R for polyacrylamides in Tables 4.38 to 4.40 appear at the void volume because of the concentration of high molecular weight chains in each polyacrylamide sample. Consequently, it was not possible to establish a relation between molecular weight and retention volume based on a steric exclusion mechanism.

According to Vivilichea (192) the surface of the silica packing will be slowly leached away in the presence of liquids having high pH. Consequently, other possible basic eluents which were compatible with polyacrylamide were considered. Formamide has been used as a solvent for polyacrylamide, see equation (2.55). If formamide is preferentially attached to the active sites,



then the surface of the packing would have a similar constitution to the structure of the polymer. It should be recalled that separations by steric exclusion with negligible interactions are obtained for polystyrene in good solvents with crosslinked polystyrene gels and for dextran in water with crosslinked dextran gels.

A ternary eluent of water/formamide/ammonia was studied. Formamide has a refractive index of 1.447. The operating range of the low index prism in the refractometer is 1.31 - 1.44. The pH of formamide is 9.21. In view of the effect of eluents with high pH on the leaching of silica, it was decided to dilute the formamide with distilled water such that a stable GPC baseline occurred at a reasonable dilution and that the pH was within a suitable operating range. Consequently, a dilution of 1 part of formamide to 5 parts of distilled water was found to give a stable baseline. The pH of this binary mixture was found to be 7.10. In the preparation of

the three component mixture, 5 parts of 1% 880 ammonia in water to 1 part of formamide was the ratio of the components in the mixture. This ternary mixture has a pH of 10.42 and gave a straight line GPC baseline. The GPC results are given in Tables 4.36 to 4.38. These results fall into the same pattern as reported for the 1% 880 ammonia experiments. The peak retention volume is at the void volume due to the significant concentration of high molecular weight polymer and the chromatogram lies between the void volume and the totally permeating volume for ethanol, see Figure 4.41. Additionally, a "ghost peak" appeared around the retention volume for ethanol, see Figures 4.42 and 4.43. This peak was irreproducible in peak shape and could have either a positive or negative deflection with respect to the polymer peak, although the polymer solutions had similar concentrations and similar injection times. In order to prove that this "ghost" peak was unconnected with the injection of polyacrylamide, an eluent injection of 1% 880 ammonia/formamide (5:1) was performed, and the "ghost" peak again occurred (see Figure 4.44). These "ghost" peaks were again irreproducible in peak height and peak width. At the time it appeared as if the GPC instrumentation might be at fault. Consequently, the eluent in the reservoir was changed to degassed distilled water and one of the initial PEO coated Porasil EL500 columns was used. This system functioned just as it did in Section 4.5.4 confirming the fact that the GPC instrumentation was operating properly.

In all separations involving formamide in binary and ternary eluents, "ghost" peaks were observed. Similar results have been reported by Berek (193) for binary eluents and refractometer detection. The observations are explained by the eluent, which is injected and appears at the totally permeating volume, having a different composition from the eluent in the reservoir for the pumping system. This change in composition may arise from polyacrylamide being preferentially solvated by one liquid component, displacement of a preferentially adsorbed component from the silica surface, evaporation of one component from the solution before injection, or adsorption

Table 4.36Porasil D1000 (uncoated) with 1% 880 ammonia/formamide (5:1)

| Solute | % concentration | Molecular weight | V _R (ml) |
|---------|-----------------|------------------|---------------------|
| Ethanol | 2.0 | 46 | 24.5 |
| PA13 | 0.152 | 40,700 | 14.0 |
| PA11 | 0.138 | 194,000 | 14.0 |
| PA18 | 0.101 | 2,482,000 | 13.5 |
| PA10 | 0.145 | 291,660 | 14.0 |
| PA30 | 0.203 | 333,000 | 13.5 |
| PA43 | 0.281 | 657,000 | 13.5 |

Table 4.37Porasil C400 (uncoated) with 1% 880 ammonia/formamide (5:1)

| Solute | % concentration | Molecular weight | V _R (ml) |
|---------|-----------------|------------------|---------------------|
| Ethanol | 2.0 | 46 | 24.5 |
| PA13 | 0.152 | 40,700 | 13.5 |
| PA30 | 0.203 | 333,000 | 14.0 |
| PA18 | 0.101 | 2,482,000 | 13.5 |

Table 4.38Porasil E1500 (uncoated) with 1% 880 ammonia/formamide (5:1)

| Solute | % concentration | Molecular weight | V _R (ml) |
|---------|-----------------|------------------|---------------------|
| Ethanol | 2.0 | 46 | 23.5 |
| PA43 | 0.281 | 657,000 | 13.0 |
| PA30 | 0.203 | 333,000 | 13.5 |
| PA18 | 0.101 | 2,482,000 | 13.0 |

FIGURE 4.41

UN-COATED PORASIL D 1000 USED WITH 1% 0.880 AMMONIA/FORMAMIDE (5:1)

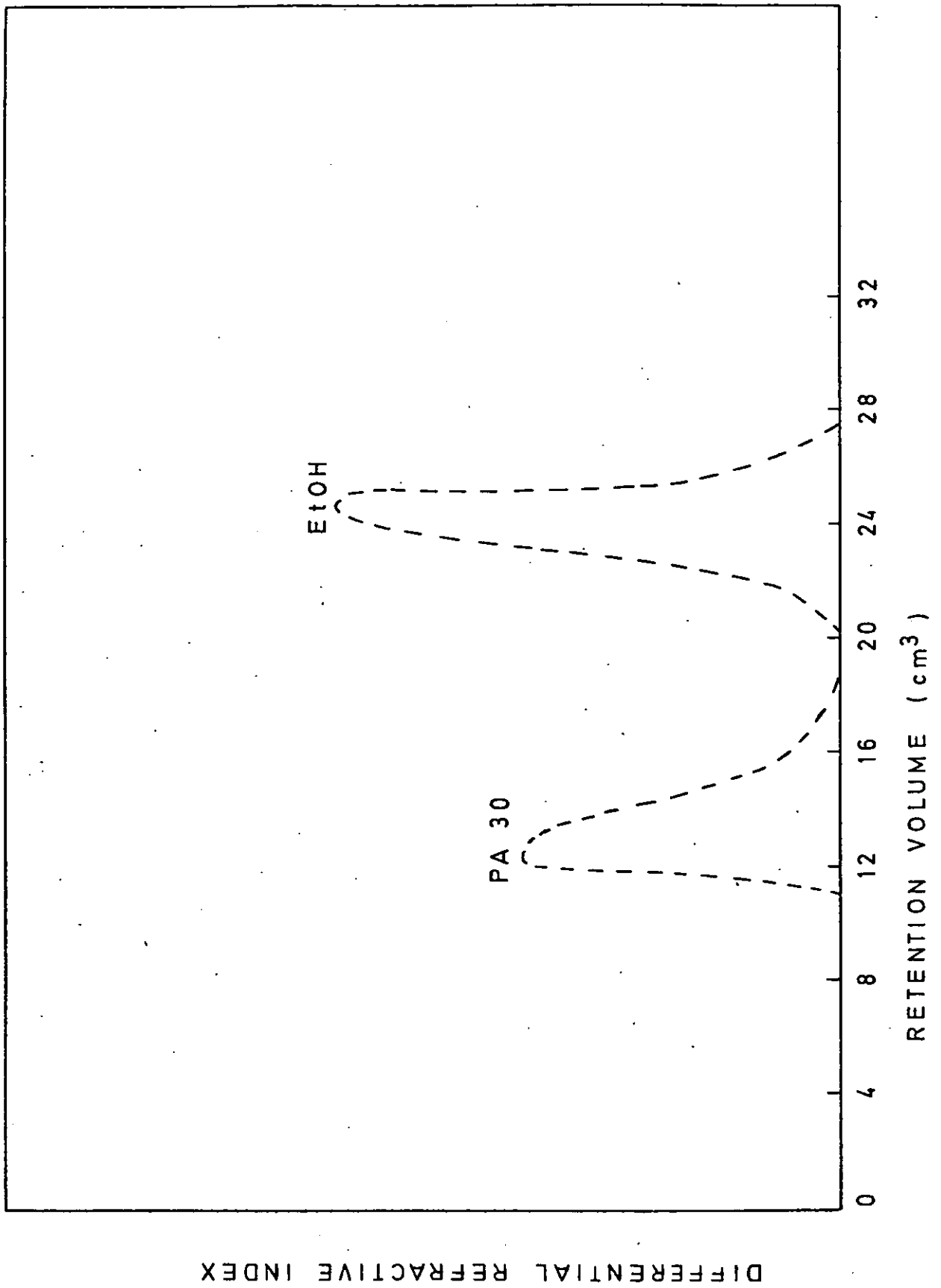


FIGURE 4.42

PORASIL D1000 USED WITH 1% 0.880 AMMONIA/FORMAMIDE (5:1)

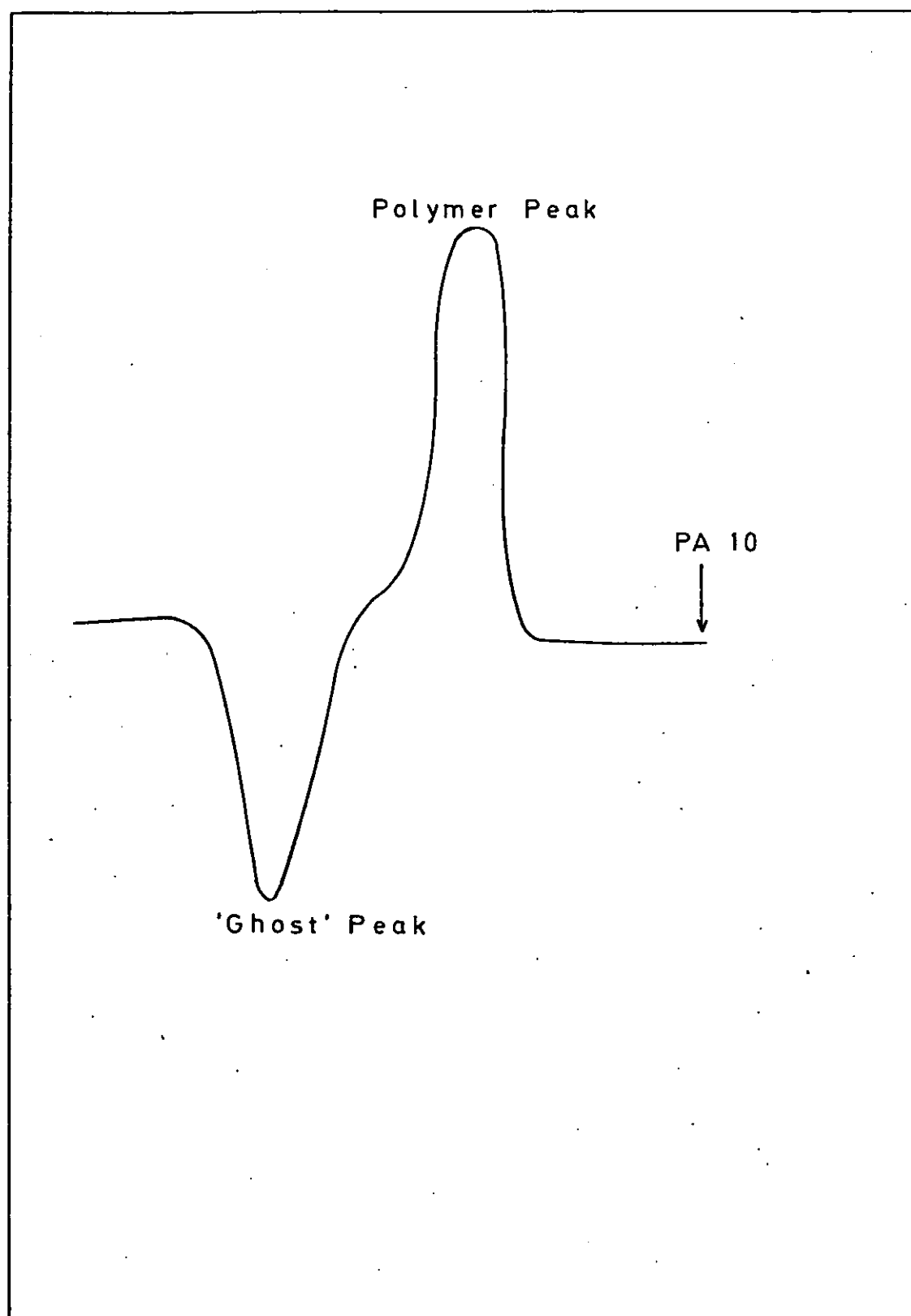


FIGURE 4.43

POLYACRYLAMIDE INJECTION USING
1% 0.880 AMMONIA/FORMAMIDE (5:1) ON PORASIL D1000 (UN-COATED)

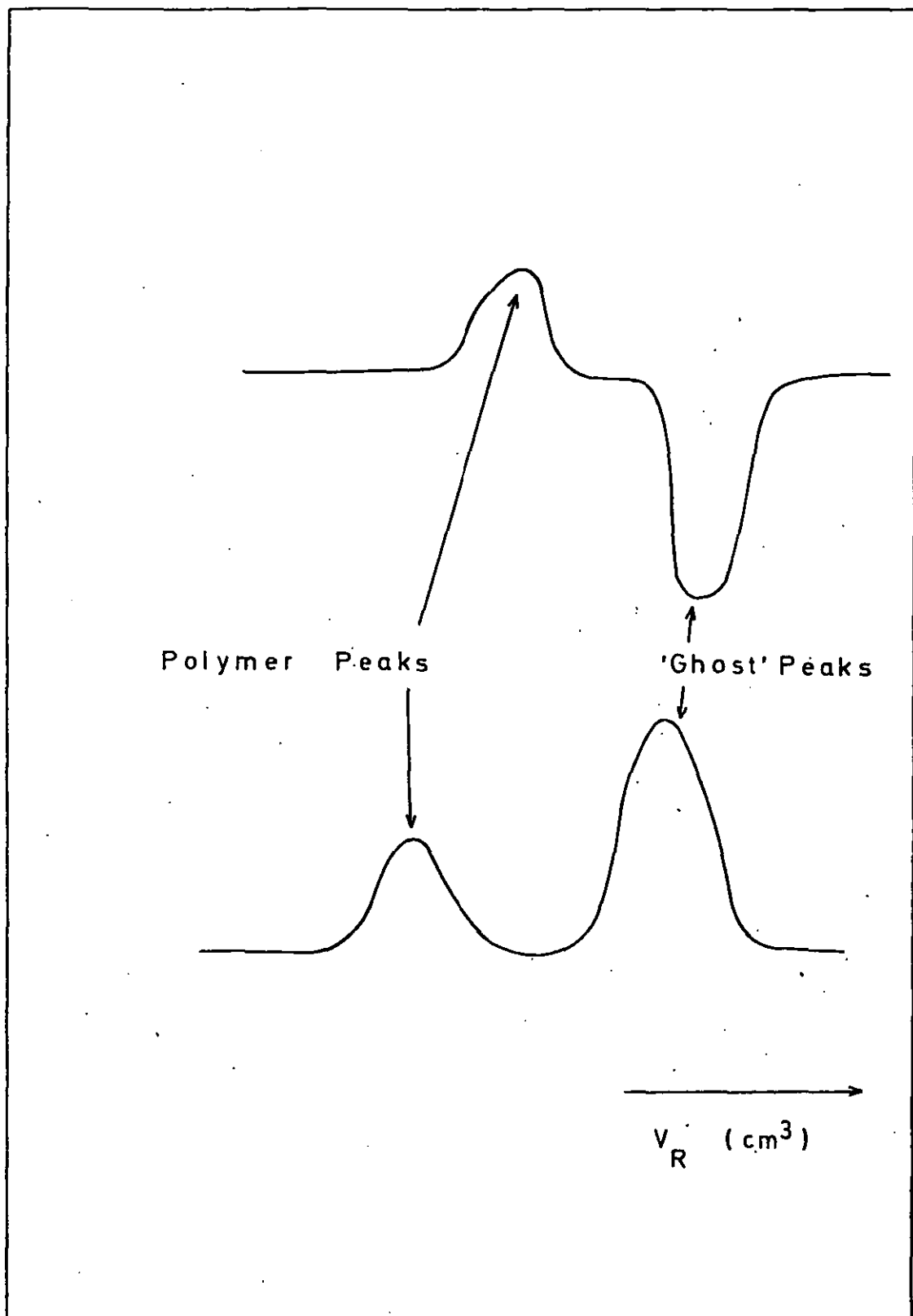
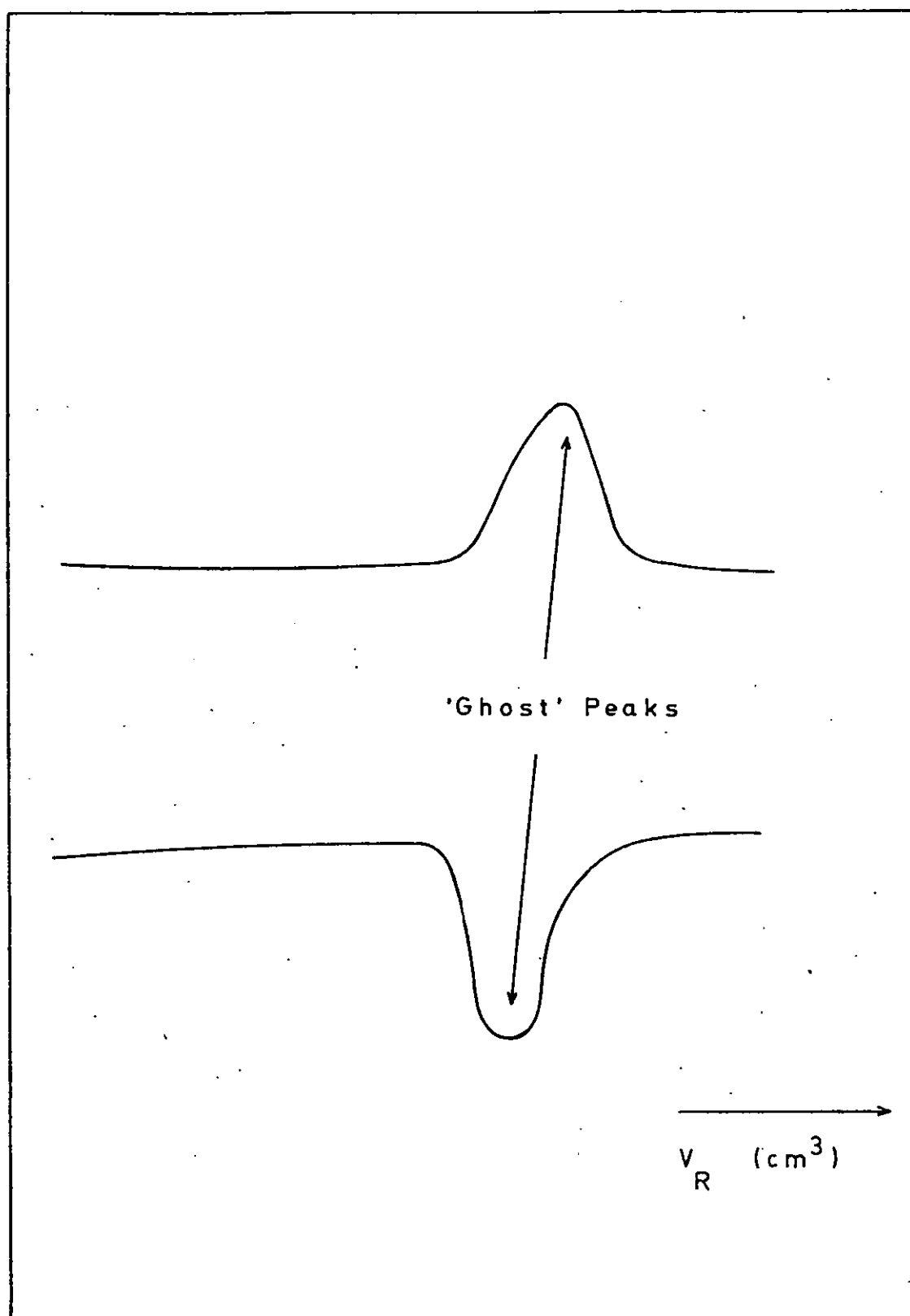


FIGURE 4.44

SOLVENT INJECTION OF 1% 0.880 AMMONIA/FORMAMIDE (5:1)
ON PORASIL D1000 (UN-COATED)



of atmospheric water during injection. Since one or more of these explanations may occur, depending on the particular conditions, "ghost" peaks which may be positive or negative are possible.

Ede (194) has reported the use of a binary eluent of m-cresol and chlorobenzene for the separation of nylon-6 with Styragel columns, since he found that m-cresol alone was not a suitable solvent. Although the polyacrylamide in the binary eluent appeared to separate by steric exclusion, the chromatograms were not always reproducible, so that accurate distributions were not easy to obtain. He did not observe any "ghost" peaks, but highlighted the fact that binary eluents were difficult to work with.

4.5.8 SG 120 silica with water/formamide as eluent

Although none of the previous GPC experiments have been entirely satisfactory, two ways of minimising polyacrylamide on silica are indicated by the results. First, the chemical bonding of a surface phase to deactivate acidic silanol groups (Bronsted acid sites). Second, the use of an eluent mixture containing a basic component to interact with other sites, such as Lewis acid sites, which do not react with silyl compounds. It was decided to use a silica which had been bonded to aminopropyl groups, in order to give a surface having a similar constitution to the structure of polyacrylamide. If the basic component in the eluent competes efficiently for the unreacted sites, then polyacrylamide separations according to steric exclusion might be expected.

Although the eluents ammonia/water and ammonia/water/formamide succeed in reducing polyacrylamide adsorption onto silica, the three component mixture has a pH of 10.42. This basic eluent could give rise to removal of the aminopropyl groups from the silica surface. It was felt preferable to eliminate ammonia from the eluent mixture. Instead, a binary eluent of water/formamide (5:1) which had a pH of 7.1 was used. Formamide will not be as effective as ammonia in deactivating acidic sites. However, the

interaction of formamide with the Lewis acid sites which remain after forming the bonded aminopropyl phase may reduce polyacrylamide adsorption to a very low level.

Silica SG 120, a laboratory sample produced at A.E.R.E., Harwell, was treated with a silyl compound by Mr. M.J. Holdoway to produce a silica with chemically bonded aminopropyl groups. This packing was slurry packed as a dispersion in methanol into a column (one foot long x 3/8" diameter). With the eluent mixture of water/formamide (5:1) having a pH of 7.1, long-term stability of the bonded phase would be expected. The eluent mixture was degassed as described in the previous section. The eluent was allowed to flush through the SG 120 column for a period of 36 hours. The column was then coupled to the detector and the following solutes, shown in Table 4.39, were injected into the column.

The chromatograms obtained here were reproducible in peak retention volume and peak shape on repeated injections. Also, the "ghost" peak appeared at a retention volume of 11.5 to 12.0 cm³ close to that of ethanol. The chromatograms for the polymers are shown in Figure 4.52, demonstrating that the separated polymer eluted between the void volume and the totally permeating volume. Contrary to the observations in previous sections, the peak elution volume did not appear at the void volume for most polyacrylamides in Figure 4.45. The plot of logarithm of molecular weight for the solutes in Table 4.39 is shown in Figure 4.46, suggesting that steric exclusion is the dominant separation mechanism. In order to establish an accurate calibration, the PA⁴⁹ fractions described in Section 4.4.2 were dissolved in water/formamide (5:1) and chromatograms were obtained with the SG 120 column. The results are shown in Table 4.40 and the chromatograms are shown in Figure 4.47.

A comparison of the chromatograms obtained from the fractions (Figure 4.47) with the chromatograms obtained from the polydisperse whole polymers

FIGURE 4.45

SG 120 (AMINO PROPYL BONDED) USED WITH FORMAMIDE/WATER (1:5)

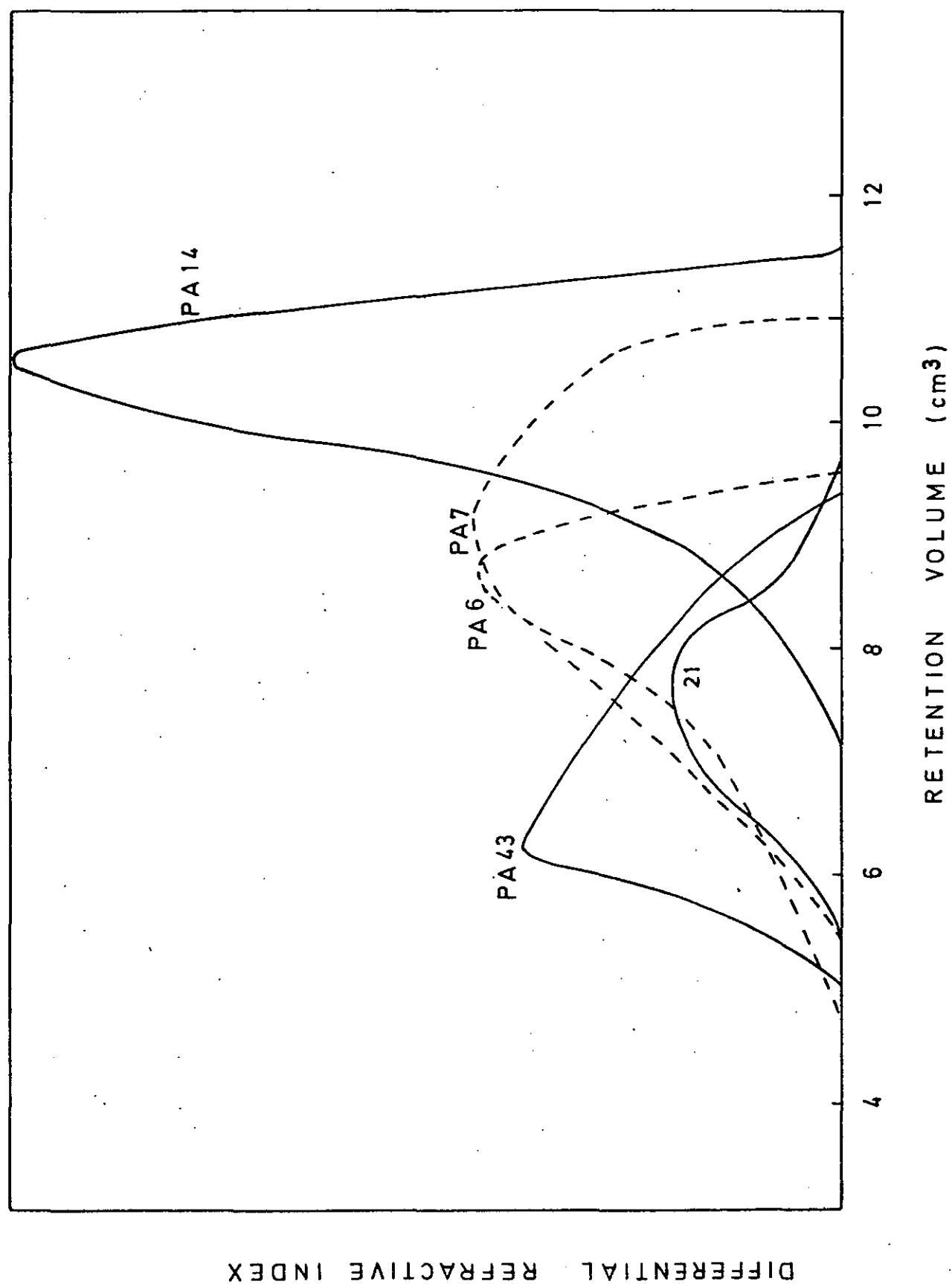


Table 4.39

SG 120 bonded with aminopropyl phase with water/formamide (5:1) as eluent

| Solute | % concentration | Molecular weight | V _R (ml) |
|-----------|-----------------|------------------|---------------------|
| Ethanol | 2.0 | 46 | 11.5 |
| Acetamide | 2.0 | 59 | 11.5 |
| PA14 | 0.390 | 13,000 | 10.25 |
| PA7 | 0.378 | 80,000 | 8.90 |
| PA21 | 0.241 | 159,900 | 7.0 |
| PA6 | 0.235 | 112,900 | 8.5 |
| PA43 | 0.309 | 658,000 | 6.3 |
| PA44 | 0.277 | 457,200 | 6.3 |
| PA5 | 0.291 | 668,000 | 6.3 |

Table 4.40

SG 120 bonded with aminopropyl phase with water/formamide (5:1) as eluent

| Solute | % concentration | Molecular weight | V _R (ml) |
|-----------|-----------------|------------------|---------------------|
| Ethanol | 2.0 | 46 | 11.5 |
| Acetamide | 2.0 | 59 | 11.5 |
| 49 F1 | 0.363 | 151,000 | 6.3 |
| 49 F2 | 0.141 | 95,000 | 7.7 |
| 49 F3 | 0.169 | 35,000 | 8.8 |

FIGURE 4.46

CALIBRATION CURVE FOR SG 120 (AMINO PROPYL BONDED)
USED WITH FORMAMIDE/WATER (1:5)

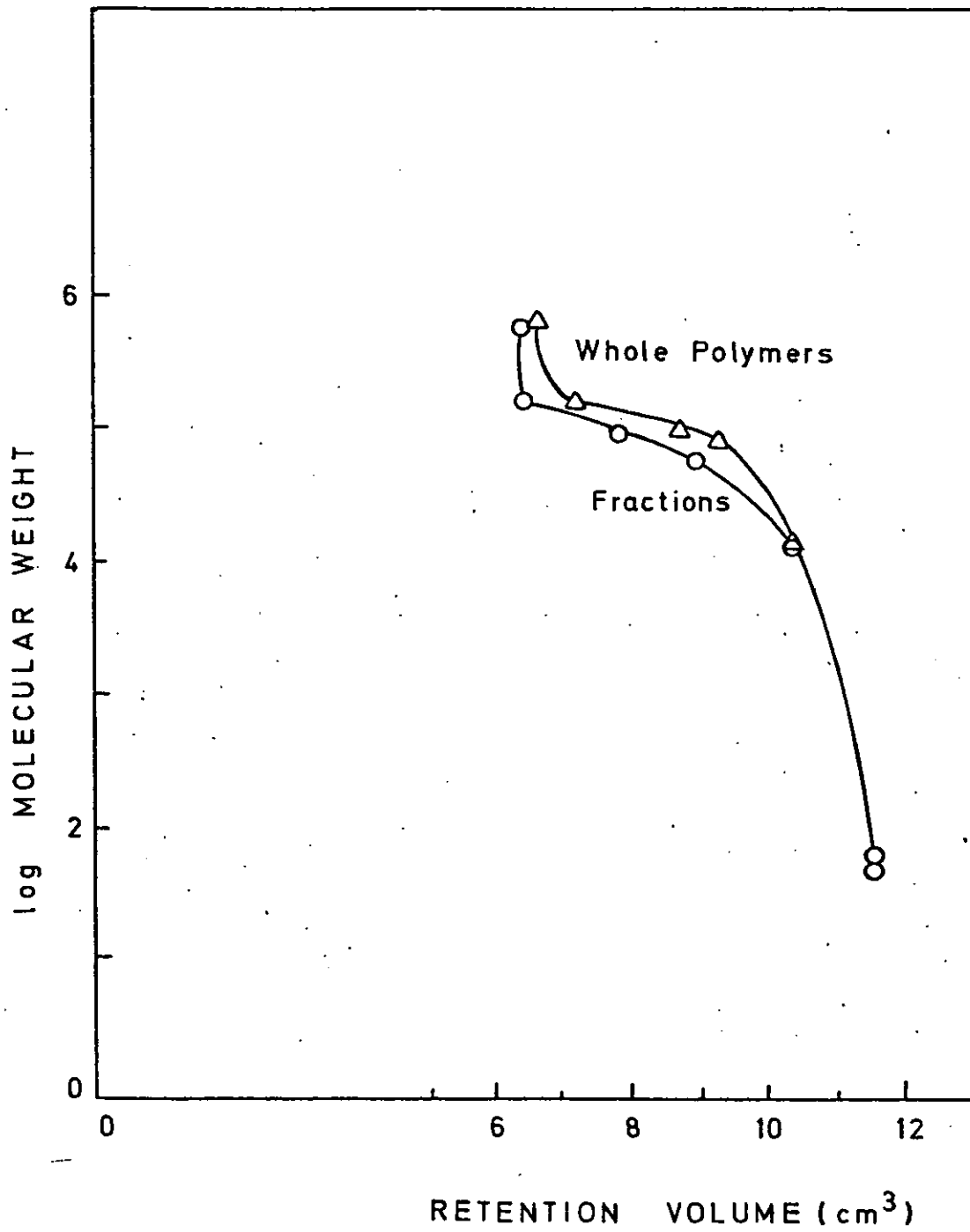
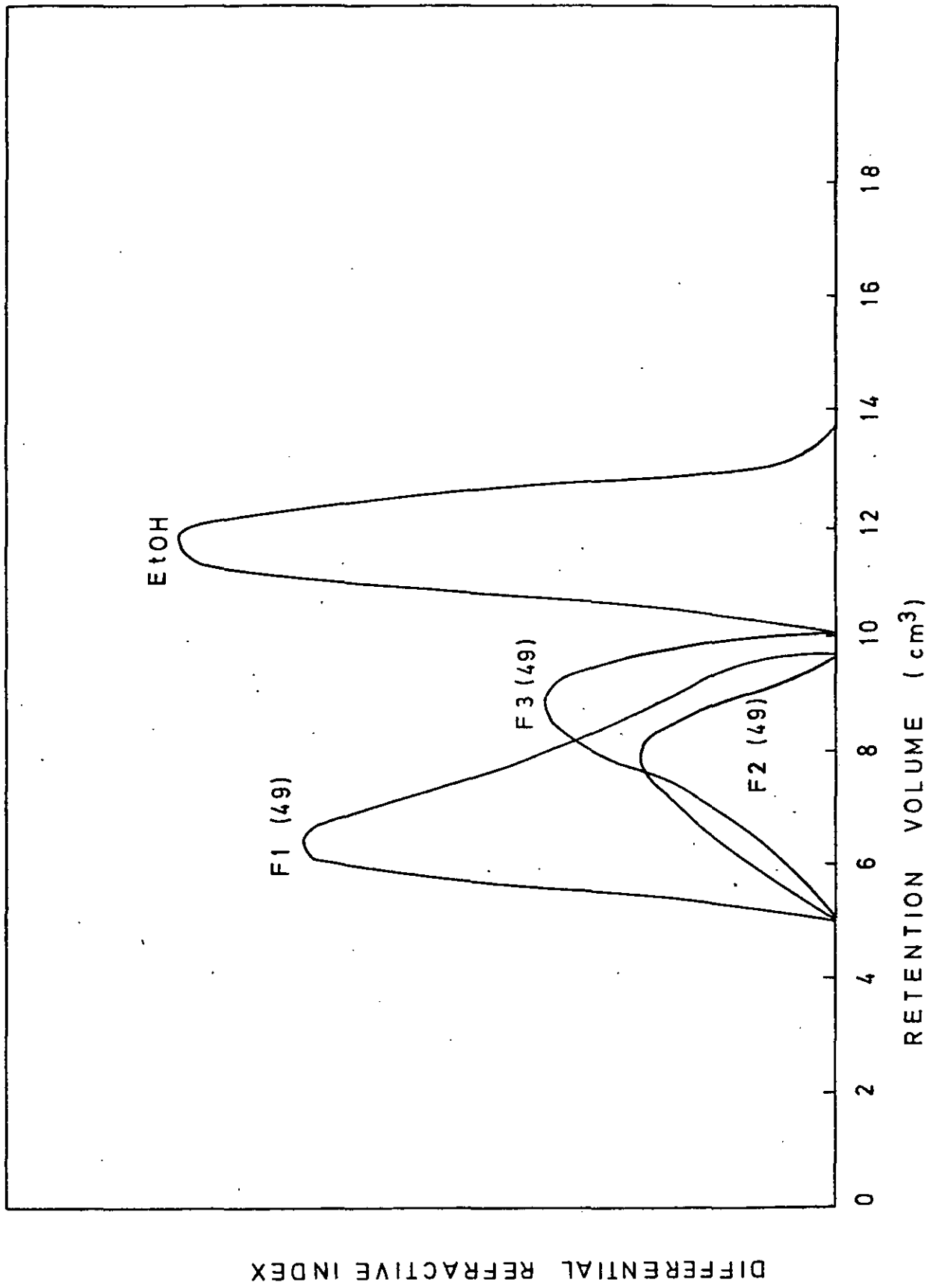


FIGURE 4.47

SG 120 (AMINO PROPYL BONDED) USED WITH FORMAMIDE/WATER (1:5)



(Figure 4.45) shows that the fractions have much narrower molecular weight distributions than the distributions for the whole polymers. The calibration curve plotted from the results given in Table 4.40 is shown in Figure 4.46, indicating that the calibration curves for fractions and whole polymers did not quite superimpose. The plots in Figure 4.46 assume that the \bar{M}_v values in Tables 4.39 and 4.40 are close to the molecular weight at the peak of the chromatograms shown in Figures 4.45 and 4.47. Whilst this may be true for the narrow distribution, it is not likely to be valid for the polydisperse unfractionated polyacrylamides. Because the distributions for the whole polymers are skewed to high molecular weight, it is probable that \bar{M}_v will be larger than the peak molecular weight. This will explain why the plateau in the calibration curve shown in Figure 4.46 is at a higher molecular weight for the whole polymers than for the fractions.

The calibration curves in Figure 4.46 suggest that the exclusion limit for the SG 120 column is just over a molecular weight of 10^5 for polyacrylamide. The same packing yields an exclusion limit for polystyrene at a molecular weight of about 10^6 (171, 173, 174). The difference may be explained in terms of the dimensions of the two polymers in solution, see equation (2.78). The unperturbed dimensions $(\langle r^2 \rangle / M)^{0.5}$ for polyacrylamide are almost 1.5 times larger than the value for polystyrene (26). Silicas with a mean pore diameter larger than 1200 Å are not prepared at A.E.R.E., Harwell. The Porasil silicas E and F which have been used in previous sections 4.5.4 have mean pore diameters of 1500 Å and 2000 Å respectively. In order to attempt to extend the useful GPC separation range for polyacrylamide to higher molecular weights than 10^5 , Porasil F was treated with a silyl compound at A.E.R.E., Harwell to give a chemically bonded aminopropyl phase. This packing was slurry packed with methanol into a one foot long column with similar dimensions to the SG 120 column. This column was flushed with the binary eluent water/formamide (5:1) and the solutes given in Table 4.41 were injected into the column.

Table 4.41

Porasil F bonded with an aminopropyl phase
with water/formamide (5:1) as eluent

| Solute | % concentration | Molecular weight | V _R (ml) |
|---------|-----------------|------------------|---------------------|
| Ethanol | 2.0 | 46 | 13.3 |
| PA14 | 0.36 | 13,000 | 12.55 |
| PA29 | 0.26 | 159,000 | 9.30 |
| PA42 | 0.21 | 307,900 | 9.0 |
| PA43 | 0.19 | 657,000 | 8.5 |

The chromatograms are shown in Figure 4.48, indicating that separation of polyacrylamides was taking place although the high molecular weight polyacrylamides had similar retention volumes. The calibration curve plotted in Figure 4.49 from the data in Table 4.41 shows that the exclusion limit for polyacrylamide is at a molecular weight just below 500,000.

Separations performed with the two aminopropyl bonded columns of SG 120 and Porasil F in series will provide a useful separation range for polyacrylamides up to a molecular weight of 10^5 . The SG 120 silica packing is about 10 μm in particle diameter and has a narrow pore size distribution. Porasil F silica packing has a diameter in the range 37-75 μm and has a somewhat broader pore size distribution than the SG 120 silica. If these two columns are in series the separation range will be amplified but the resolution of separation will be lower than with SG 120 alone owing to the greater chromatogram broadening of the Porasil F column. The results given in Table 4.42 were obtained with the two columns in series and the binary eluent of water/formamide (5:1).

The chromatograms obtained for some of the whole polymers given in Table 4.42 are shown in Figure 4.50. The results in Table 4.42 are plotted out to give a calibration curve as shown in Figure 4.51. For low molecular weight solutes, e.g. PA14, PA49 (3), PA58 (3), the low molecular weight tails of the chromatograms were camouflaged by the "ghost" peak appearing at the totally permeating volume of the gel, concealing the true distribution of the polyacrylamide. However, when these experiments were performed separately on the SG 120 columns, little interference was obtained. The interference obtained with the two columns in series could be attributed to the poor resolution expected from the Porasil F column, so that broadened chromatograms were obtained.

Table 4.42

Water/formamide as eluent used on SG 120 and Porasil F,
each bonded with an aminopropyl phase and packed into separate columns

| Solute | % concentration | Molecular weight | V _R (ml) |
|----------------------|-----------------|------------------|---------------------|
| Ethanol | 2.0 | 46 | 23.5 |
| Acetamide | 2.0 | 59 | 23.5 |
| PA58 (1) | 0.19 | 811,000 | 16.0 |
| PA58 (2) | 0.24 | 534,200 | 16.0 |
| PA58 (3) | 0.16 | 18,800 | 21.5 |
| PA58 (whole polymer) | 0.38 | 316,100 | 16.5 |
| PA9 | 0.17 | 152,000 | 18.0 |
| PA50 | 0.43 | 123,000 | 18.5 |
| PA56 | 0.278 | 420,300 | 16.5 |
| PA54 | 0.318 | 564,000 | 16.0 |
| PA29 | 0.26 | 159,000 | 18.0 |
| PA49 (1) | 0.435 | 151,000 | 17.5 |
| PA49 (2) | 0.169 | 95,000 | 19.0 |
| PA49 (3) | 0.203 | 35,100 | 20.0 |
| PA57 | 0.16 | 100,000 | 19.5 |

FIGURE 4.48

PORASIL F (AMINO PROPYL BONDED) USED WITH FORMAMIDE/WATER (1:5)

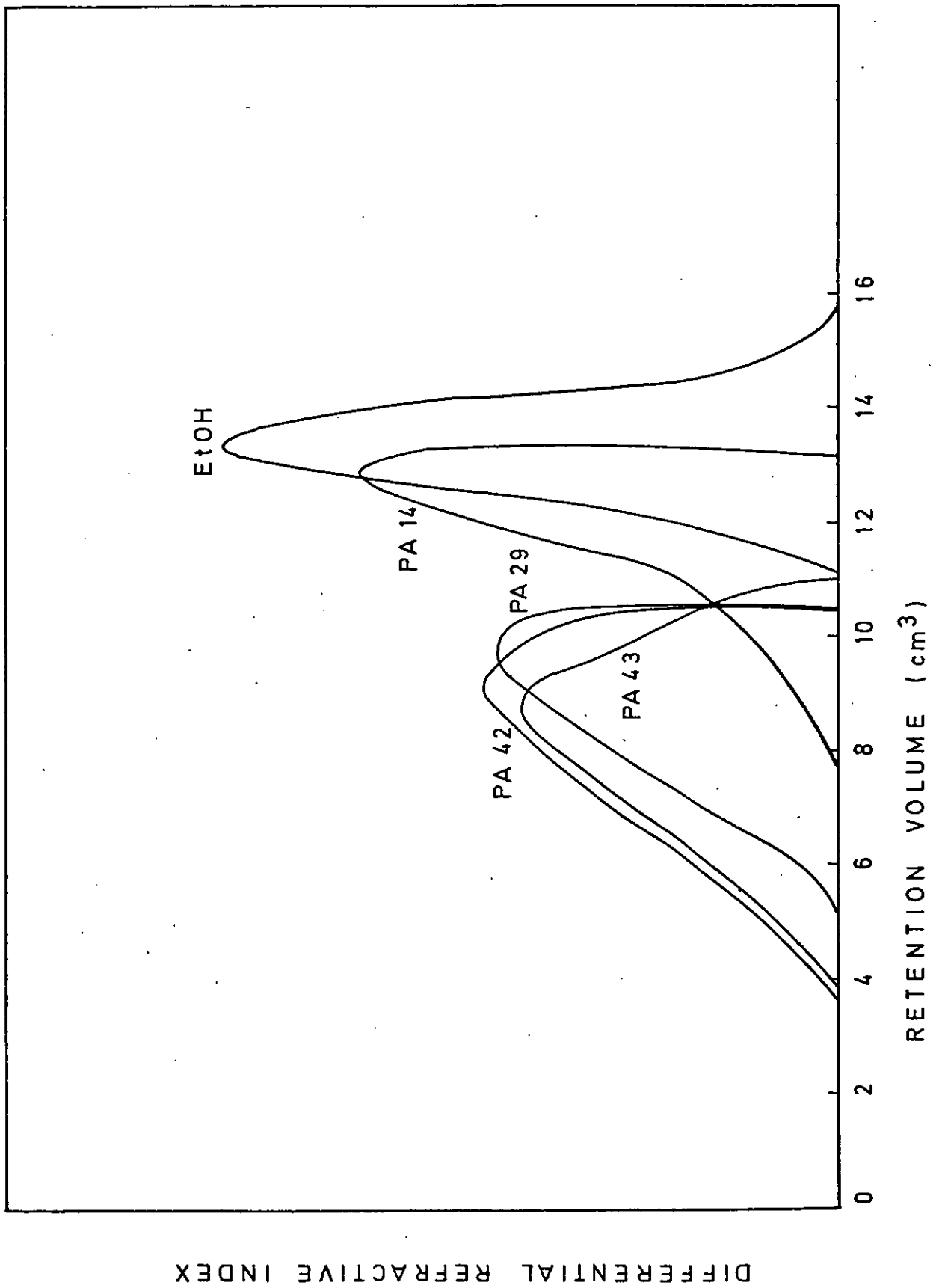


FIGURE 4.49

CALIBRATION CURVE FOR PORASIL F (AMINO PROPYL BONDED)

USING FORMAMIDE/WATER (1:5)

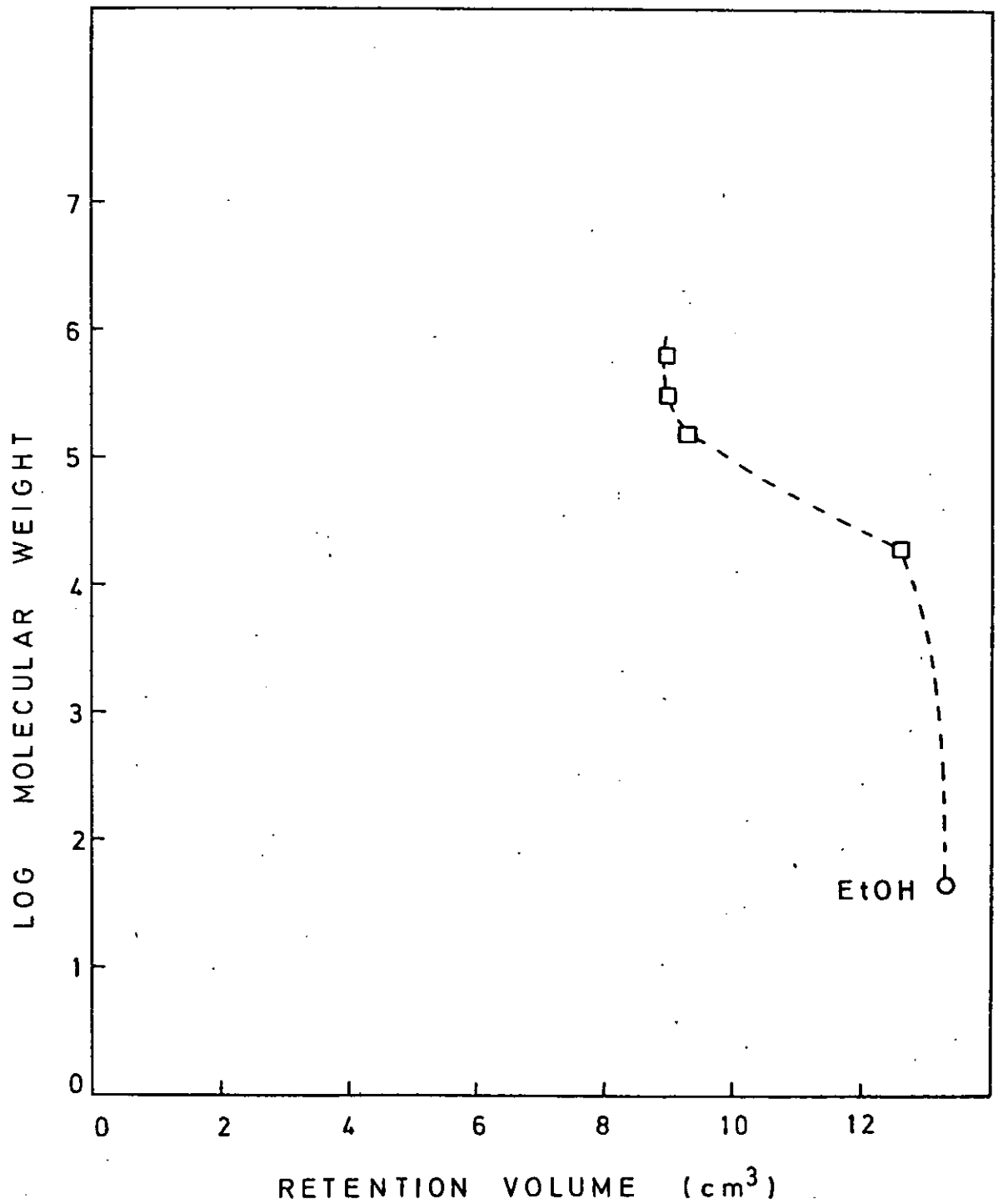


FIGURE 4.50

SG 120 AND PORASIL F (AMINO PROPYL BONDED) USING FORMAMIDE/WATER (1:5)

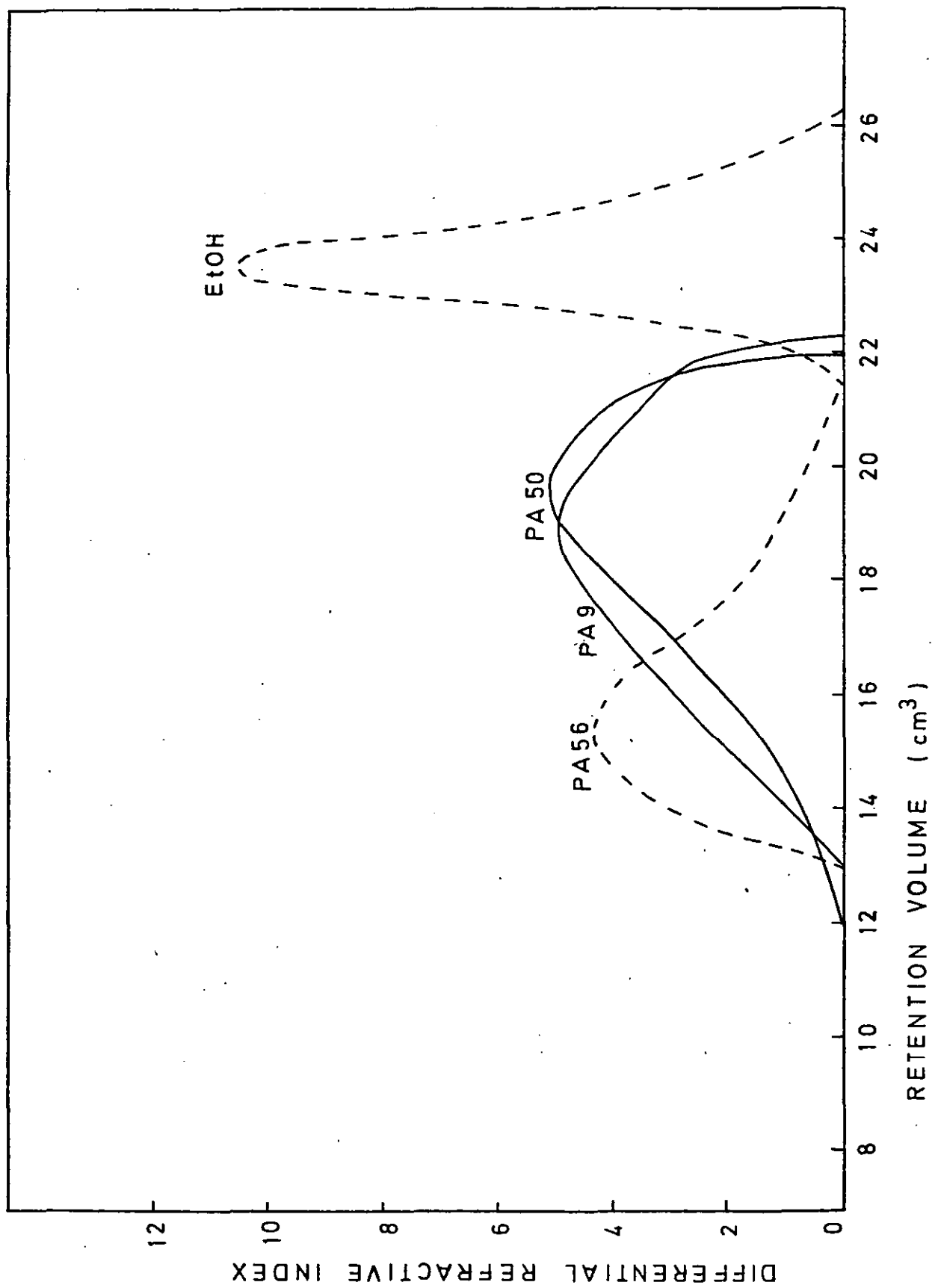
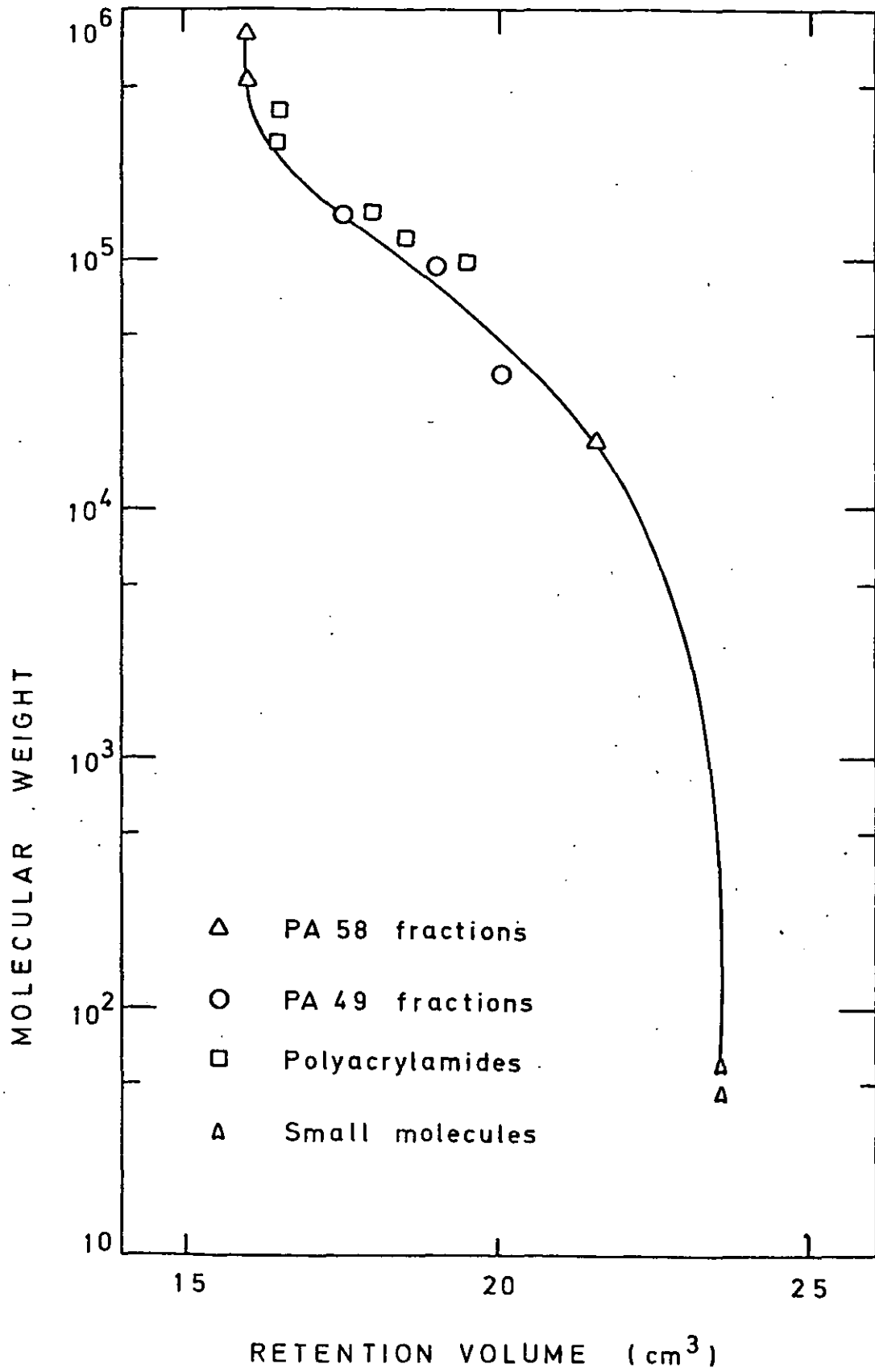


FIGURE 4.51

GPC CALIBRATION OF SG 120 AND PORASIL F
(AMINO PROPYL BONDED) USING FORMAMIDE/WATER (1:5)



4.5.9 Molecular Weight Distribution

In view of the successful GPC separations of polyacrylamide described in the previous section, an attempt was made to determine accurate molecular weight distributions for comparison with the distribution predicted for an acrylamide polymerisation, as in Section 4.1. It was felt that the aminopropyl bonded Porasil F column was unsuitable for quantitative studies of distributions because the particle size of the packing did not give efficient separations, leading to excessive chromatogram broadening. The best column was therefore the aminopropyl bonded SG 120 column which yielded the calibrated curve shown in Figure 4.46. From this curve, a suitable polymer for distribution calculations must have a chromatogram which suggests very few polyacrylamide chains with molecular weights above 10^5 . Consequently, polyacrylamide PA14 in Table 4.39 was chosen. This low molecular weight polyacrylamide will be representative of the polymerisation conditions, since the filtration problems associated with high molecular weight polymers in Section 4.2.1 should be greatly reduced.

Chromatogram heights as a function of retention volume were determined from the chromatogram of polyacrylamide PA14, see Figure 4.45. The low molecular weight tail of the chromatogram merged with the "ghost" peak. The tail was resolved by referring to the appearance of the "ghost" peak from a solvent injection in the absence of polymer. Because of the curved calibration plot in Figure 4.45, the procedure described by Rodriguez (195) and Pickett (196) must be used in the calibration of the differential weight distribution $w(M)$ as a function of molecular weight M as given by

$$w(M) = \frac{d I(V)}{dV} \cdot \frac{dV}{d(\log.M)} \cdot \frac{d(\log.M)}{dM} \quad (4.1)$$

where $I(V)$ is the weight fraction eluted up to elution volume V , $dI(V)/dV$ is equivalent to the height of the chromatogram, and $d(\log.M)/dM$ is $1/M$. In equation (4.1) $d(\log.M)/dV$ is the slope of the calibration curve, which

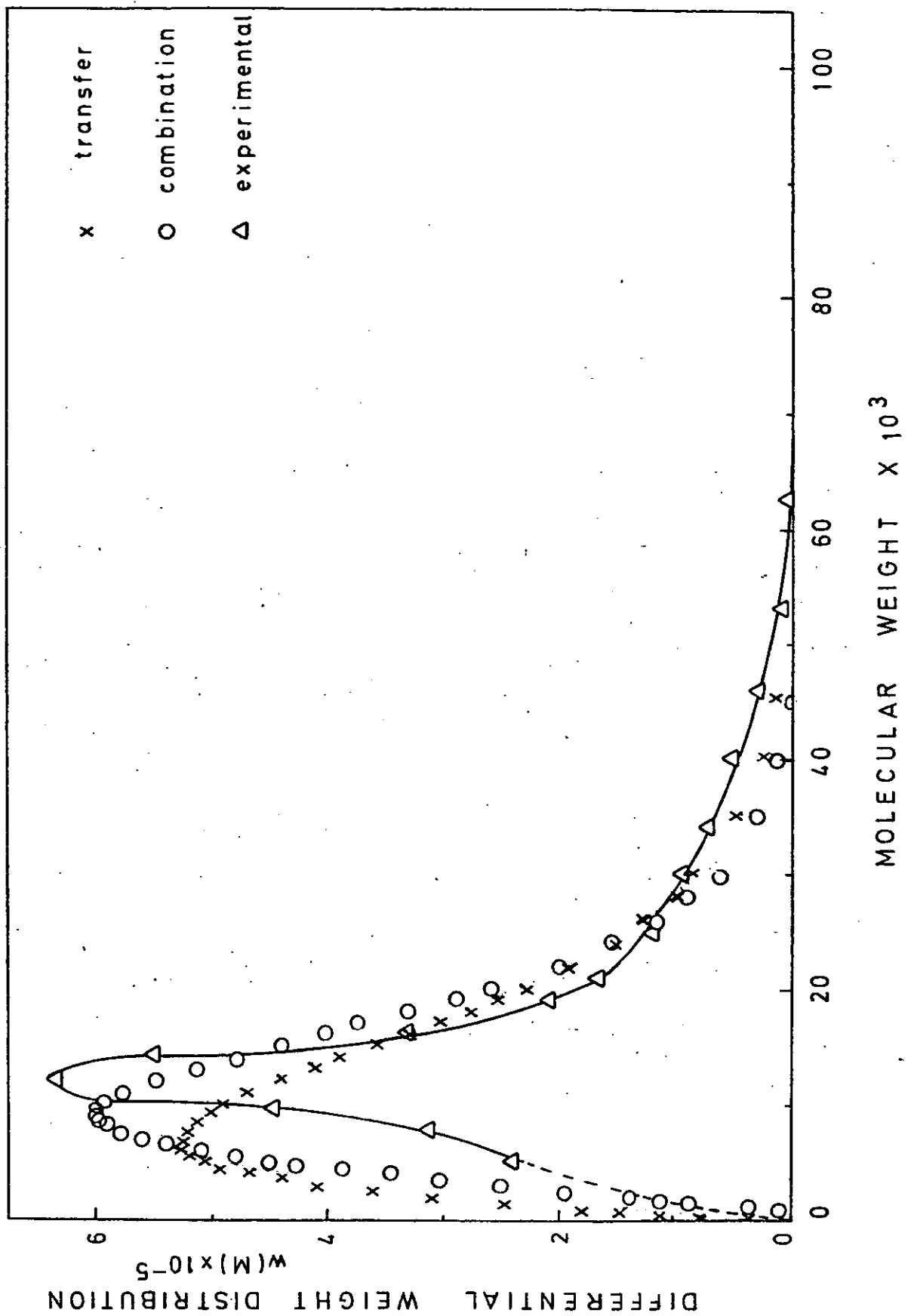
depends on V as shown in Figure 4.46. From the chromatogram heights and the calibration curve for fractions in Figure 4.46, values of $w(M)$ were calculated with a computer program developed by Croucher (197) based on the program first described by Pickett and coworkers (196). The distribution curve is shown in Figure 4.52.

Theoretical distribution functions given by equations (2.20) and (2.21) were compared with the experimental distribution determined for polyacrylamide PA14. These functions require values of \bar{M}_n which was not determined experimentally because polymer PA14 has a molecular weight below the lower limit for membrane osmometry. However, the value of \bar{M}_n in equations (2.20) and (2.21) may be calculated from an experimental value of \bar{M}_v , since relations depending on the Mark-Houwink exponent a are available for estimating \bar{M}_v/\bar{M}_n for the two distribution functions (198). Values of \bar{M}_v/\bar{M}_n of 1.45 and 1.90 were used to calculate \bar{M}_n in equations (2.20) and (2.21) from $\bar{M}_v = 13,000$. The theoretical distributions are plotted in Figure 4.52, showing only fair agreement with the experimental distribution. The experimental distribution in Figure 4.52 could not be established accurately at low molecular weights because the tail of the chromatogram merged with the "ghost" peak. The deviation of the experimental distribution from the theoretical distributions in Figure 4.52 is partly explained by the polymerisation conversion of 38% monomer which was obtained in the preparation of PA14. Average molecular weights calculated from the experimental distribution $w(M)$ with the program of Croucher (197) suggest that the experimental distribution with a polydispersity of 2.68 is broader than the two theoretical distributions given by equations (2.20) and (2.21). Average molecular weights calculated from the experimental distribution are given in Table 4.43, showing good agreement between the experimental value of \bar{M}_v and the value of \bar{M}_v determined from the molecular weight distribution.

The polydispersity of polyacrylamide fraction PA49 (3) in Table 4.40 was calculated from the chromatogram in Figure 4.47 with the calibration

FIGURE 4.52

MOLECULAR WEIGHT DISTRIBUTION OF PA14



curve for fractions in Figure 4.46. The value of 1.48 was found to be much lower than the polydispersity of 2.68 calculated for polyacrylamide PA14, confirming the success of the fractionation, as suggested by the qualitative comparison of the chromatograms in Figures 4.45 and 4.47.

Table 4.43Calculated molecular weight averages for PA14 on SG 120

| | | |
|------------------------------------|---|--------|
| Number average molecular weight | = | 5,740 |
| Peak average molecular weight | = | 9,400 |
| Viscosity average molecular weight | = | 13,600 |
| Weight average molecular weight | = | 15,400 |
| Polydispersity ratio | = | 2.68 |

CHAPTER 5

CONCLUSIONS

From this research important observations may be stated about the radical polymerisation of acrylamide, the characterisation of polyacrylamide, and the fractionation of polyacrylamide by gel permeation chromatography. In view of the lack of publications describing reliable results for the behaviour of polyacrylamide in solution, several problems in the synthesis, characterisation and fractionation experiments had to be solved before reproducible results could be obtained.

In the polymerisation work, it was found that polyacrylamides with average molecular weights in the range 10^4 - 10^6 could be produced. Control over molecular weight and the degree of conversion of monomer into polymer was achieved by adjusting the temperature, monomer concentration and reaction time. The initiator potassium persulphate was used so that the polymerisation kinetics followed closely the theoretical scheme, thus avoiding the complex behaviour that follows from the use of multicomponent initiators which have been widely studied recently.

The problems of handling aqueous polyacrylamide solutions were demonstrated by the observations that polymer may be lost during filtration operations and that the solution properties may depend on the previous history of the sample. Filtration was a necessary procedure in order to prevent the blockage of the GPC instrumentation with very high molecular weight polyacrylamide, so that the polymer concentration in solution had to be accurately monitored after the filtration process. In order to obtain reproducible properties, the solutions were prepared by a well documented procedure, and the polymer was stored in solution in order to avoid the changes in solution properties which apparently occur after the polymer has been stored in the dry state.

The care required in preparing aqueous polyacrylamide solutions was again encountered in the solution viscosity measurements. Experiments utilising the internal dilution method in an Ubbelohde viscometer yielded unsatisfactory plots of specific and inherent viscosity data, and it was found that all solutions for viscosity measurements had to be prepared externally by an identical procedure. Having developed this method, it was found that reliable and reproducible results were easily obtained. More severe difficulties were observed in osmotic pressure determinations. Instrumental and membrane problems prevented satisfactory operation of the osmometer with either pure water or pure formamide. It was found that results could be obtained with binary solvent mixture of water/formamide (3:1), but extreme care was required in order to obtain reliable data. Consequently, although some satisfactory molecular weight data were obtained, it was not possible to use the osmometer with aqueous solutions on a routine basis.

The development of a GPC system for the satisfactory fractionation of polyacrylamide involved much effort. It was established that polyacrylamide adsorbed from water onto the surface of the porous silica packing, so that reproducible GPC behaviour according to an exclusion mechanism was not possible. Polyacrylamide adsorption was reduced by coating the silica surface physically with poly(ethylene oxide) or Aerosol OT. Although more satisfactory GPC behaviour resulted, the coating was not stable over a long period of time. It was also found that more satisfactory GPC behaviour also resulted if a basic compound such as ammonia was included in the eluent in order to interact preferentially with the acidic sites on the silica surface. From these experiments, it was decided to deactivate the Bronsted acid sites by chemically bonding a silyl compound to the surface of the silica and to use a binary eluent mixture containing a basic component which would interact with the remaining sites such as Lewis acid sites. The only drawback of this system was the appearance of a "ghost"

peak for each polyacrylamide separation at the totally permeating volume. This peak merged with the low molecular weight tail of the polyacrylamide chromatogram.

Successful GPC separations were obtained with a chemically bonded aminopropyl phase and a water/formamide (5:1) eluent mixture. The pore surface environment was then similar to polyacrylamide, minimising partition and adsorption effects. Successful GPC separations of polyacrylamide were then obtained. This represents the first demonstration that polyacrylamide may be separated by a steric exclusion mechanism. This was confirmed by preparing polyacrylamide fractions by fractional precipitation, and GPC studies with these fractions gave the full GPC calibration curve. Molecular weight distributions were calculated from the chromatograms for a fraction and a whole polymer, demonstrating the success of the fractional precipitation technique. The distribution for the whole polymer was in fair agreement with theoretical distributions calculated from the polymerisation mechanism.

Whilst this research represents a major step forward in the GPC characterisation of polyacrylamide, only chains with molecular weights up to 5×10^5 could be separated with the porous silicas used in this work. Although other silicas which are now available will raise this molecular weight exclusion limit, it is unlikely that they will be entirely satisfactory for the separation of polyacrylamides having molecular weights of several million which are widely used commercially as flocculants. Polyacrylamides are highly extended in water and water/formamide (5:1). The size of polyacrylamide may be reduced by choosing a poorer solvent which if used as a GPC eluent would lead to a higher exclusion limit. Therefore, further GPC work with pure formamide, Mark-Houwink exponent = 0.54 for polyacrylamide, will be of interest.

Although the chemically bonded aminopropyl phase would appear to be satisfactory for the GPC separation of polyacrylamide, it is possible that other silyl compounds might be superior. A further improvement would be to choose a silyl compound containing an acrylic group. Having chemically bonded such compounds to the silica surface, the acrylic groups could be polymerised to give a thin polymeric layer to cover the pore surface. Such a layer would cover both Bronsted and Lewis acid sites, and if polyacrylamide GPC separations occurred solely by steric exclusion, then the use of a binary liquid mixture as eluent would not be necessary.

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APPENDIX(1) Safety Precautions in Handling Acrylamide Monomer

The chief hazard is a characteristic toxicity involving neuro-muscular disorders of varying severity (28), consequently the reactor was assembled in an efficient fume cupboard in order to reduce any form of ingestion, inhalation or body contact. Disposable gloves were worn in the procedures involving acrylamide monomer and during the synthesis of monomer into polymer. Since the polymer does not degrade to monomer on heating, no hazard was expected from the polymer unless the polymer was contaminated by residual monomer. For example, polyacrylamide has been approved as a coagulant aid in potable water treatment (1).

(2) Calculation of Intrinsic Viscosity of Polyacrylamide in a Binary Solvent of Water/Formamide (5:1)

Using Collinson's values of K and a (Mark Houwink constants) for polyacrylamide in water are 68×10^{-5} and 0.66. For a polymer having a molecular weight of 10^5 the intrinsic viscosity would be 1.357. Kotera's (112) values of K and a for polyacrylamide using formamide as solvent are 1.08×10^{-3} and 0.54. Therefore for a polymer having a molecular weight of 10^5 the intrinsic viscosity would be 0.542. If formamide and water are mixed together in a ratio of 1:5 then polyacrylamide in this binary solvent should have an intrinsic viscosity of

$$[\eta] = \frac{0.542 \times 5(1.357)}{6} = 1.22 \text{ dl g}^{-1}$$

This relation assumes a simple linear relation between intrinsic viscosity and solvent power for the polyacrylamide. It is probable that just above theta solvent conditions the change in intrinsic viscosity with polymer-solvent interactions will be greater than for a good solvent (22). Con-

sequently, the value of 1.22 dl g^{-1} will be the minimum value. Therefore, it is not surprising that the experimental values for water and water/formamide (5:1) are almost identical.

