

Supplementary Information For:
Fluorous Bulk Membranes for Potentiometric Sensors
With Wide Selectivity Ranges: Observation of
Exceptionally Strong Ion Pair Formation

*Paul Boswell and Philippe Bühlmann**

University of Minnesota, Department of Chemistry 207 Pleasant St. SE, Minneapolis, Minnesota 55455

buhlmann@chem.umn.edu

Materials and Instrumentation

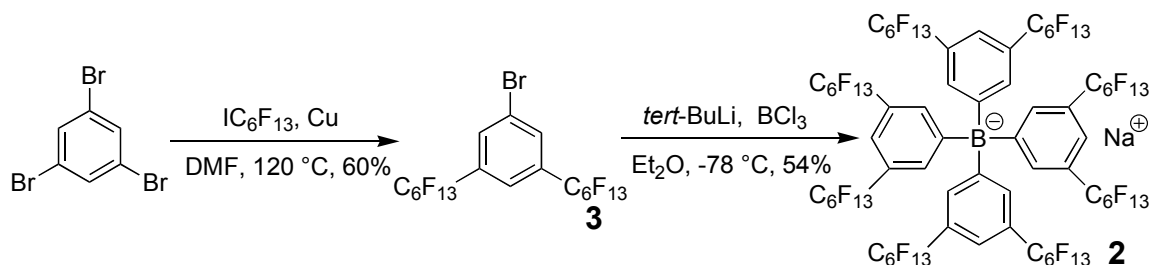
Synthesis

All reagents and solvents for chemical synthesis were purchased from Aldrich (Milwaukee, WI), Oakwood (West Columbia, SC), or Lancaster (Windham, NH) and were used without purification.

Conductimetric and Potentiometric Measurements

Sample solutions were made with deionized and charcoal-treated water (≥ 18.2 M Ω cm specific resistance) obtained with a Milli-Q PLUS reagent-grade water system (Millipore, Bedford, MA). Double-junction sleeve-type Ag/AgCl reference electrodes (DX200, Mettler Toledo, Switzerland) and EMF 16 16-Channel Data Acquisition System potentiometers (Lawson Labs, Malvern, PA) were used

for all potentiometric and conductimetric measurements. Mitex™ membrane filters made of pure Teflon® (13 mm diameter, 10 μm pore size, 125 μm thick) were obtained from Millipore.



Scheme I. Synthesis of sodium tetrakis[3,5-bis(perfluorohexyl)phenyl]borate (**2**).

1-Bromo-3,5-bis(perfluorohexyl)benzene (3):

Compound **3** was prepared with 60% yield using a literature procedure describing the synthesis of 1-bromo-3,5-bis(perfluorooctyl)benzene.¹

Sodium tetrakis[3,5-bis(perfluorohexyl)phenyl]borate (2):

A raw product of **2** was prepared according to a literature procedure.² The greenish-brown oil, which was previously reported² to be the pure product, was further purified by thorough drying under vacuum and recrystallization from perfluorohexanes to give the product as colorless crystals. ¹H NMR (500 MHz, acetone-*d*₆, δ): 7.72 (s, 8H), 7.59 (s, 4H). MS *m/z* (relative intensity): 2861.0 (20.6%), 2862.0 (100%), 2863.0 (71.6%), 2864.0 (25.2%), 2865.0 (6.5%). Anal. Cald. for C₇₂H₁₂BF₁₀₄Na: C, 29.96; H, 0.42; B, 0.37. Found: C, 30.05; H, 0.60; B, 0.87. Boron analysis was performed by ICP-AES (Quantitative Technologies Inc., Whitehouse, NJ).

Potentiometric Measurements

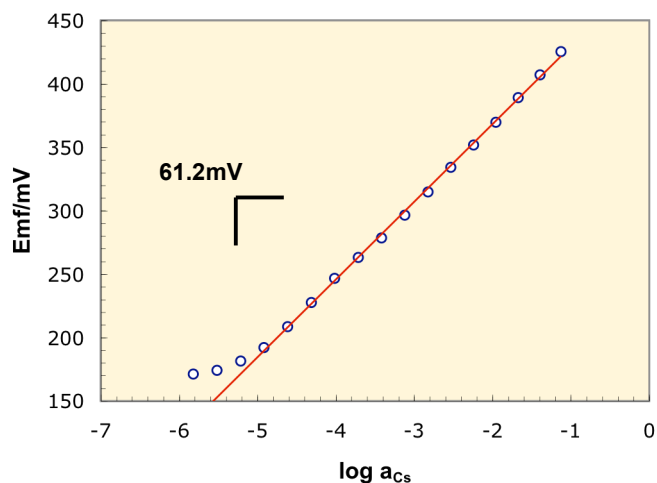


Figure 1. Cs⁺ Calibration Curve Acquired With Supported Perfluoroperhydrophenanthrene Phase Containing 1.4 mM Cesium Tetrakis[3,5-bis(perfluorohexyl)-phenyl]borate

Three types of polymeric membranes were fabricated by the usual method³ and characterized simultaneously with the fluorous liquid-phase membranes. Each polymeric membrane contained plasticizer and poly(vinyl chloride) in a 2:1 ratio. The lipophilic salts potassium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (KFPB) or potassium tetrakis(4-chlorophenyl)borate (KCIPB) were added to the *o*-NPOE (0.2%, w/w) or chloroparaffin (0.3%, w/w) membranes to provide for ionic sites.

The fluorous liquid-phase membranes were prepared by transferring 12 μ L of a saturated solution of **2** in perfluoroperhydrophenanthrene, **1**, onto the surface of a porous Teflon[®] filter, into which this solution was quickly absorbed. Each filter soaked with solution of **2** in **1** was then placed in a custom electrode body and mechanically sealed around the perimeter, leaving an exposed region 8.3 mm in diameter. Figure 1 shows a typical calibration curve of one of these fluorous electrodes.

Perfluoroperhydrophenanthrene, **1**, was chosen because it has a sufficiently high boiling point and low pour point (-20 °C) to make it useful as a fluorous liquid phase and possibly as a fluorous plasticizer for

fluorous polymeric membranes. Linear perfluorinated alkanes have ranges between their melting and boiling points that are too narrow to be useful as fluorous phases, and branched perfluorinated alkanes are not readily available.

Selectivity coefficients were determined by the fixed interference method⁴ for Li^+ , Na^+ , K^+ , NH_4^+ , and H^+ , while the separate solution method⁴ was employed for Ca^{2+} , Ag^+ , $(\text{CH}_3\text{CH}_2\text{CH}_2)_4\text{N}^+$, and $(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2)_4\text{N}^+$. Nernstian responses were confirmed for all ions in the range where selectivities were tested. Activity coefficients were calculated according to a two-parameter Debye-Hückel approximation.⁵ Table 1 shows a complete list of selectivity measurements made with the electrodes described in this study. For all these selectivity measurements Cs^+ was considered as the primary ion, and the inner filling solution of the ISE contained 1 mM CsCl.

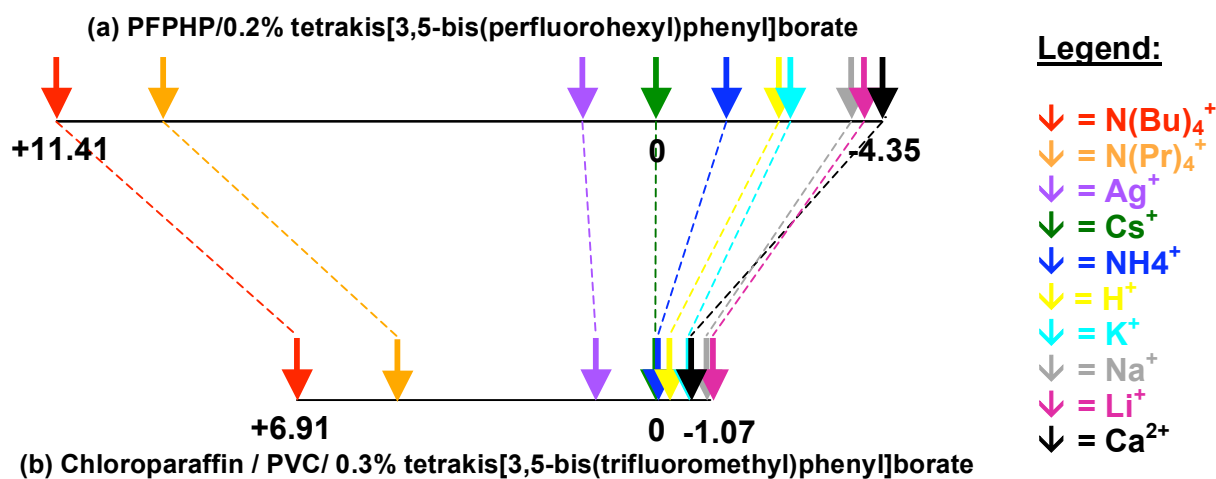


Figure 2. Selectivity Diagram Comparing the Logarithmic Selectivity Coefficients of Several Cations Referenced to Cs^+ Between (a) a Fluorous Membrane, and (b) a Chloroparaffin/PVC Membrane.

Table 1. Potentiometrically Determined Logarithmic Selectivity Coefficients, $\log K_{Cs,J}^{pot}$, Referenced to Cs^+ for Fluorous, Nonfluorous Ion Exchanger, and Ionophore-based ISE Membranes

Membrane Type	$\log K_{Cs,J}^{pot}$								
	Ca^{2+}	Li^+	Na^+	K^+	H^+	NH_4^+	Ag^+	$N(Pr)_4^+$	$N(Bu)_4^+$
I (Fluorous)	-4.35	-4.01	-3.75	-2.59	-2.27	-1.35	+1.43	+9.08	+11.41
II (Chloroparaffin, KFPB)	-0.69	-1.07	-0.99	-0.65	-0.28	-0.07	+1.15	+5.88	+6.91
III (<i>o</i> NPOE, 2)	-3.85	-3.66	-2.85	-1.06	-2.66	-1.36	-0.89	+4.76	+4.33
IV (<i>o</i> NPOE, KCIPB)	-3.79	-3.66	-2.90	-1.07	-2.72	-1.33	-0.25	+5.48	+4.41

Conductimetric Measurements

Due to the high resistance of solutions of **2** in perfluoroperhydrophenanthrene, conductivity cells with an acceptable cell constant and sample volume are not commercially available. Instead, we used a conductivity cell with a fluorous liquid phase supported by a porous Teflon[®] filter (cell constant = 0.034 cm^{-1}), as described above for the potentiometric measurements. All conductivities were determined with a potentiometer (input impedance 10 T Ω) using the method of potential reduction by a known shunt.⁶

The fluorous, supported liquid-phase conductivity cells were made by transferring 12 μ L of a solution of **2** in perfluoroperhydrophenanthrene, **1**, onto the surface of a Teflon[®] filter, into which it was quickly absorbed. These membranes were then allowed to equilibrate with 10 mL of a 100 mM solution of a chloride salt of the primary ion for 1.5 to 2.5 h.

They were then placed in an electrode body of the same type used for the potentiometric measurements and immersed in a 100 mM solution of the primary ion chloride. The total resistance of the electrochemical cell without the fluorous supported liquid-phase membranes is negligible since it is more than six orders of magnitude smaller than the resistance of the fluorous membranes. Shunts used for these measurements had resistances in the range of 1.0–10 G Ω .

In order to ensure complete conditioning of the membranes, the time required for equilibration of membranes upon contact with cation solutions was determined by two independent methods. When membranes containing **2** were exposed in a Petri dish to 10 mM CsCl or NaCl solutions (one side of the

membrane contacting the solution) and allowed to equilibrate with those solutions for 1-hour increments of time up to 5 hours, membrane resistances approached a final value within one hour. No significant difference between resistances measured after 1, 2, 3, 4, and 5 hours were observed. These observations suggest that these thin fluoruous phases equilibrate with the solutions within less than one hour. This conclusion is consistent with potentiometric results. When membranes containing **2** were placed into electrode bodies of the same type used for potentiometric measurements and immersed into 100 mM CsCl solutions, stabilization of the membrane potentials required less than 25 min.

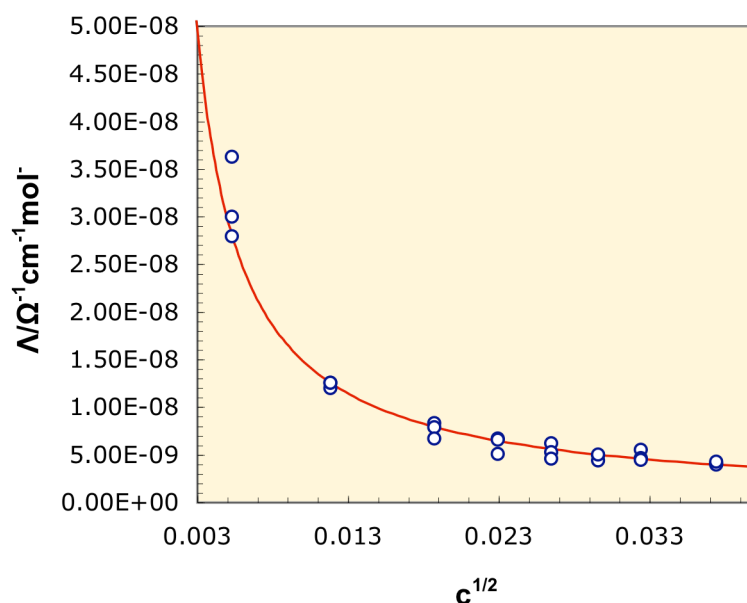


Figure 3. Molar Conductivity, Λ , Plotted as a Function of the Square Root of the Concentration of the Cs^+ Salt of **2**, Shown With a Fuoss–Kraus Fit.

The relation between molar conductivity and fluoruous salt concentration in **1** can be fitted with the Fuoss–Kraus theory⁷

$$\Lambda = \frac{\lambda_0}{c^{1/2} K_{ip}^{1/2}} + \frac{\lambda_{0,t} c^{1/2} K_t}{K_{ip}^{1/2}} \quad (\text{Ia})$$

where Λ is the molar conductivity, c is the salt concentration, λ_0 and $\lambda_{0,t}$ are the limiting molar conductivities for free and triple ions, respectively, K_{ip} is the ion pair formation constant, and K_t is the triple ion formation constant. $\lambda_{0,t}$ is commonly approximated with $2\lambda_0/3$.⁸

$$\Lambda = \frac{\lambda_0}{c^{1/2}K_{ip}^{1/2}} + \frac{2\lambda_0c^{1/2}K_t}{3K_{ip}^{1/2}} \quad (\text{Ib})$$

More complex theory can compensate for free ion activities, changes in viscosity with the total salt concentration, and formation of quadrupoles consisting of two cations and two anions. However, only a small range of salt concentrations was available experimentally for conductivity measurements. The relatively low solubility of **2** in **1** limits the upper range of salt concentrations available for conductivity measurement, and the extremely high resistance of the perfluoroperhydrophenanthrene solutions limits the accuracy of conductivity measurements at low salt concentrations. While the small range of salt concentrations allowed accurate measurements of K_{ip} , the constants for the formation of triple ions (and quadrupoles, when fitting with more complex models) are associated with larger errors and are not discussed here. Importantly, the more complex models show that taking into account the formation of any complexes larger than ion pairs does not change the estimated values of K_{ip} significantly.

As Equation Ib shows, values for the limiting molar conductivities, λ_0 , are required to determine K_{ip} from fits as illustrated by Fig. 3. Due to the strong ion pair formation in **1** and the limited salt concentration range for accurate conductivity measurement, the direct measurement of limiting molar conductivities is not feasible.⁸

Therefore, limiting ionic molar conductivities were determined by the Stokes–Einstein approximation, which is known to have greater accuracy in solvents of lower dielectric constant:⁸

$$\lambda_0^i = \frac{z_i^2 F^2}{6N_A \pi \eta r_i} \quad (\text{II})$$

where F is the Faraday constant, N_A is Avogadro's constant, r is the crystallographic ion radius, and η is the viscosity of the solvent (25 °C, 28.4 cP⁹). This approximation was used previously for the determination of ion pair formation constants in media of very low dielectric constants.¹⁰ The limiting molar conductivity of the salt is given by $\lambda_0 = \lambda_0^+ + \lambda_0^-$ for a 1:1 electrolyte. Crystallographic ionic radii from the literature¹¹ were used for cations, and the radius of the fluorophilic borate was approximated to be 10 pm. Even a comparatively large error in the radius of the borate would not affect the calculated ion pair formation constants significantly because the conductivities are dominated by the smaller, more mobile cations.

References

- (1) Cavazzini, M.; Manfredi, A.; Montanari, F.; Quici, S.; Pozzi, G. *Eur. J. Org. Chem.* **2001**, 4639.
- (2) Van den Broeke, J.; Deelman, B. J.; van Koten, G. *Tetrahedron Lett.* **2001**, 42, 8085.
- (3) Bühlmann, P.; Yahya, L.; Enderes, R. *Electroanalysis.* **2004**, 16, 973.
- (4) Bakker, E.; Pretsch, E.; Bühlmann, P.; *Anal. Chem.* **2000**, 72, 1127.
- (5) Meier, P. C. *Anal. Chim. Acta.* **1982**, 136, 363.
- (6) Oesch, U.; Simon W. *Anal. Chem.* **1980**, 52, 692. Ammann, D.; Pretsch, E.; Simon, W.; Lindner, E.; Bezegh, A.; Pungor, E. *Anal. Chim. Acta.* **1985**, 171, 119.
- (7) Kraus, C.; Fuoss, R. *J. Am. Chem. Soc.* **1933**, 55, 21. Kraus, C.; Fuoss, R. *J. Am. Chem. Soc.* **1933**, 55, 21.
- (8) Izutsu, K. *Electrochemistry in Nonaqueous Solutions*; Wiley: Weinheim, **2002**; pp 209-210.
- (9) Maciejewski, A. *J. Photochem. Photobiol. A* **1990**, 51, 87.
- (10) Abbott, A. P.; Griffith, G. A.; Harper, J. C. *J. Chem. Soc. Faraday Trans.* **1997**, 93, 577.
- (11) Marcus, Y. *Ion Properties*; Marcel Dekker: New York, **1997**.