

Electrical Conductivity and Solubility of KF in *N,N*-Dimethylformamide up to 125 °C

Gavin Macfie,[†] Richard. G. Compton,[†] and Horacio R. Corti^{*,‡}

Physical and Theoretical Chemistry Laboratory, Oxford University, Oxford OX1 3QZ, United Kingdom, and Unidad de Actividad Química, Comisión Nacional de Energía Atómica, Av.Gral. Paz 1499, (1650) San Martín, Argentina

The solubility of potassium fluoride (KF) in dimethylformamide (DMF) and the dielectric constant of the solvent have been determined in the temperature range (25–125) °C by means of electrical conductivity and capacity measurements. The solubility of KF in this aprotic solvent seems to be almost temperature independent (mean value $(0.33 \pm 0.03) \times 10^{-3} \text{ mol}\cdot\text{dm}^{-3}$). The speciation of KF in DMF is also discussed in relation to the concentration dependence of the molar conductance. It is concluded that ion pairs could account for around 50 to 70% of the species and that triple ions could be present in the concentration range studied.

Introduction

An important technique for substituting fluorine into organic molecules is the nucleophilic transfer method using an alkali metal fluoride.¹ This technique finds widespread application in many areas, including the pharmaceutical, agrochemical, and dyestuff industries, and is often carried out under conditions of phase-transfer catalysis using alkali metal fluorides such as KF. In protic solvents this reaction often leads to the formation of non-fluorine-containing products;² therefore, dipolar aprotic solvents are preferred. Other advantages include their high boiling points, good thermal stabilities, and limited fluoride solvation.

In this paper we present a detailed study of the solubility of KF in a dipolar aprotic solvent, dimethylformamide (DMF), at different temperatures, to assess its effect in nucleophilic aromatic fluorination. The solution thermodynamics of alkali metal fluorides in nonaqueous solvents, including solubility, has been reviewed by Hefter,³ but the work is restricted to 25 °C. We have adopted a conductometric technique instead of the direct analytical determination of fluoride or the alkali metal concentration in the solution to avoid the problems related to the presence of traces of finely divided solid in the solution and also to prevent the hydration of the solvent during sample manipulation. Moreover, the conductometric method allowed information on ion pair formation of the fluoride salt in DMF to be obtained. This is expected to be important because the solvent has a dielectric constant significantly lower than that of water.

Experimental Section

The electrical conductivity method used to determine the solubility of KF in DMF at a given temperature relies on the very precise measurement of the electrical resistance of solutions having variable concentrations of salt, up to and including the saturated solution.

The measured electrical resistance, R , is related to the specific conductivity, κ , of the solution through the cell constant, a , of the cell, by

$$R = \frac{a}{\kappa} \quad (1)$$

a is a geometric factor approximately equal to the ratio between the distance and the area of the electrodes.⁴

The specific conductivity of the solution for a given salt is proportional to the concentration of free (nonassociated) ions in the solution.⁴ Due to the very low solubility of KF in DMF, the specific conductivity of the saturated solution is very low. Therefore, to measure the resistance of the solution with high accuracy, that is resistance in the range 10^3 to $10^4 \Omega$, the cell needs to have a very small value of a .

In this work we used a stainless steel cell with a concentric-cylindrical geometry whose main features have been described elsewhere.⁵ The electrical insulation between the electropolished cylinders and the grounded support is provided by sapphire spheres. The constant of the cell, $a = (0.2747 \pm 0.0003) \text{ m}^{-1}$, was determined by measuring its capacitance under vacuum, C_0 :

$$C_0 = \frac{\epsilon_0}{a} \quad (2)$$

where ϵ_0 is the electric permittivity of a vacuum ($8.85418 \times 10^{-12} \text{ F}\cdot\text{m}^{-1}$).

Due to the particular geometry of the cell, a is almost independent of the temperature and was determined to vary by less than 0.3% between 25 °C and 125 °C.

The cell is essentially a capacitor, and it was also used to determine the electric permittivity of the DMF as a function of temperature using a Wayne Kerr analyzer. The results agree within 2% with those reported in the literature⁶ between 15 °C and 35 °C, as shown in Figure 1.

The procedure to prepare a KF solution of known concentration in DMF is illustrated in Figure 2. The cell was rinsed by flowing pure methanol with a high-pressure pump (Gilson, model 365) through valves F and A (valves B, G, and H closed) and discharging through valve E. The remaining methanol in the cell was removed with a vacuum

* To whom correspondence should be addressed. E-mail: hrcorti@cnea.gov.ar. Fax: 5411-4754-7121.

[†] Oxford University.

[‡] Comisión Nacional de Energía Atómica.

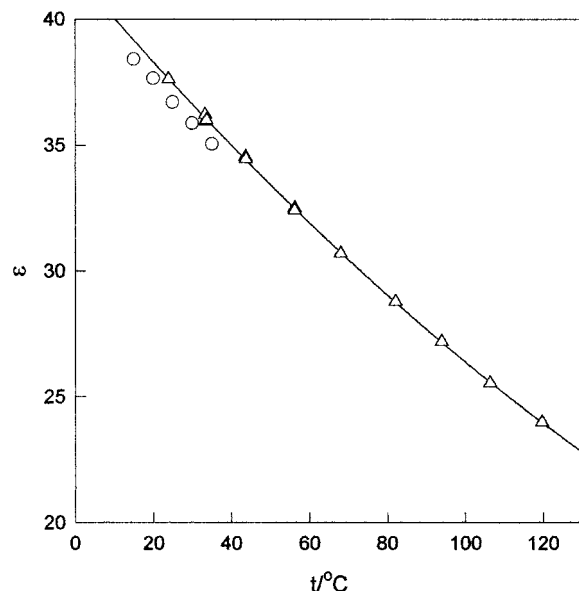


Figure 1. Electric permittivity of DMF as a function of temperature: Δ , this work; \circ , ref. 5.

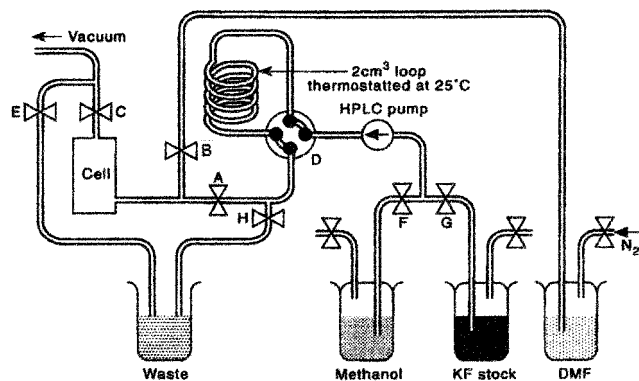


Figure 2. Experimental setup for the preparation of the KF/DMF solutions and filling of the conductivity cell.

pump (valve C open; A, B, and E closed) until the measured resistance was higher than 100 M Ω . Valve F was then closed, and the calibrated 2 cm³ loop immersed in a thermostated bath at 25 °C was filled with the stock solution of KF in methanol, around 0.01 to 0.1 mol·dm⁻³, by pumping this solution through valves G and H.

The calibrated loop is isolated from the rest of the system by means of a four-port valve (D). The remaining stock solution was then displaced from the tubing with pure methanol. Valves G and H were then closed and the KF/methanol solution in the loop was injected into the cell by pumping pure methanol through valves F and A. The methanol was then removed by vacuum, leaving only the KF solid in the cell. Finally, pure DMF was injected into the cell through valve B (valve A closed) by pressurizing with nitrogen.

The cell has a magnetic stirrer at the bottom, which allowed the solubility equilibrium to be reached within 30 min at room temperature. Finally, the cell was immersed in a thermostated oil bath, as indicated in Figure 3. The runs were then performed at several temperatures at a fixed molality. It should, however, be noted that the molarity of the solution changed during heating due to the thermal expansion of the solvent. From the known initial concentration and the density of DMF at the working temperature⁷ it was possible to calculate the KF molarity at each temperature.

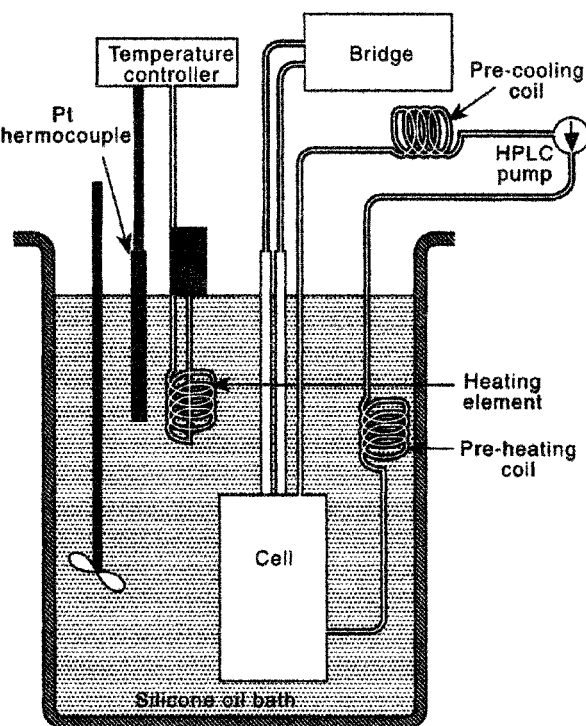


Figure 3. Scheme of the temperature control system and the closed recirculation loop.

Figure 3 also shows the closed loop, which allowed recycling of the solution to achieve rapid equilibration. The setup includes a cooling loop (immersed in an ice bath) to cool the solution at room temperature before it enters the pump inlet and a preheating coil to increase the temperature of the solution very close to the working temperature before entering the cell. Once a stable value of the resistance was obtained for a period of 10–15 min, the temperature of the bath was increased and a new point was measured.

After the measurement was completed, the procedure was repeated. Variation of the KF stock concentration allowed the initial concentration of KF in the cell to be altered.

The conductivities of pure DMF and of the saturated solution (prepared with a concentrated methanol stock solution) were also measured.

The KF (Merck, Suprapur), DMF (EM Science, Omnisolv, 0.003% water), and methanol (J.T.Baker, HPLC solvent) were used as received.

Results and Discussion

The specific conductivity of the pure DMF was determined between 25 °C and 125 °C as described above. In this temperature range it can be described to within 1% by the following polynomial expression:

$$\kappa^{\circ}/\text{S}\cdot\text{cm}^{-1} = (1.5971 \times 10^{-7}) + (9.4569 \times 10^{-9})t^{\circ}\text{C} - (1.0465 \times 10^{-10})(t^{\circ}\text{C})^2 + (8.1689 \times 10^{-13})(t^{\circ}\text{C})^3 \quad (3)$$

The specific conductivities of pure DMF and KF solutions of concentration (0.0768, 0.151, and 0.251) $\times 10^{-3}$ mol·dm⁻³ at 25 °C and a saturated solution in the (25–125) °C range are shown in Figure 4. The molar concentrations at temperatures other than 25 °C were calculated using the density of the solvent reported in the literature⁷ up to 80 °C and linearly extrapolated up to 125 °C.

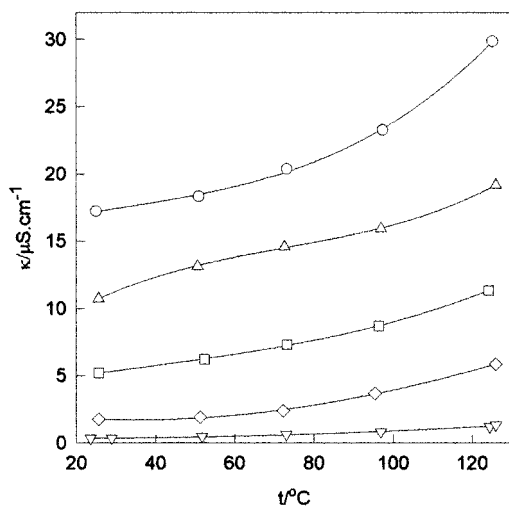


Figure 4. Specific conductivity of the KF/DMF solutions as a function of temperature. Concentration at 25 °C from bottom to top: pure DMF, $0.0768 \times 10^{-3} \text{ mol}\cdot\text{dm}^{-3}$, $0.151 \times 10^{-3} \text{ mol}\cdot\text{dm}^{-3}$, $0.251 \times 10^{-3} \text{ mol}\cdot\text{dm}^{-3}$, saturated solution.

Table 1. Properties of DMF and Infinite Dilution Molar Conductivity of KF in DMF as a Function of Temperature

$T/^\circ\text{C}$	$\rho^a/\text{g}\cdot\text{cm}^{-3}$	$\eta^a/\text{mPa}\cdot\text{s}$	ϵ	$\Lambda^\circ_{\text{KF}}/S\cdot\text{cm}^2\cdot\text{mol}^{-1}$
25	0.945 43	0.8135	36.4	64
50	0.921 09	0.6125	33.4	90
75	0.896 91	0.4844	29.8	108
100	0.872 54 ^c	0.3994 ^c	26.4	124
125	0.848 23 ^c	0.3384 ^c	23.2	143

^a Reference 7. ^b See text. ^c Extrapolated values.

The properties of DMF used in this work are presented in Table 1 as a function of temperature. Although the viscosity of DMF has been reported only up to 80 °C,⁷ the use of an Arrhenius plot permitted reliable extrapolations at higher temperatures.

In view of the low concentration of the KF in the DMF solutions, we used the properties of the pure solvent as representative of the corresponding solutions.

The specific conductivities of the four solutions at round temperatures (25, 50, 75, 100, and 125) °C were obtained from the regression of the results showed in Figure 4.

Supporting Information is available containing the experimental data of Figure 4 at the measured temperatures.

Because the ionic conductivity at infinite dilution of the KF in DMF is not known, we could not use the recommended procedure to evaluate the solubility of the electrolyte from conductivity measurements.⁸

To obtain the solubility of KF at each temperature, we plotted in Figure 5 the specific conductivity as a function of the salt concentration. The points where the curves obtained intercept the horizontal lines representing the conductivity of the saturated solution correspond to the solubility at each temperature.

In this procedure the specific conductivity of the KF solutions need not be corrected by the conductivity of the pure solvent at each temperature because the solvent contribution only displaces the curves upward without modifying the interception point.

Table 2 summarizes the results obtained along with the uncertainty estimated from the difference between a quadratic and a linear extrapolation of the undersaturated solution data to the saturation conductivity.

The solubility seems to have a wide minimum close to 50 °C, but the temperature dependence of the solubility is

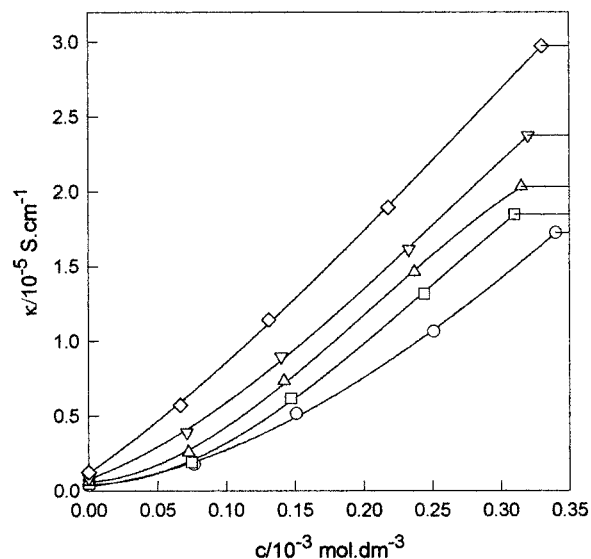


Figure 5. Specific conductivity of KF/DMF solutions as a function of concentration at several temperatures. From bottom to top: (25, 50, 75, 100, and 125) °C. The horizontal lines correspond to the conductivities of the saturated solutions at each temperature.

Table 2. Solubility s of KF in DMF at Several Temperatures

$T/^\circ\text{C}$	$s/10^{-3} \text{ mol}\cdot\text{dm}^{-3}$
25	0.34 ± 0.02
50	$0.31 \pm 0.01_5$
75	$0.31 \pm 0.01_5$
100	0.32 ± 0.01
125	0.33 ± 0.01

negligible, indicating a very small enthalpy of dissolution for KF in DMF.

The solubility of KF in DMF reported by Wynn et al.⁹ is $0.12 \times 10^{-3} \text{ mol}\cdot\text{dm}^{-3}$ at 24 °C, which is lower than our results at 25 °C ($0.34 \times 10^{-3} \text{ mol}\cdot\text{dm}^{-3}$). These authors used flame emission spectrometry to determine the solubility of alkali metal fluorides in nonaqueous solvents with a precision between 1 and 10%, and they discuss the effect of traces of moisture on the solubility. For instance, the solubility of KF in acetonitrile containing 100 $\mu\text{g}/\text{cm}^3$ of water is $0.014 \times 10^{-3} \text{ mol}\cdot\text{dm}^{-3}$, but increases to $0.031 \times 10^{-3} \text{ mol}\cdot\text{dm}^{-3}$ in acetonitrile containing 400 $\mu\text{g}/\text{cm}^3$ of water. These authors treated DMF with KOH and distilled it from barium oxide under reduced pressure, but the final water content was not quoted. The water content of the DMF used in our work was less than 30 $\mu\text{g}/\text{cm}^3$, so it is not clear whether the difference in the reported values can be attributed to moisture effects.

Atherton¹⁰ reported a solubility of $0.6 \times 10^{-3} \text{ mol}\cdot\text{dm}^{-3}$ for KF in DMF at 120 °C, which is double that measured in this work in this temperature region. No details are given in that work of the method of determination or the water content of DMF.

It should be emphasized that the concentrations shown in Figure 5 are the total concentration of KF, that is, the sum of the free and associated fluoride and potassium ion concentrations. The behavior of the molar conductivity of KF in DMF with concentration, obtained from $\Lambda = \kappa_c/c$ (where κ_c is the solvent-corrected specific conductivity of the solution), is shown in Table 3. The expected decrease of molar conductivity with increasing concentration of KF due to ion interactions and ion pair formation is not observed. In fact, the molar conductivity of KF increases with concentration all over the range of concentrations studied.

Table 3. Specific and Molar Conductivity of KF in DMF as a Function of Concentration at Several Temperatures

$T/^\circ\text{C}$	$c/10^{-3} \text{ mol}\cdot\text{dm}^{-3}$	$\kappa/\mu\text{S}\cdot\text{cm}^{-1}$	$\Lambda/\text{S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$
25	0.0768	1.42	18.5
25	0.151	4.81	31.8
25	0.251	10.3	41.0
25	saturated	16.9	
50	0.0747	1.43	19.1
50	0.147	5.70	38.8
50	0.244	12.7	52.0
50	saturated	18.0	
75	0.0725	1.96	27.0
75	0.142	6.71	47.2
75	0.237	14.0	59.1
75	saturated	19.7	
100	0.0712	3.06	43.0
100	0.140	8.11	57.9
100	0.233	15.3	65.7
100	saturated	22.9	
125	0.0667	4.48	67.2
125	0.131	10.2	77.9
125	0.218	17.7	81.2
125	saturated	28.5	

^a Corrected by solvent conductivity.

This kind of behavior has been reported for electrolytes in solvents of very low electric permittivity,^{11–14} and it could be ascribed to the formation of a charged triple ion (KF_2^- and K_2F^+ in this case) as the concentration increases, reducing the relative population of nonconducting ion pairs. The fact that we observed this kind of behavior in DMF, a solvent of relatively high dielectric constant, could be related to the peculiar properties of the fluoride ion.

The onset of triple ion formation is characterized by a minimum in the molar conductivity as the concentration of the electrolyte increases. The electrolyte concentration at the minimum can be approximated by¹¹

$$c_{\min} = \frac{3}{2K_T} \quad (4)$$

where K_T is the formation constant of triple ions.

For the KF/DMF system we did not observe the minimum, which implies that, at the concentrations studied, the ion association could involve not only ion pairs but also triple ions or larger aggregates. The set of data is not sufficiently large or accurate to make possible the application of common methods¹⁵ to obtain both the ion pair formation constant, K_A , and K_T from the conductivity data.

It is more convenient to describe the KF speciation in DMF in terms of ion pair formation and to assess the degree of ion dissociation of ion pairs, α , from the ratio Λ/Λ° . Because Λ° is not available for KF in DMF, its value at 25 °C was obtained from the known ionic limiting conductivity of fluoride and potassium ions in water reported in the literature⁴ by assuming that the ratio of the molar conductivities of KF in DMF and water is given by the expression obtained by comparing the molar ion conductivities of potassium and sodium (isoelectronic with fluoride) in water with those reported in DMF¹⁶

$$\frac{\Lambda_{\text{DMF}}^\circ}{\Lambda_{\text{w}}^\circ} = 2.2 \frac{\eta_{\text{w}}}{\eta_{\text{DMF}}} \quad (5)$$

where η_{w} and η_{DMF} are the viscosities of water¹⁷ and DMF, respectively.

The estimated accuracy of this prediction is 10%, and it is assumed that the same relationship applies at higher temperatures. Thus, using the infinite dilution molar

conductivity of KF in water calculated from the correlations by Oelkers and Helgeson¹⁸ at high temperatures, we could estimate the Λ° values in DMF shown in Table 1.

By adopting the crude assumption that $\alpha = \Lambda/\Lambda^\circ$, we obtain values of α ranging from 0.28 at 25 °C up to 0.47 at 125 °C at the lowest concentrations used in this work, where one expects the larger ratio of ion pairs to triple ions. Thus, around 50 to 70% of the F^- and K^+ ions form ion pairs in DMF. The expected increase in ion association with increasing temperature due to the reduction of the solvent dielectric constant was not observed. This could be due to the limited accuracy of the estimation of Λ° of KF in DMF or, more likely, to the increased formation of triple ions as the temperature increases.

Conclusions

The solubility of KF in dimethylformamide (DMF) has been determined in the temperature range 25 to 125 °C by means of electrical conductivity measurements. The solubility of KF in this aprotic solvent seems to be almost temperature independent (mean value $0.33 \times 10^{-3} \text{ mol}\cdot\text{dm}^{-3}$). The degree of ion pairing has been estimated to be on the order of (50 to 70)%, but from the observed concentration dependence of the KF molar conductivity, it is plausible that in the studied concentration region triple ions could be present.

Supporting Information Available:

Table of the measured specific conductances of pure DMF and KF/DMF solutions at different temperatures in the range 25 °C to 125 °C. This material is available free of charge via the Internet at <http://pubs.acs.org>.

Literature Cited

- (1) Clark, J. H.; Macquarrie, D. Substrate dependent solvent effect in nucleophilic fluorine transfer reactions. *J. Fluorine Chem.* **1987**, *35*, 591–596.
- (2) Clark, J. H. Fluoride ion as a base in organic synthesis. *Chem. Rev.* **1980**, *80*, 429–452.
- (3) Hefter, G. T. Solvation of Fluoride Ions. 3. A Review of Fluoride Solvation Thermodynamics in Nonaqueous and Mixed Solvents. *Rev. Inorg. Chem.* **1989**, *10*, 185–223.
- (4) Robinson, R. A.; Stokes, R. H. *Electrolyte Solutions*; Butterworth: London, 1955.
- (5) Fernández, D.; Goodwin, A. R. H.; Levelt Sengers, J. M. H. Measurement of the Static Relative Permittivity of Ambient-Pressure High-Purity Water at Frequencies from 0.1 to 10 kHz and Temperatures from 273 to 373 K. *Int. J. Thermophys.* **1995**, *16*, 929–955.
- (6) Leader, G. T.; Gormley, J. F. The Dielectric Constant of *N*-Methylamides. *J. Am. Chem. Soc.* **1951**, *73*, 5731–5733.
- (7) Corradini, F.; Marchetti, A.; Tagliazucchi, M.; Tassi, L.; Tosi, G. Kinematic Viscosity Studies of the Binary Ethane-1,2-diol/*N,N*-Dimethylformamide Solvent System at Various Temperatures. *Can. J. Chem. Eng.* **1993**, *71*, 124–129.
- (8) Fernández Prini, R.; Justice, J. C. Evaluation of the Solubility of Electrolytes from Conductivity Measurements. *Pure Appl. Chem.* **1984**, *56*, 541–547.
- (9) Wynn, D. A.; Roth, M. M.; Pollard, B. D. The solubility of Alkali-Metal Fluorides in Non-Aqueous Solvents with and without Crown Ethers, as Determined by Flame Emission Spectrometry. *Talanta* **1984**, *31*, 1036–1040.
- (10) Atherton, J. H. Mechanism in Two Phase Reaction Systems: Coupled Mass Transfer and Chemical Reaction. *Research in Chemical Kinetics*; Compton, R. G., Hancock, G., Eds.; Elsevier Science B.V.: Amsterdam, 1994; Vol. 2.
- (11) Barthel, J.; Gerber, R.; Gores, H.-J. The Temperature Dependence of the Properties of Electrolyte Solutions. VI. Triple Ion Formation in Solvents of Low Permittivity Exemplified by LiBF_4 Solutions in Dimethoxyethane. *Ber. Bunsen-Ges. Phys. Chem.* **1984**, *88*, 616–622.
- (12) Chen, Z.; Hojo, M. Relationship between Triple Ion Formation Constants and the Salt Concentration of the Minimum in the Conductometric Curves in Low-Permittivity Solvents. *J. Phys. Chem. B* **1997**, *101*, 10896–10902.

- (13) Geblewicz, G.; Schiffrin, D. J.; Solvent Properties of Polyaromatic Hydrocarbons. *J. Chem. Soc., Faraday Trans. 1* **1988**, *84*, 561–574.
- (14) Abbott, A. P.; Claxton, T. A.; Fawcett, J.; Harper, J. C. Tetrakis-(decyl)ammonium Tetrphenylborate: a Novel Electrolyte for Nonpolar Media. *J. Chem. Soc., Faraday Trans. 1* **1996**, *92*, 1747–1749.
- (15) Fernández Prini, R. *Physical Chemistry of Organic Solvent Systems*; Covington, A. K., Dickinson, T., Eds.; Plenum Press: New York, 1973.
- (16) Krungalz, B. S. Separation of Limiting Conductances into Ionic Contributions in Nonaqueous Solutions by Indirect Methods. *J. Chem. Soc., Faraday Trans. 1* **1983**, *79*, 571–587.
- (17) Watson, J. T. R.; Basu, R. S.; Sengers, J. V. An Improved Representative Equation for the Dynamic Viscosity of Water Substance. *J. Phys. Chem. Ref. Data* **1980**, *9*, 1255–1290.
- (18) Oelkers, E. H.; Helgeson, H. C. Calculation of the Thermodynamic and Transport Properties of Aqueous Species at High Pressures and Temperatures: Aqueous Tracer Diffusion Coefficients of Ions to 1000 °C and 5 kbar. *Geochim. Cosmochim. Acta* **1988**, *52*, 63–92.

Received for review January 22, 2001. Accepted June 7, 2001. The authors are grateful to British Council for financial support of this project. H.R.C. is a member of Carrera del Investigador Científico del Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET). G.M. thanks the EPSRC for a studentship and Avicia for providing support through a CASE award.

JE0100241