

# Conductivity of (C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N BF<sub>4</sub> in Liquid and Supercritical Hydrofluorocarbons

Andrew P. Abbott\* and Christopher A. Eardley

Chemistry Department, University of Leicester, Leicester LE1 7RH, U.K.

Received: January 27, 2000; In Final Form: July 13, 2000

The conductivity of tetrabutylammonium tetrafluoroborate in 1,1,1,2-tetrafluoroethane (HFC 134a) in the liquid state at 30 °C and in difluoromethane (HFC32) in the liquid, near critical and supercritical states is presented as a function of concentration and pressure. The data are fitted to a Fuoss–Kraus model and the ion pair and triple ion dissociation constants are analyzed as a function of temperature and pressure. It is shown that the ionic equilibria are controlled by the relative permittivity of the media irrespective of the state of the fluid. The change in ion pair and triple ion dissociation constants with pressure are used to discuss the solvation of charged and neutral species in liquid and supercritical fluids.

## Introduction

Early investigations into the electrical conductivity of supercritical media focused on measurements in aqueous solutions. In the 1950s, Franck measured the conductometric properties of a variety of electrolytes in aqueous solution at temperatures up to 800 °C and at pressures as high as 400 MPa.<sup>1</sup> Marshall and co-workers then made a number of similar measurements.<sup>2</sup> The limiting molar conductivities of several electrolytes at supercritical conditions were consequently calculated.

The electrical conductivities of electrolytes in nonaqueous supercritical media have received relatively little attention in comparison to the aforementioned aqueous systems. The conductivity of the hydrophobic electrolyte tetrakis(decyl)-ammonium tetraphenylborate (TDATPhB) in supercritical CO<sub>2</sub> (sc CO<sub>2</sub>) has been investigated previously.<sup>3</sup> The low conductivities observed were attributed to pronounced ion association, which results from the very low relative permittivity ( $\epsilon \approx 1.8$ ). TDATPhB, for example, exhibited an electrical conductivity of only  $1.5 \mu\text{S cm}^{-1}$  at a concentration of 19.2 mM in sc CO<sub>2</sub> at 70 °C and 300 bar. Under these conditions the ion pair and triple ion dissociation constants were found to be  $7.12 \times 10^{-13}$  and  $4.27 \times 10^{-4} \text{ mol dm}^{-3}$ , respectively. The conductivities measured in the supercritical phase were then compared to those of the same electrolyte in liquid cyclohexane, a medium of very similar relative permittivity to that of sc CO<sub>2</sub>. Although the ion pair and triple ion dissociation constants were very similar in the two media, the conductivity of TDATPhB in scCO<sub>2</sub> was approximately 5 times that in cyclohexane at the same temperature. Hence, it was shown that the molar conductivity of an electrolyte can be enhanced in the supercritical phase because the low viscosity of the supercritical medium leads to high ionic mobilities.

Olsen and Tallman measured the conductivity of tetrabutylammonium tetrafluoroborate, TBABF<sub>4</sub>, in the dipolar supercritical fluid, chlorodifluoromethane.<sup>4</sup> When electrolyte concentrations of 6–12 mM were employed, the molar conductivity of supercritical chlorodifluoromethane increased with the square root of the TBABF<sub>4</sub> concentration at fixed temperature and pressure. It was consequently proposed that triple ions constitute

the majority of charge carriers under such conditions, although no mathematical fits of the conductivity data to the Fuoss–Kraus equation were performed.

In recent work we have shown that HFC 32 and 134a are useful solvents for electrochemical investigations in both the liquid and supercritical states.<sup>5</sup> The unprecedented electrochemical stability of these solvents coupled with the relatively mild critical conditions makes them ideal media for studies of electron-transfer processes in the supercritical state. To analyze electrochemical data it is important to quantify the conductivity of electrolytes in these media. The current work shows that both liquid and supercritical HFC 32 can be made conducting via the dissolution of TBABF<sub>4</sub>. The conductivity of this electrolyte is presented in liquid HFC 134a and both liquid and supercritical HFC 32. In particular, the associative behavior of the electrolyte ions in supercritical HFC 32 is examined.

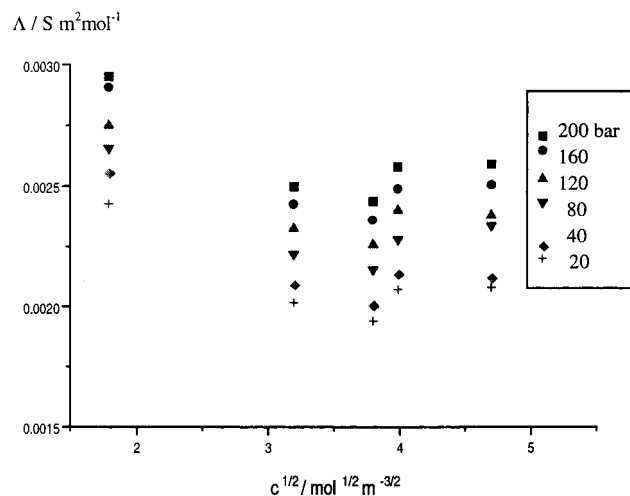
## Experimental Section

The solvents HFC 134a and HFC 32 (ICI Klea group, 99.99%) were used as received. The cell was flushed with HFC gas prior to use to remove traces of oxygen. The electrolyte tetrabutylammonium tetrafluoroborate (TBABF<sub>4</sub>) (Fluka, electrochemical grade) was dried in vacuo before use. The high pressure cell used to measure solution conductivity was similar to that reported previously.<sup>3</sup> An ac impedance method was applied to measure the solution resistance, employing a 1286 potentiostat and a 1254 frequency response analyzer (both Solartron Instruments) controlled by ZPLOT software. A 20 mV ac amplitude was used to record impedance spectra in the frequency range 65000–1000 Hz. The acquired data were analyzed using ZVIEW software. The uncompensated solution resistance was obtained by extrapolation to infinite frequency and the average solution resistance from five experimental runs was used to calculate the conductivity. The cell constant was calibrated with an aqueous solution of 0.01 mol dm<sup>-3</sup> KCl at 30 °C, where the absolute conductivity of this solution was taken from the literature.<sup>6</sup>

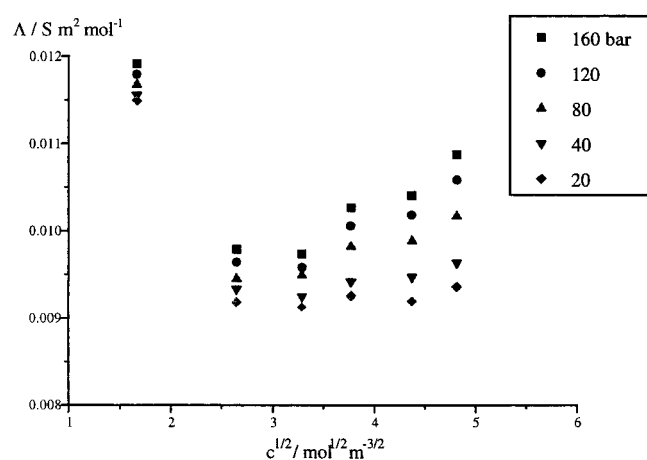
## Results and Discussion

Figures 1 and 2 show the molar conductivity,  $\Lambda$ , as a function of the square root of electrolyte concentration for TBABF<sub>4</sub> in

\* Corresponding author. Fax: UK + 116 252 3789. E-mail: andrew.abbott@le.ac.uk.



**Figure 1.** Molar conductivity of TBABF<sub>4</sub> in HFC 134a as a function of concentration at 30 °C and a variety of fluid pressures.



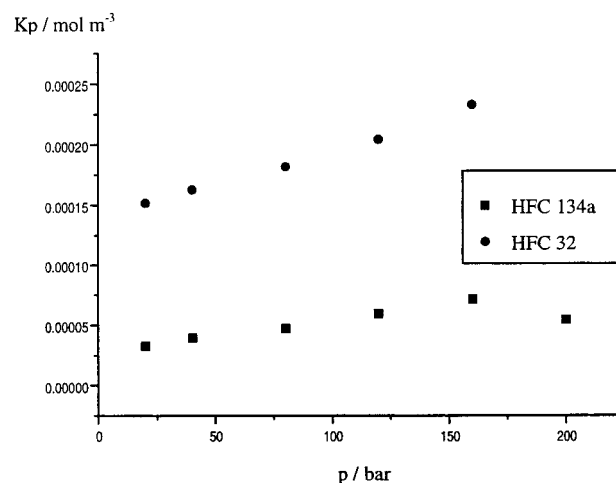
**Figure 2.** Molar conductivity of TBABF<sub>4</sub> in HFC 32 as a function of concentration at 30 °C and a variety of fluid pressures.

**TABLE 1: Comparison of the Molar Conductivity of TBABF<sub>4</sub> in Liquid DCE, HFC 134a and HFC 32 at a Similar Concentration, *c*, at 30 °C and 120 Bar**

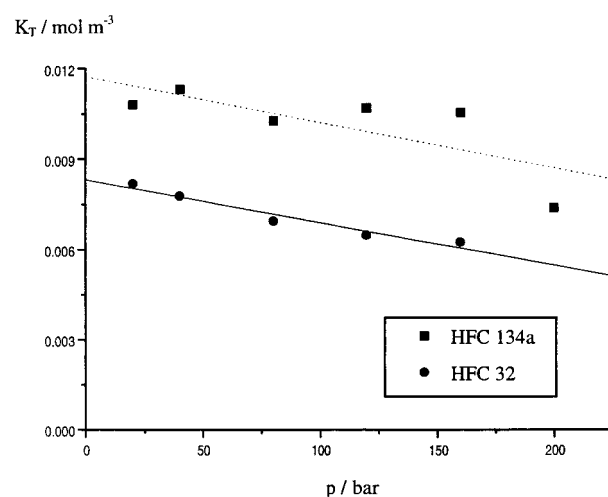
solvent	ε	η/cP	<i>c</i> /mM	Λ × 10 <sup>3</sup> /S m <sup>2</sup> mol <sup>-1</sup>
DCE <sup>a</sup>	10.4	0.505	14.2	2.05
HFC 134a	9.7	0.221	14.4	2.26
HFC 32	13.4	0.130	14.2	10.06

<sup>a</sup> Measured at 1 bar.

liquid HFC 134a and HFC 32, respectively, at 30 °C and a range of pressures. The form of both plots is very similar to that presented for other liquid solvents of similar relative permittivity.<sup>7</sup> The molar conductivity in both HFC solvents is larger than that in 1,2-dichloroethane (DCE) (ε = 10.4)<sup>8</sup> despite the similar relative permittivity (see Table 1). This is clearly a consequence of the reduced solution viscosity in the HFC solvents. The molar conductivity of TBABF<sub>4</sub> is considerably greater in liquid HFC 32 than HFC 134a over the studied concentration range. This difference can be ascribed to the higher relative permittivity and lower viscosity of HFC 32, as shown in Table 1. The increase in molar conductivity with pressure is due to the increase in solvent relative permittivity and the consequent decrease in the extent of electrolyte ion association. This is, however, in contrast to many nonaqueous liquid electrolytes, where an increase in the pressure results in a decrease in the molar conductivity due to the concomitant increase in fluid viscosity.<sup>9</sup> This shows that for HFC fluids over



**Figure 3.** *K<sub>p</sub>* as a function of pressure for TBABF<sub>4</sub> in HFC 134a and HFC 32 at 30 °C.



**Figure 4.** *K<sub>T</sub>* as a function of pressure for TBABF<sub>4</sub> in HFC 134a and HFC 32 at 30 °C.

the pressure range studied at 30 °C the change in solvent viscosity is small compared with the change in relative permittivity.

Both Figures 1 and 2 show minima in the region of 0.01 to 0.015 mol dm<sup>-3</sup>, showing that the principle charge carriers are single ions and triple ions. These data were fitted to the Fuoss–Kraus equation, to obtain the equilibrium constants for ion pair dissociation, *K<sub>p</sub>*, and triple ion dissociation, *K<sub>T</sub>*

$$\frac{\Lambda\sqrt{c}}{\Lambda_0} = \sqrt{K_p} + \frac{2c\sqrt{K_p}}{3K_T} \quad (1)$$

where *c* is the concentration of electrolyte and Λ<sub>0</sub> is the limiting molar conductivity of the single ions. Values of the limiting molar conductivity of TBABF<sub>4</sub> in HFC 134a and HFC 32 were calculated using Walden's rule, where the Walden constant was taken as 4.34 × 10<sup>-6</sup> S kg m mol<sup>-1</sup> s<sup>-1</sup>.<sup>7,10</sup> The viscosity of HFC 134a was calculated from the equation of state of Okubo et al.,<sup>11</sup> whereas that of HFC 32 was computed from the equation of Steil and Thodos<sup>12</sup> using literature values of the dilute gas viscosity.<sup>13</sup> The resulting plots of *K<sub>p</sub>* and *K<sub>T</sub>* as a function of pressure are shown in Figures 3 and 4, respectively, for TBABF<sub>4</sub> in both liquid HFC 134a and HFC 32 at 30 °C.

The *K<sub>p</sub>* values for TBABF<sub>4</sub> in HFC 32 are considerably larger than those in HFC 134a at 30 °C, as expected. Ion-pairing is

less favored in HFC 32 because of the higher relative permittivity of the medium.<sup>14</sup> In both solvents, however,  $K_P$  increases roughly linearly with pressure. The increased relative permittivity of HFC 32 will enable the solvent to stabilize the charged species.  $K_T$ , however, exhibits a lower sensitivity to pressure than  $K_P$  in both the HFC 134a and HFC 32 liquid electrolytes. This phenomenon may result from the lower sensitivity of  $K_T$  to changing relative permittivity, as has been previously observed for TBABF<sub>4</sub> in liquid media of low relative permittivity.<sup>7</sup>

In solution at constant temperature, the pressure dependence of an equilibrium constant,  $K$ , can be expressed by the following thermodynamic relation<sup>15</sup>

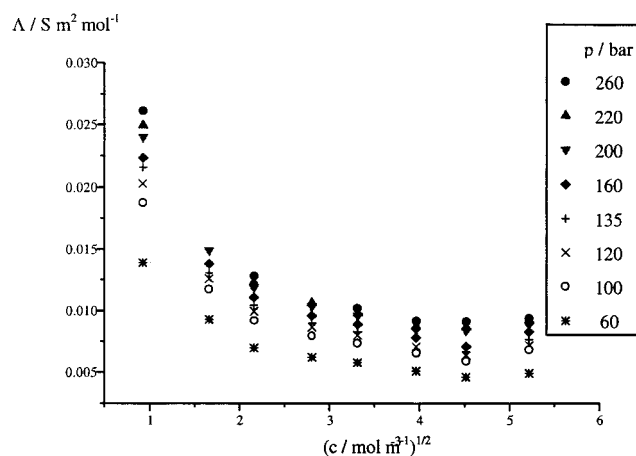
$$\left(\frac{\partial \ln K}{\partial p}\right)_T = -\frac{\Delta V^\theta}{RT} \quad (2)$$

where  $\Delta V^\theta$  is the standard volume of reaction, the change in volume between the standard states of the reactants and products. The slope of a plot of  $\ln K_P$  versus pressure at constant temperature should, therefore, provide the volume of reaction associated with ion pair dissociation. At 30 °C the plot is linear ( $r = 0.999$ ) over the pressure range studied with a slope yielding a volume of reaction of  $-75.3 \text{ cm}^3 \text{ mol}^{-1}$ . The corresponding change in volume for HFC 134a is  $-136.5 \text{ cm}^3 \text{ mol}^{-1}$ . These values are similar in magnitude to  $\Delta V^\theta$  values previously calculated for tetrabutylammonium picrate in a variety of liquid media of low relative permittivity.<sup>16,17</sup> The decrease in  $\Delta V^\theta$  calculated in the current work can be largely attributed to the change in ion solvation during ion pair dissociation.<sup>18</sup> Over the same pressure range the change in solvent volume for HFC 32 and HFC 134a is only  $-3.3$  and  $-4.5 \text{ cm}^3 \text{ mol}^{-1}$ , respectively. It is interesting to note that the ratio of the change in volume arising from ion pair dissociation in the two solvents is exactly the same as the ratio of the molecular volumes of the two solvents ( $V_{134a} = 75.0 \text{ \AA}^3$  and  $V_{32} = 40.8 \text{ \AA}^3$ ). This suggests that in these two media the change in solvation number following dissociation is the same.

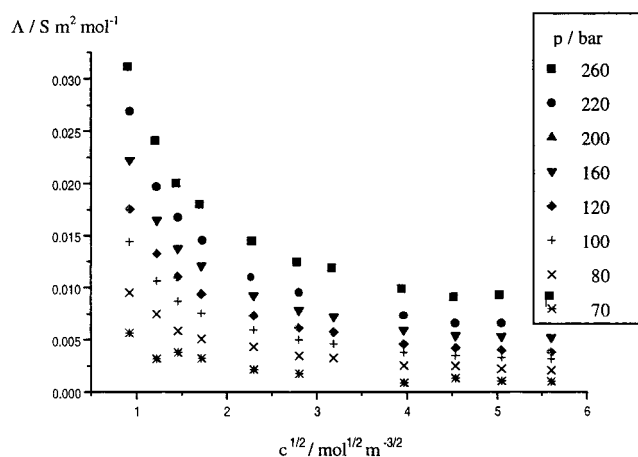
The molar conductivity of TBABF<sub>4</sub> has been shown to be far greater in liquid HFC 32 than in liquid HFC 134a at 30 °C. Since our interest in supercritical electrolyte solutions is for electrochemical applications, HFC 32 was studied in the near critical and super critical regions because it exhibits a lower critical temperature ( $T_c = 78.11 \text{ °C}$ ), than HFC 134a. The molar conductivity of TBABF<sub>4</sub> in liquid HFC 32 at 70 °C and supercritical HFC 32 at 90 °C is shown in Figures 5 and 6, respectively, as a function of the square root of the concentration at various pressures.

From a practical perspective it is interesting to note that the conductivities of TBABF<sub>4</sub> solutions at 30, 70, and 90 °C are of the same order of magnitude as shown in Figure 7. It is, therefore, implied that the increase in ion mobility expected at higher temperatures is offset by an increase in ion aggregation caused by the reduction in solvent relative permittivity. The pressure dependence of the conductivity is highest in the supercritical phase, where the high compressibility of the fluid leads to large changes in relative permittivity with pressure.<sup>14</sup>

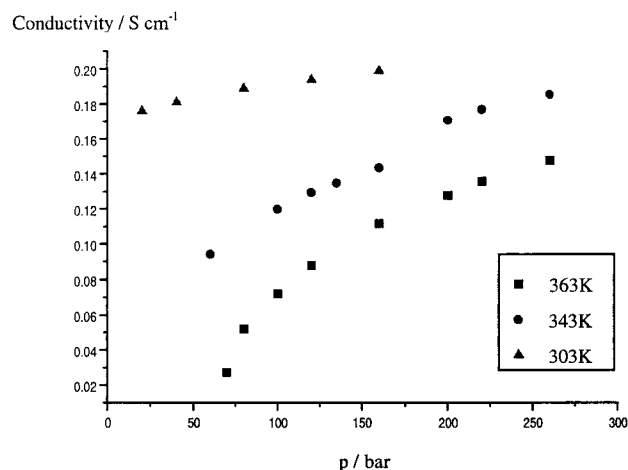
The relatively high molar conductivity of TBABF<sub>4</sub> in supercritical HFC 32 suggests that this solvent–electrolyte system may be particularly suited for use in supercritical electrochemistry. The conductivity of this supercritical medium is far greater than that of the same electrolyte in supercritical chlorodifluoromethane (CDFM), a medium recently recommended for its high electrical conductivity and low critical



**Figure 5.** Molar conductivity of TBABF<sub>4</sub> in HFC 32 as a function of concentration at 70 °C and a variety of fluid pressures.



**Figure 6.** Molar conductivity of TBABF<sub>4</sub> in supercritical HFC 32 as a function of concentration at 90 °C and a variety of fluid pressures.

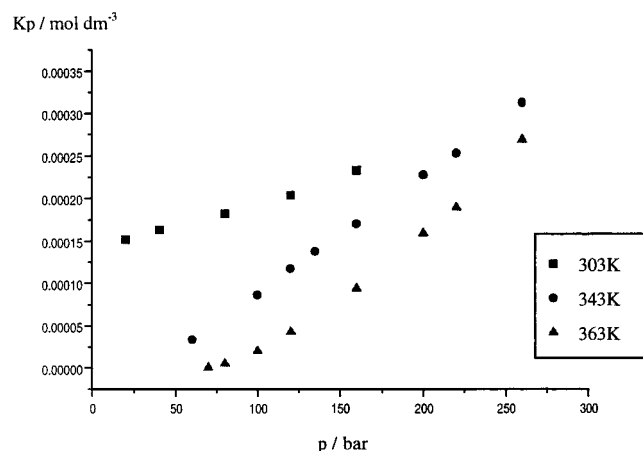
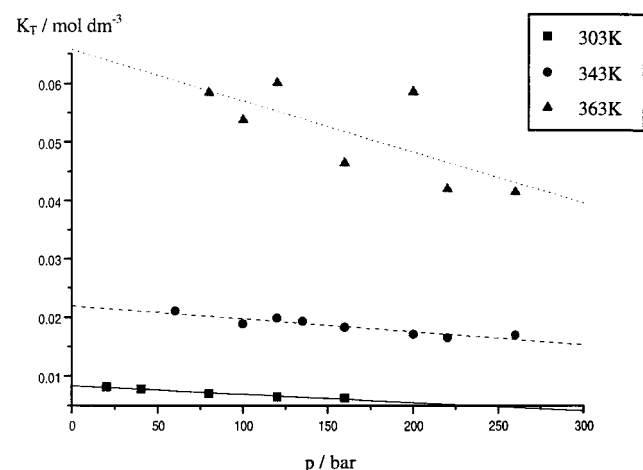


**Figure 7.** Conductivity of  $0.02 \text{ mol dm}^{-3}$  TBABF<sub>4</sub> in HFC 32 as a function of pressure at various temperatures.

temperature.<sup>4</sup> This difference can be ascribed to the higher relative permittivity and lower viscosity of HFC 32, as shown in Table 2. HFC 32 also holds the advantage of a lower critical temperature than CDFM. This result shows categorically that the voltammetric artifacts observed recently in supercritical fluids<sup>5</sup> do not arise from uncompensated solution resistance. This supports the idea that the artifacts originate from a change in the double layer structure.<sup>19</sup>

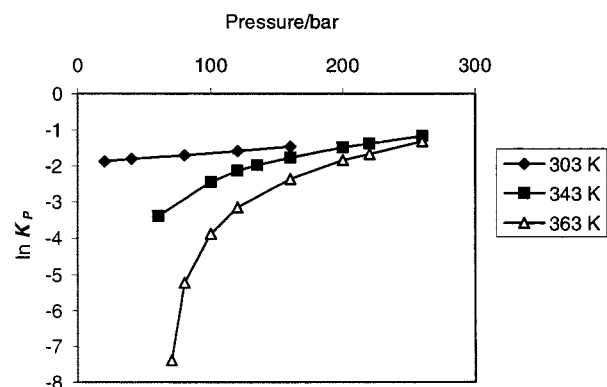
**TABLE 2: Comparison of the Molar Conductivity of TBABF<sub>4</sub> in Supercritical HFC 32 and CDFM at Similar Concentrations and Reduced Temperatures**

solvent	$T_c/^\circ\text{C}$	$\epsilon_c$	$T/^\circ\text{C}$	$p/\text{bar}$	$\eta/\text{cP}$	$c/\text{mM}$	$\Lambda \times 10^{-4}/\text{S m}^2 \text{mol}^{-1}$
HFC 32	78.11	6.0	90	100	0.0488	10.2	46.3
CDFM	96.15	2.31	115	100	0.0691	10.0	1.89

**Figure 8.**  $K_p$  as a function of pressure for TBABF<sub>4</sub> in HFC 32 at different temperatures.**Figure 9.**  $K_T$  as a function of pressure for TBABF<sub>4</sub> in HFC 32 at a variety of different temperatures.

Figures 8 and 9 display the pressure dependence of  $K_p$  and  $K_T$ , calculated from eq 2 for TBABF<sub>4</sub> in HFC 32 at 30, 70, and 90 °C. At each temperature,  $K_p$  increases roughly linearly with increasing pressure. This phenomenon can again be attributed to the increase in the relative permittivity of the medium with increasing pressure. The same effect causes an increase in  $K_p$  with decreasing temperature.<sup>14</sup>

Plots of  $\ln K_p$  vs  $p$  are shown for TBABF<sub>4</sub> in both liquid and supercritical HFC 32 in Figure 10. When the temperature is increased to 70 °C, the plot is nonlinear, implying that the volume change associated with ion pair dissociation becomes more negative with decreasing pressure. In the supercritical phase at 90 °C, the curvature of the plot is even more pronounced and divergence increases as the pressure approaches that of the critical point. It appears that the volume change corresponding to ion pair dissociation increases significantly as the pressure of the supercritical system is lowered. This could be accounted for by a decrease in the solvation of the ion pair because of the low solvent density; i.e., the solvation sheath around the ion pair becomes less ordered whereas the individual

**Figure 10.** The pressure dependence of  $\ln K_p$  for TBABF<sub>4</sub> in both liquid and supercritical HFC 32.

ions remain strongly solvated. It must also be noted, however, that the isothermal compressibility,  $\Delta\beta^\theta$ , of the fluid describes the pressure dependence of  $\Delta V^\theta$ .<sup>15</sup>

$$\left(\frac{\partial \Delta V^\theta}{\partial p}\right)_T = -\Delta\beta^\theta \quad (3)$$

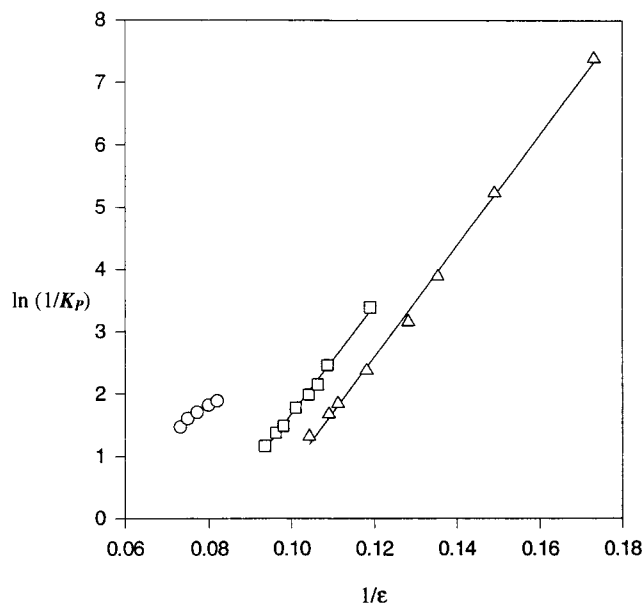
Hence the divergence exhibited in the supercritical plot of Figure 10 can also be partially ascribed to the divergence of the compressibility as the pressure tends toward  $p_c$ . As the temperature of the system is lowered to 303 K, the isothermal compressibility of the fluid will decrease significantly, yielding a volume of ion pair dissociation that is relatively independent of pressure. Carrying out the same analysis of the triple ion dissociation constant yields quite different results. For HFC 32 at each of the temperatures studied there is a linear relationship between  $\ln K_T$  and  $p$ . The volume change for triple ion dissociation are 49.9, 38.2, and 53.1 cm<sup>3</sup> mol<sup>-1</sup> at 303, 343, and 363 K, respectively. It should be noted that not only is the volume change associated with triple ion dissociation smaller than that for ion pair dissociation but also the volume change is negative for the ion pair and positive for the triple ion dissociation. This provides an insight into the solvation of the species in solution. Clearly, the solvation of neutral and charged species is markedly different and considerably more solvent molecules are required to solvate the single ions than the neutral pairs. It would also seem apparent that the solvation of the triple ion is similar to that of the single ion.

Fuoss and Kraus studied ion association in media over a wide range of relative permittivity.<sup>20</sup> It can be shown that the dissociation constant of a nondipolar 1–1 electrolyte can generally be expressed as

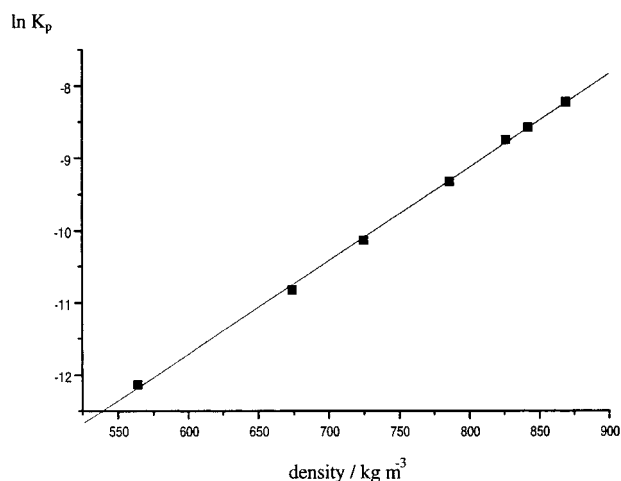
$$\ln\left(\frac{1}{K_p}\right) = \ln A_0 + \left(\frac{e^2}{4\pi\epsilon\epsilon_0 k_B T}\right) \quad (4)$$

where  $A_0$  is a preexponential constant,  $e$  is the charge of an electron, and  $a$  is the distance of closest approach of the two ions. A plot of  $\ln(1/K_p)$  versus  $1/\epsilon$  should, therefore, be linear for systems that can be described by the thermodynamic approach of Fuoss and Kraus.<sup>21</sup> Figure 11 shows plots of this type for TBABF<sub>4</sub> in liquid HFC 32 at 30 and 70 °C, and in supercritical HFC 32 at 90 °C. Good linear correlations ( $r > 0.988$ ) are observed at each temperature. These results suggest that at each temperature  $a$  is independent of pressure over the studied range. At the temperatures of 30, 70, and 90 °C the calculated  $a$  values are 11.68, 5.61, and 5.16 Å, respectively. The  $a$  values at 70 and 90 °C are in reasonable agreement with





**Figure 11.** Variation of  $\ln(1/K_p)$  with  $1/\epsilon$  for TBABF<sub>4</sub> in HFC 32 at 30 °C (O), 70 °C (□), and 90 °C (Δ).



**Figure 12.**  $\ln K_p$  as a function of solution density for TBABF<sub>4</sub> in HFC 32 at 363 K.

those previously published for TBABF<sub>4</sub> in media of low relative permittivity and show that penetrating ion pairs are formed.<sup>7</sup> The strong linear correlation at 90 °C ( $r = 0.999$ ) also suggests that at a fixed concentration ion association is purely governed by the temperature and relative permittivity of the medium, independent of whether the conducting phase is liquid or supercritical. The high  $a$  value at 30 °C is a consequence of the high relative permittivity, allowing solvent shared ion pairs to form.

Johnston and co-workers<sup>22</sup> showed that in supercritical water local density augmentation can have a significant effect on ionic mobility. We have previously shown<sup>23</sup> that local density augmentation can occur in supercritical HFC 32 at 90 °C at densities close to critical. Figure 12 shows that there is, however, a strong linear correlation ( $r = 0.998$ ) between  $\ln K_p$  and reduced density for TBABF<sub>4</sub> in supercritical HFC 32 at 90 °C. If solvation of the species had an effect upon the ion-pairing equilibrium, a plot of  $\ln K_p$  against solvent reduced density would display two density regions indicative of solvent density inhomogeneities.<sup>24</sup> It can be concluded that under the conditions studied the local environment around the solute does not have a significant effect upon ion association in the supercritical phase. It is useful therefore to note that when analyzing the

conductometric response of near critical and supercritical ionic solutions, the simple dielectric model developed for liquid solvents is valid. It should, however, be noted that linear density augmentation is not particularly marked in HFC 32 at the conditions used since  $\rho > \rho_c$ <sup>23</sup> and that measurements closer to the critical point are difficult to make.

These studies have shown that highly conducting solutions can be obtained with TBABF<sub>4</sub> in both HFC 134a and HFC 32. Charge is carried by both single and triple ions, the proportions of which are governed by the overall electrolyte concentration and the relative permittivity of the solution in both the liquid and supercritical states.

## Conclusion

It has been shown that by the addition of a tetrabutylammonium tetrafluoroborate electrolyte to liquid and supercritical hydrofluorocarbons, the conductivity of the medium is sufficient to allow the study of electrochemistry. Both single ions and triple ions have been shown to be responsible for transport of charge in liquid and supercritical HFC 32. The ion pair dissociation constant changes markedly with pressure whereas the triple ion dissociation constant is largely unaffected.

## References and Notes

- (1) Franck, E. U. Z. *Phys. Chem., N. F.* **1956**, 8, 92. Franck, E. U. Z. *Phys. Chem., N. F.* **1956**, 8, 107. Franck, E. U. Z. *Phys. Chem., N. F.* **1956**, 8, 192.
- (2) Dunn, L. A.; Marshall, W. L. *J. Phys. Chem.* **1969**, 73, 723. Dunn, L. A.; Marshall, W. L. *J. Phys. Chem.* **1969**, 73, 2619. Frantz, J. D.; Marshall, W. L. *Am. J. Sci.* **1984**, 282, 1666. Frantz, J. D.; Marshall, W. L. *Am. J. Sci.* **1984**, 284, 651. Quist, A. S.; Marshall, W. L. *J. Phys. Chem.* **1965**, 69, 2984. Quist, A. S.; Marshall, W. L. *J. Phys. Chem.* **1966**, 70, 3714. Quist, A. S.; Marshall, W. L. *J. Phys. Chem.* **1966**, 72, 3122. Yeatts, L. B.; Dunn, L. A.; Marshall, W. L. *J. Phys. Chem.* **1971**, 75, 1099. Yeatts, L. B.; Marshall, W. L. *J. Phys. Chem.* **1972**, 76, 1053. Marshall, W. L. *J. Chem. Eng. Data* **1987**, 32, 221.
- (3) Abbott, A. P.; Harper, J. C. *J. Chem. Soc., Faraday Trans.* **1996**, 92, 3895.
- (4) Olsen, S. A.; Tallman, D. E. *Anal. Chem.* **1996**, 68, 2054.
- (5) Abbott, A. P.; Eardley, C. A.; Harper, J. C.; Hope, E. G. *J. Electroanal. Chem.* **1998**, 457, 1.
- (6) Robinson, R. A.; Stokes, R. H. *Electrolyte Solutions*; Butterworth: London, 1959.
- (7) Abbott, A. P.; Schiffrin, D. J. *J. Chem. Soc., Faraday Trans.* **1990**, 86, 1453.
- (8) Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents: Solvent Properties and Methods of Purification*, 4th ed.; J. Wiley and Sons: New York, 1986.
- (9) Glugla, P. G.; Byon, J. H.; Eckert, C. A. *J. Chem. Eng. Data* **1981**, 26, 80.
- (10) Bein, G. S.; Fuoss, R. M.; Kraus, C. A. *J. Am. Chem. Soc.* **1934**, 56, 1860.
- (11) Okubo, T.; Hasuo, T.; Nagashima, A. *Int. J. Thermophys.* **1992**, 13, 931.
- (12) Steil, L. I.; Thodos, G. *AIChE J.* **1964**, 10, 275.
- (13) Geller, V. Z.; Paulaitis, M. E.; Bivens, D. B.; Yokozeiki, A. *Int. J. Thermophys.* **1996**, 17, 75.
- (14) Abbott, A. P.; Eardley, C. A.; Tooth, R. *J. Chem. Eng. Data* **1999**, 44, 112.
- (15) Blandamer, M. J.; Burgess, J.; Robertson, R. E.; Scott, J. M. W. *Chem. Rev.* **1982**, 82, 259.
- (16) Everaert, J.; Persoons, A. *J. Phys. Chem.* **1982**, 86, 546.
- (17) Marcus, Y. Z. *Naturforsch.* **1983**, 38a, 247.
- (18) Marcus, Y. *Ion Solvation*; Wiley: New York, 1985.
- (19) Abbott, A. P.; Eardley, C. A. *J. Phys. Chem. B* **1999**, 103, 6157.
- (20) Fuoss, R. M.; Kraus, C. A. *J. Am. Chem. Soc.* **1957**, 79, 3304.
- (21) Bockris, J. O'M.; Reddy, A. K. N. *Modern Electrochemistry*; Plenum Press: New York, 1970.
- (22) Balbuena, P. B.; Johnston, K. P.; Rossky, P. J.; Hyun, J. K. *J. Phys. Chem. B* **1998**, 102, 3806.
- (23) Abbott, A. P.; Eardley, C. A.; *J. Phys. Chem. B* **1999**, 103, 2504.
- (24) Tucker, S. C.; Maddox, M. W. *J. Phys. Chem. B* **1998**, 102, 2437.