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Determination of Viscosity in Ethanol and HFA 134a Mixtures

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INTRODUCTION

Knowledge of formulation liquid properties is beneficial when modelling internal transient flows of pMDI HFA 134a and ethanol binary mixtures during atomization [1, 2]. Non-linear expressions are available that correlate saturated vapor pressure, density and surface tension to HFA 134a-ethanol composition [3, 4]. In this study, experimentally determined dynamic viscosity is presented for ethanol-HFA 134a mixtures at 20.4 ± 1.2°C.

MATERIALS AND METHODS

Viscosity can be described as a fluid's resistance to shear strain when submitted to a shear stress. For a sphere travelling within a closed capillary containing a liquid, the dynamic viscosity, μ, of the liquid is given by

$$\mu = K(\rho_s - \rho_L)\, t \qquad\qquad \textit{Equation 1}$$

where K is the viscometer constant; ρ_s and ρ_L are the densities of the sphere and liquid respectively; and t is the time of travel of the sphere between two fixed graduation lines. Equation 1 is valid for non-turbulent flow where the sphere is travelling at terminal velocity.

To determine the viscosity of HFA 134a (Mexichem Fluor, Runcorn, UK), absolute ethanol (Fisher Scientific, Loughborough, UK) and mixtures, formulations were packaged within a Comes DM density measuring device with a 90 mL Pyrex inner tube (DH Industries Limited, Laindon, UK). The Comes DM device (Figure 1) was fitted with a Bespak BK 357 valve (Bespak

Limited, King's Lynn, UK) to allow HFA 134a addition using a Pamasol P2016 Laboratory Plant (DH Industries Limited, Laindon, UK). A Borosilicate glass Meterate tube (VWR International Limited, Lutterworth, UK) was secured inside the Comes DM device (clean and dry) prior to addition of the test formulation; providing a sphere within a closed capillary. The diameter and mass of the sphere was determined to be 0.316cm (CD-6 CSX, Mitutoyo, Andover, UK) and 0.05174g (Mettler Toledo Leicester, UK); giving the sphere density to be 3.13 g/mL.
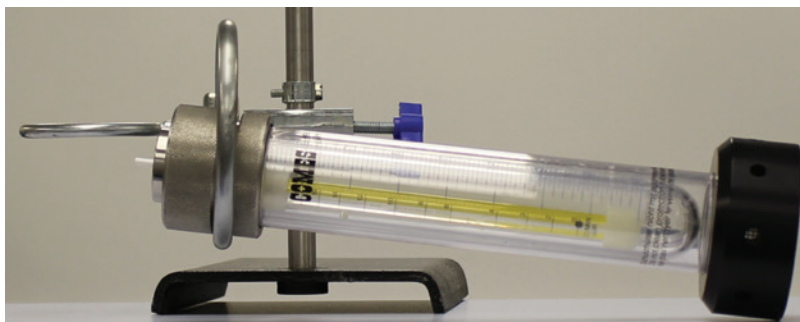

Figure 1.   Comes DM density measuring device with a 90 mL Pyrex inner tube containing a Meterate tube (7° to horizontal) and 3.13g/mL sphere.

A predetermined volume of ethanol was dispensed directly into the inner tube of the Comes DM device and the mass determined by weight difference (± 0.1 g, Mettler Toledo Leicester, UK). Similarly, a pre-determined volume of HFA 134a was filled through the Bespak valve into the Comes DM device and the mass again determined by weight difference (± 0.1 g). All formulations evaluated were mixed by inversion and left to equilibrate for five minutes prior to viscosity measurements. Compositions were expressed as %w/w. In all cases, formulations were filled into the Comes DM device such that the remaining headspace volume was less than 10%; i.e., HFA 134a vapor mass was negligible (<0.25% of total formulation weight). The density of ethanol-HFA 134a mixtures were determined in accordance with Johnson et al. (2018) [4]. The time of travel (n = 10; %RSD < 2.3%) of the sphere between two fixed graduation marks (distance between start mark and end mark = 8.3cm) within the Meterate tube was determined, in duplicate, at an incline (7° to horizontal; to optimize time of travel and measurement accuracy) using a calibrated stopwatch (VWR International, Lutterworth, Limited, UK). The viscometer constant, K, was determined to be 0.0235 ± 0.0004 mNmkg^{-1} using solutions of known viscosity (0.389cP, 1.200cP, 0.594cP) and density (0.782g mL, 0.789g/mL, 0.792g/mL); acetonitrile, ethanol, and methanol respectively (Fisher Scientific, Loughborough, UK) [5-7]. Viscosity measurements for the pure components were within 1.2% of published values [6, 8] verifying non-turbulent flow conditions and terminal velocity of the sphere during timed period of travel.

RESULTS AND DISCUSSION

Table 1 and Figure 2 present the viscosity of ethanol and HFA 134a mixtures at 10% w/w intervals (20.4 ± 1.2°C). Terminal velocity of the sphere was confirmed for 20%w/w ethanol content and above, by ensuring that observed travel times were proportional to distance traveled, i.e. when the start-mark was located closer to the end-mark (total distance traveled, and travel time, both reduced by 40 ± 1%). Therefore, for completeness, Figure 2 includes Solvay's previously published value of HFA 134a viscosity (0.211cP at 20°C) [8]. Reid *et al.* [9] suggest the following mixing rules for viscosity:

$$ln(\mu_m) = x_e ln(\mu_e) + (1 - x_e)ln(\mu_{HFA}) \qquad\qquad \textit{Equation 2a}$$

$$\mu_m^n = x_e \mu_e^n + (1 - x_e)\mu_{HFA}^n \qquad\qquad \textit{Equation 2b}$$

where x_e = mole fraction of ethanol in mixture, μ_e = viscosity of ethanol, μ_{HFA} = viscosity of HFA134a, and μ_m = viscosity of the mixture.

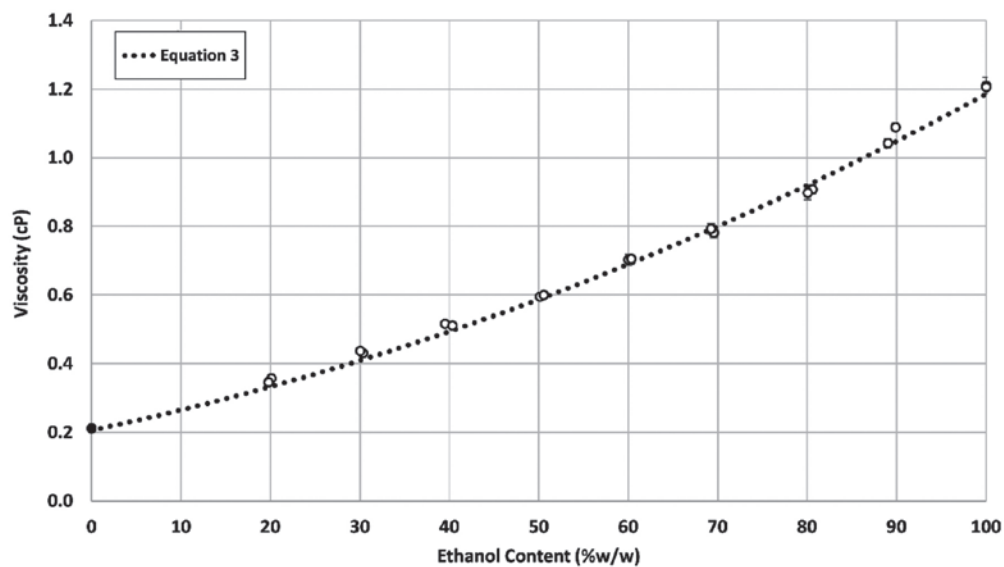| Table 1.			
Viscosity of ethanol and HFA 134a mixtures at 20.4 ± 1.2°C.			
Ethanol %(w/w)	**Viscosity (cP)**	**Ethanol %(w/w)**	**Viscosity (cP)**
20	0.352	70	0.787
30	0.434	80	0.903
40	0.514	90	1.066
50	0.598	100	1.209
60	0.704		

Figure 2. Viscosity of ethanol and HFA 134a mixtures at 20.4 ± 1.2°C. Error bars are standard deviation and at most ethanol concentrations fall within the plot symbol; n=10 for each duplicate. (○ data from this study; ● previously published data [8]).

The logarithmic Equation 2a was proposed by Arrhenius. Exponent *n* in power law Equation 2b is adjustable; Reid *et al.* [9] suggest *n* = +1 and *n* = -1. Neither the Arrhenius expression, nor the power law equation with the recommended values of *n* were found to represent the data very well. Adjustment of the exponent to *n* = -0.45 was found to best represent the data, which leads to the following mixing rule for viscosity:

$$\mu_m^{-0.45} = x_e \mu_e^{-0.45} + (1 - x_e)\mu_{HFA}^{-0.45} \qquad\qquad \textit{Equation 3}$$

The quadratic least-squares fit of the viscosity data (Figure 2) has a sum-of-squares error of 2.05×10^{-3} and a maximum error of 6.1%. Equation 3 gives a sum-of-squares error of 2.64×10^{-3} and a maximum error of 5.1%.

Equation 3 involves a single adjustable exponent and its assumed form ensures that the viscosity of ethanol and HFA 134a are exactly matched with the measured values at $y_e = 0$ and $y_e = 1$. This is a desirable property when data from sources with different levels of confidence are combined (e.g., properties of pure substances known to high accuracy and measurements of mixture properties with higher uncertainty).

CONCLUSIONS

The viscosity of ethanol and HFA 134a mixtures has been experimentally determined at 20.4 ± 1.2°C. A power-law mixing rule was successfully found to capture the behavior of the viscosity data. This expression is useful for models of the internal transient flow and atomization of pMDI formulations based on HFA 134a-ethanol mixtures [1, 2].

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