

$$K_1 = K_{ap}(1 + K_{D,1}/[Na^+])^2 \quad (\text{see text})$$

where

$$[Na^+] = \{K_{D,Na^+,BPh_4^-} [Na^+,BPh_4^-]\}^{1/2}$$

Inspection of the data given in Table VII reveals:

(1)  $K_{ap}$  values observed in the experiments performed in the absence of sodium boride fit the line shown in Figure 3.

(2) The addition of  $Na^+BPh_4^-$  increases  $K_{ap}$  if  $[Na^+,BPh_4^-] < 10^{-2} M$ . This is to be expected since an increase in  $[Na^+]$  depresses the concentration of  $T^-$  and  $T^{2-},Na^+$  ions. In fact, the  $K_1$  values calculated from the equation involving  $[Na^+]$  are consistent with those obtained by the linear extrapolation shown in Figure 3, *viz.*,  $K_1 = 400$ .

(3) For a high concentration of  $Na^+,BPh_4^- (>10^2 M)$ , *i.e.*, for a relatively high concentration of  $Na^+$  and  $BPh_4^-$  ions,  $K_{ap}$  decreases. Under these conditions, one expects a substantial proportion of triple ions, *i.e.*,  $(T^{2-},2Na^+)Na^+$ ,  $(T^{2-},2Na^+)BPh_4^-$ ,  $(T^-,Na^+)Na^+$ , and  $(T^-,Na^+)BPh_4^-$ . The binding of  $Na^+$  or  $BPh_4^-$  by

$T^-,Na^+$  arises from a dipole-charge interaction, that of  $T^{2-},2Na^+$  with the free ions has to be attributed to a quadrupole-charge interaction. The former is stronger than the latter, and therefore the formation of triple ions removes from the system a greater fraction of  $T^-,Na^+$  than of  $T^{2-},2Na^+$ . This decreases the  $K_{ap}$  in accordance with our observations.

Let us summarize our findings. The formation of triple ions distorts the value of  $K_{ap}$  at rather high concentration of the free ions. It seems that this effect is negligible in the absence of  $Na^+,BPh_4^-$ , even in the experiments which were performed at the highest concentration of  $T^{2-},2Na^+$ . However, had this effect been important it would decrease the  $K_{ap}$ . Therefore, any corrections which would account for the triple ion formation could only amplify the discrepancy between Garst's and our  $K_1$ .

*Acknowledgment.* We wish to thank Dr. Garst for his constructive comments. This work was supported by the National Science Foundation and by the U. S. Army Research Office, Durham.

## Studies of Solvation Phenomena of Ions and Ion Pairs in Dimethoxyethane and Tetrahydrofuran

C. Carvajal, K. J. Tölle, J. Smid, and M. Szwarc

*Contribution from the Department of Chemistry, State University College of Forestry at Syracuse University, Syracuse, New York 13210. Received August 12, 1965*

Density, viscosity, and dielectric constant of dimethoxyethane (DME) and tetrahydrofuran (THF) were investigated in the temperature range  $+25$  to  $-70^\circ$  and found to be remarkably similar for both solvents. Conductance of tetraphenylboride salts of  $Na^+$ ,  $Cs^+$ , and  $Bu(Am)_3N^+$  were investigated in both media, down to  $5 \times 10^{-6} M$  concentration and over the whole temperature range of  $+25$  to  $-70^\circ$ . The respective  $\lambda_0^+$ ,  $K_{dis}$ , and  $-\Delta H_{dis}$  showed that  $Bu(Am)_3N^+,BPh_4^-$  forms contact ion pairs in both solvents and dissociates into free  $Bu(Am)_3N^+$  and  $BPh_4^-$  ions not coordinated with solvent. The simple "sphere in continuum" model accounts for the quantitative behavior of this salt in DME and THF. However, to account for the behavior of  $Na^+,BPh_4^-$ , it is necessary to assume that in both media the salt forms mainly solvent-separated pairs which dissociate into solvent-coordinated  $Na^+$  ions. While the behavior of  $Bu(Am)_3N^+,BPh_4^-$  or  $Na^+,BPh_4^-$  is similar in THF and DME, that of  $Cs^+,BPh_4^-$  is different in DME from that in THF. It was shown that the medium-size, free  $Cs^+$  ion is coordinated with DME but not with THF, whereas the  $Cs^+,BPh_4^-$  forms mainly contact ion pairs in both solvents. Therefore, the "sphere in continuum" model reasonably accounts for the dissociation of  $Cs^+,BPh_4^-$  in THF but not in DME. At ambient temperatures the dissociation constant of  $Cs^+,BPh_4^-$  is  $\sim 20$  times greater in DME than in THF. Lowering the temperature leads to conversion of contact ion pairs to solvent-separated pairs as shown by the substantial decrease in  $-\Delta H_{dis}$ .

In reactions involving ions or ion pairs, the role played by solvent cannot be overestimated. Even a small modification of its structure may cause a large change in the rate and in the pattern of an investigated process. Propagation of anionic polymerization may serve as an example. The reaction involves free ions, *e.g.*,  $\sim\text{styrene}^-$ , and ion pairs such as  $\sim\text{styrene}^-,Na^+$ . The latter grow rapidly in tetrahydrofuran,<sup>1</sup> the respective  $k_{p\pm}$  being 80 l./mole sec., but slowly in dioxane,<sup>2</sup>  $k_{p\pm} = 3-5$  l./mole sec. Moreover, in THF the  $\sim\text{styrene}^-,Li^+$  ion pair is the most reactive and the  $\sim\text{styrene}^-,Cs^+$  the least. In dioxane the pattern is reversed,  $\sim\text{styrene}^-,Cs^+$  being the most reactive and  $\sim\text{styrene}^-,Li^+$  the most inert ion pair.

It seems that a thorough characterization of solvents is required before quantitative understanding of their role can be contemplated. Therefore, we started a comprehensive program of characterization of ethereal solvents, and in this communication our findings for tetrahydrofuran (THF) and dimethoxyethane (DME) are reported. The physical properties of these solvents, *i.e.*, density ( $d$ ), dielectric constant ( $\epsilon$ ), and viscosity ( $\eta$ ) were determined for a temperature range of  $-70$  up to  $+25^\circ$ . In addition, the conductance of  $Na^+$ ,  $Cs^+$ , and  $(i-Am)_3BuN^+$  ( $i-Am = \text{isoamyl}$ ) salts of  $BPh_4^-$  was investigated in the same temperature range.

(1) D. N. Bhattacharyya, C. L. Lee, J. Smid, and M. Szwarc, *J. Phys. Chem.*, **69**, 612 (1965).

(2) D. N. Bhattacharyya, J. Smid, and M. Szwarc, *ibid.*, **69**, 624 (1965).

The  $(i\text{-Am})_3\text{BuN}^+$  salt was chosen, since it was shown<sup>3</sup> that the transference number of this cation is then 0.5. Hence, the experimental  $\Lambda_0$  gives  $\lambda_0^-$  of  $\text{BPh}_4^-$  and therefore the  $\lambda_0^+$  for cations may be calculated from the respective  $\Lambda_0$  values.

## Experimental Section

Dimethoxyethane (DME) and tetrahydrofuran (THF) were acquired commercially and purified by standard procedures. The purified solvents were distilled on a 3-ft. long fractionation column after being refluxed overnight on sodium-potassium alloy. It was found that traces of moisture do not affect their dielectric constant or solvating power and contribute only insignificantly to their conductance. In view of this, the investigation was carried out in a closed system but not on a high-vacuum line.

The densities were determined pycnometrically in a constant temperature bath, viscosities in a Ubbelohde-type viscosimeter which was calibrated with liquids of known viscosity, and the dielectric constant by means of a Q-meter (Radio Corp.) operating on 50–150 kc. The reliability of the latter was checked by determining the known dielectric constants of some pure liquids. The results seem to be accurate within 1%.

Sodium tetraphenylboride, acquired from Fisher Scientific Co. (99.7%), was thrice reprecipitated from ethylene dichloride by slow addition of cyclohexane. The absence of other alkali salts was checked by flame spectrophotometry. The preparation of  $\text{Cs}^+$  and  $\text{Bu}(i\text{-Am})_3\text{N}^+$  salts followed the procedure described in a previous paper.<sup>4</sup>

Conductance was measured in glass cells immersed in a constant temperature bath filled with isooctane. The temperature was measured with a thermocouple immersed in a pocket located in the vicinity of the electrodes. The bridge used in this work and its operation were described.<sup>4</sup> The unit was cooled to  $-70^\circ$  with solid carbon dioxide and the conductance measured after the system attained its thermal equilibrium. Thereafter, the temperature was raised by means of an electric heater by  $\sim 10^\circ$ , and the conductance measured again after a new thermal equilibrium was established. This procedure was repeated over and over again until the temperature of the bath reached  $25^\circ$ . Thus, the resistance of the cell was determined as a function of temperature for a constant salt concentration (the contraction of the volume of the liquid was taken into account in the calculation). We estimated the reliability of temperature measurements at  $\pm 0.2^\circ$ . The uncertainty arises from the difficulty of ascertaining whether the thermal equilibrium is attained. Therefore, in several experiments the resistance was redetermined as the temperature was lowered and the results were found to be consistent with the previous one. This assures us of the reliability of our results.

The cell constant was determined at  $25^\circ$  with a KCl solution. The calculation, based on the cell dimension and the respective expansion coefficients, indicated that the cell constant is insignificantly changed (by about 1%) by lowering the temperature from  $+25$  to

$-70^\circ$ . To establish this point, we measured the conductance in three cells of widely different separation of the electrodes and their areas. Since the ratios of the resistances determined at  $25$  and  $-70^\circ$  were constant, no corrections were introduced.

The stock solutions were prepared by weighing the investigated salts. The dilution factors were calculated from the weights of the solution and of the added solvent. The conductance was measured down to concentrations of  $\sim 5 \times 10^{-6} M$  and the resistance of the pure solvent checked; the appropriate corrections were then introduced.

The smoothed curves giving  $\Lambda$  as  $f(T)$  for constant  $C$  were used to intrapolate  $\Lambda$  as a  $f(c)$  for series of  $T$ . Using a computer program, we calculated from these values the respective Fuoss variables  $F/\Lambda$  and  $f^2c\Lambda/F$ , and their plots led to  $\Lambda_0$  and  $K_{\text{dis}}$  at the desired temperatures.

## Results

The densities, viscosities, and dielectric constants of DME and THF were found to be remarkably similar (see Tables I and II). On lowering the temperature, the increase of the viscosity and of the dielectric constant of DME is slightly greater than that of THF, e.g.,  $d \ln \epsilon/d \ln T = -1.28$  for the former and  $-1.16$  for the latter solvent. The log of  $\epsilon$  is linear with log  $T$  over

**Table I.** Physical Properties of Dimethoxyethane (DME) as Functions of Temperature<sup>a</sup>

Temp., °C.	$d$ , g./cc.	$\eta \times 10^3$ , poises	$\epsilon$
25	0.859	4.55	7.20
10	0.874	5.30	7.60
5	0.879	5.55	7.75
0	0.883	6.10	8.00
-10	0.893	6.70	8.45
-20	0.903	7.80	8.85
-25	0.908	8.60	9.05
-30	0.913	9.30	9.30
-40	0.923	11.30	9.85
-50	0.932	13.80	10.45
-60	0.942	16.9	11.05
-70	0.952	21.0	11.75
-75	0.957	...	12.15

<sup>a</sup>  $d \ln \epsilon/d \ln T = -1.28$ ;  $\epsilon = -2.83 + 2950/T$ ;  $\log \eta = -3.773 + 425/T$ ;  $d \ln \nu/dT = 0.00114$ , where  $\nu$  denotes the molar volume of the liquid.

**Table II.** Physical Properties of Tetrahydrofuran (THF) as Functions of Temperature<sup>a</sup>

Temp., °C.	$d$ , g./cc.	$\eta \times 10^3$ , poises	$\epsilon$
25	0.880	4.61	7.39
10	0.894	5.42	7.88
0	0.904	6.08	8.23
-10	0.914	6.90	8.60
-20	0.924	7.91	9.00
-30	0.934	9.16	9.43
-40	0.945	10.75	9.91
-50	0.955	12.8	10.43
-60	0.966	15.5	10.98
-70	0.978	19.1	11.58

<sup>a</sup>  $d \ln \epsilon/d \ln T = -1.16$ ;  $\epsilon = -1.495 + 2659/T$ ;  $\log \eta = -3.655 + 393/T$ ;  $d \ln \nu/dT = 0.001085$ , where  $\nu$  denotes the molar volume of the liquid.

(3) M. A. Coplan and R. M. Fuoss, *J. Phys. Chem.*, **68**, 1177 (1964).

(4) D. N. Bhattacharyya, C. L. Lee, J. Smid, and M. Szwarc, *ibid.*, **69**, 608 (1965).

**Table III.** Conductivities of  $\text{Na}^+(\text{BPh}_4)^-$ ,  $\text{Cs}^+(\text{BPh}_4)^-$ , and  $(\text{N}(i\text{-Am})_3\text{Bu})^+(\text{BPh}_4)^-$  in Dimethoxyethane (DME)

Temp., °C.	$\text{Na}^+(\text{BPh}_4)^-$			$\text{Cs}^+(\text{BPh}_4)^-$			$(\text{N}(i\text{-Am})_3\text{Bu})^+(\text{BPh}_4)^-$		
	$\Lambda_0$ , cm. <sup>2</sup> /ohm equiv.	$\Lambda_{07}$ $\times 10^2$	$K_{\text{dis}}$ $\times 10^5$ , moles/l.	$\Lambda_0$ , cm. <sup>2</sup> /ohm equiv.	$\Lambda_{07}$ $\times 10^2$	$K_{\text{dis}}$ $\times 10^5$ , moles/l.	$\Lambda_0$ , cm. <sup>2</sup> /ohm equiv.	$\Lambda_{07}$ $\times 10^2$	$K_{\text{dis}}$ $\times 10^5$ , moles/l.
25	102.0	46.4	5.46	100.0	45.5	2.86	92.6 (?)	42.1 (?)	3.47 (?)
10	87.0	46.1	5.95	84.7	44.9	3.97	77.5	41.0	4.72
0	76.3	46.5	6.76	74.0	45.1	5.18	67.1	40.9	5.66
-10	66.3	46.0	7.70	64.1	43.0	6.54	58.9	39.4	6.81
-20	56.0	43.7	9.08	54.2	42.2	8.70	48.9	38.1	8.25
-30	47.1	43.8	10.00	45.5	42.3	10.1	41.2	38.3	9.72
-40	38.3	43.2	11.91	37.6	42.5	11.6 (?)	33.8	38.2	11.09
-50	30.4	42.0	13.3	30.0	41.4	14.6	27.0	37.3	12.67
-60	23.0	39.0	15.8	23.1	39.1	16.5	20.8	35.1	13.67
-70	16.4	34.4	15.6 (?)	16.7	35.1	16.2	15.45	32.0	14.33
-75	13.8	...	16.5	...	...	...	...	...	15.26

**Table IV.** Conductivities of  $\text{Na}^+(\text{BPh}_4)^-$ ,  $\text{Cs}^+(\text{BPh}_4)^-$ , and  $(\text{N}(i\text{-Am})_3\text{Bu})^+(\text{BPh}_4)^-$  in Tetrahydrofuran (THF)

Temp., °C.	$\text{Na}^+(\text{BPh}_4)^-$			$\text{Cs}^+(\text{BPh}_4)^-$			$(\text{N}(i\text{-Am})_3\text{Bu})^+(\text{BPh}_4)^-$		
	$\Lambda_0$ , cm. <sup>2</sup> /ohm equiv.	$\Lambda_{07}$ $\times 10^2$	$K_{\text{dis}}$ $\times 10^5$ , moles/l.	$\Lambda_0$ , cm. <sup>2</sup> /ohm equiv.	$\Lambda_{07}$ $\times 10^2$	$K_{\text{dis}}$ $\times 10^5$ , moles/l.	$\Lambda_0$ , cm. <sup>2</sup> /ohm equiv.	$\Lambda_{07}$ $\times 10^2$	$K_{\text{dis}}$ $\times 10^5$ , moles/l.
25	86.2	39.7	8.82	120.0 <sup>a</sup>	55.2	0.149	82.0	37.8	5.52
10	71.6	39.1	10.7	100.0	54.6	0.181	68.9	37.6	6.25
0	62.9	38.5	12.0	88.6	54.2	0.206	61.1	37.5	7.04
-10	55.1	38.2	12.9	76.9	53.7	0.235	53.7	37.2	7.67
-20	47.5	37.7	14.0	66.7	53.0	0.255	46.6	37.0	8.29
-30	40.8	37.2	14.1 (?)	57.8	52.7	0.280	39.9	36.4	9.55
-40	34.4	36.8	14.2 (?)	48.8	52.3	0.308	33.6	36.1	10.79
-50	28.8	36.3	15.1	40.0 (?)	50.4 (?)	0.331 (?)	28.0	35.5	11.95
-60	23.1	35.9	16.5	33.9	51.5	0.363	22.8	35.3	13.06
-70	18.5	35.6	15.3 (?)	25.0	48.1	0.390	18.3	35.3	14.15

<sup>a</sup> This value is higher than the one previously reported (ref. 4).

**Table V.**  $\lambda_0^+$  and Stokes Radii in Dimethoxyethane

Temp., °C.	$\text{Na}^+$		$\text{Cs}^+$		$\text{Bu}(\text{Am})_3\text{N}^+$	
	$\lambda_0^+$	$0.82/\eta\lambda_0^+$	$\lambda_0^+$	$0.82/\eta\lambda_0^+$	$\lambda_0^+$	$0.82/\eta\lambda_0^+$
25	55.7	3.2	53.7	3.35	46.3	3.9
10	48.2	3.2	45.9	3.4	38.8 (?)	3.8 (?)
0	42.8	3.2	40.5	3.3	33.5	4.0
-10	36.9	3.3	34.7	3.5	29.4	4.15
-20	31.6	3.3	29.8	3.5	24.4	4.3
-30	26.5	3.3	24.9	3.5	20.6	4.3
-40	21.4	3.4	20.7	3.65	16.9	4.25
-50	16.9	3.65	16.5	3.6	13.5	4.4
-60	12.6	3.85 (?)	12.7	3.8	10.4	4.65
-70	...	...	9.0	4.3 (?)	7.7	5.05 (?)

**Table VI.**  $\lambda_0^+$  and Stokes Radii in Tetrahydrofuran

Temp., °C.	$\text{Na}^+$		$\text{Cs}^+$		$\text{Bu}(\text{Am})_3\text{N}^+$	
	$\lambda_0^+$	$0.82/\eta\lambda_0^+$	$\lambda_0^+$	$0.82/\eta\lambda_0^+$	$\lambda_0^+$	$0.82/\eta\lambda_0^+$
25	45.2	3.95	79.0	2.25	41.0	4.35
10	37.1	4.05	65.5	2.3	34.5	4.35
0	32.3	4.15	58.0	2.3	30.6	4.35
-10	28.2	4.2	50.0	2.35	26.9	4.4
-20	24.2	4.25	43.4	2.4	23.3	4.4
-30	20.8	4.3	37.8	2.4	20.0	4.45
-40	17.6	4.35	32.0	2.4	16.8	4.55
-50	14.8	4.4	26.0	2.5	14.0	4.65
-60	11.7	4.5	22.5	2.35 (?)	11.4	4.65
-70	9.35	4.55	15.9	2.65	9.15	4.65

the whole temperature range, but a good linear relation is found also between  $\epsilon$  and  $1/T$ . For DME the latter relation shows a slight curvature, while for THF both relations are equally good and no preference can be made on the basis of experimental data.

Tables III and IV list the respective  $\Lambda_0$  values, Walden products, and  $K_{\text{dis}}$  of the studied salts as functions of temperature. Assuming  $\lambda_0^+ = \lambda_0^-$  for the  $\text{Bu}(i\text{-Am})_3\text{N}^+\text{BPh}_4^-$ , we calculate the  $\lambda_0^+$  for  $\text{Na}^+$ ,  $\text{Cs}^+$ , and  $\text{Bu}(i\text{-Am})_3\text{N}^+$  cations. The latter are listed in Tables V and VI. Finally, Figures 1 and 2 give  $\log K_{\text{dis}}$  as a function of  $1/T$  for all of the investigated salts in DME and THF, respectively.

## Discussion

Before discussing the significance of our data, we have to assess their reliability. Although there are some uncertainties in the temperature determination, the

smoothing operation applied in plotting the cell resistance vs.  $T$  (see Figure 3) eliminates them to a great extent. Nevertheless, we estimate the uncertainties in  $\Lambda_0$  as  $\pm 3\text{--}5\%$  and in  $K_{\text{dis}}$  as about  $\pm 10\%$ . The effect of these errors on our final conclusions will be discussed later.

The assumption that  $\lambda_0^+ = \lambda_0^-$  for  $(i\text{-Am})_3\text{BuN}^+$ ,  $\text{BPh}_4^-$  permits us to calculate the Stokes' radii,  $R$ , for  $\text{Na}^+$ ,  $\text{Cs}^+$ , and  $(i\text{-Am})_3\text{BuN}^+$  in THF and DME. The classic equation gives  $R = 0.82/\eta\lambda_0^+$  in Å. The validity of Stokes law may be questioned; however, for large spherical ions of low surface charge density, e.g.,  $\text{Bu}(i\text{-Am})_3\text{N}^+$  or  $\text{Bu}_4\text{N}^+$ , it is likely to be reliable, although the appropriate coefficient may differ somewhat from  $1/6\pi$ . In fact, the calculations of Robinson and Stokes<sup>5</sup> indicate that Stokes radii give the proper

(5) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Academic Press Inc., New York, N. Y., 1959.

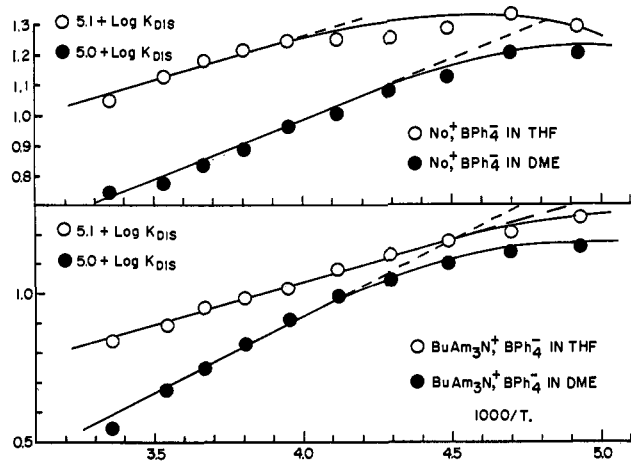


Figure 1.  $\text{Log } K$ , as a function of  $1/T$ .

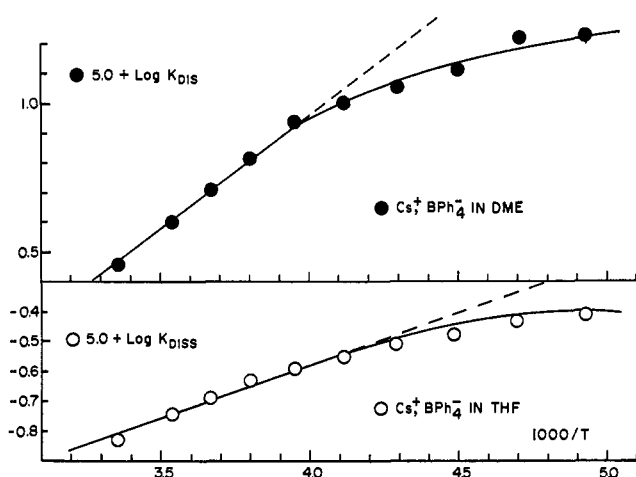


Figure 2.  $\text{Log } K_{\text{dis}}$  as a function of  $1/T$ .

dimensions for  $R \geq 5 \text{ \AA}$ ., whereas for smaller ions the equation apparently underestimates the ionic dimensions. In spite of these reservations, we shall use the classic equation for the purpose of this discussion.

Figure 4 shows that for any dielectric constant the Stokes radius of  $\text{Bu}(i\text{-Am})_3\text{N}^+$  ion is virtually the same in DME and THF. An error of  $\pm 3\text{--}5\%$  in  $\Delta_0$  results in an error of  $\pm 10\text{--}15\%$  in Stokes radii, and most of the observed deviations are smaller than that. In our experiments the decrease of  $1/\epsilon$  is caused by lowering the temperature of the medium, and therefore the lines shown in Figure 4 should be steeper if we correct for the effect predicted by the theories of Boyd<sup>6a</sup> or Zwanzig.<sup>6b</sup> It is probable that the observed increase of  $R$  reflects increasing participation of solvent with the motion of the ions (electrostriction) at lower temperatures. The magnitude of  $R$  for the  $(i\text{-Am})_3\text{BuN}^+$  ion, and a negligible solvent effect on its size, indicate that neither DME nor THF coordinates with it to any significant degree.

The situation is very different for  $\text{Na}^+$  and  $\text{Cs}^+$  ions. The radius of a  $\text{Na}^+$  ion in THF (for  $1/\epsilon = 0.11$ ) is  $\sim 4.3 \text{ \AA}$ ., but only  $\sim 3.4 \text{ \AA}$ . in DME. Since both radii are substantially larger than that expected for a bare  $\text{Na}^+$  ion, one must conclude that, in contradistinction to the ammonium ion, a  $\text{Na}^+$  ion is co-

(6) Their theories predict a slight decrease in  $R$  at higher  $\epsilon$ : (a) R. H. Boyd, *J. Chem. Phys.*, **35**, 1281 (1961); (b) R. Zwanzig; *ibid.*, **38**, 1603 (1963).

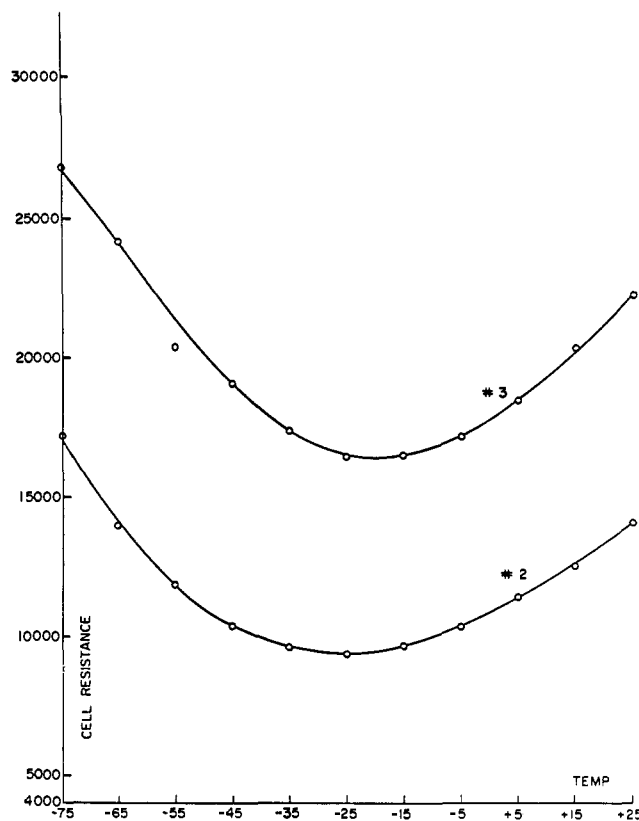


Figure 3. Cell resistance at constant  $c$  as a function of temperature.

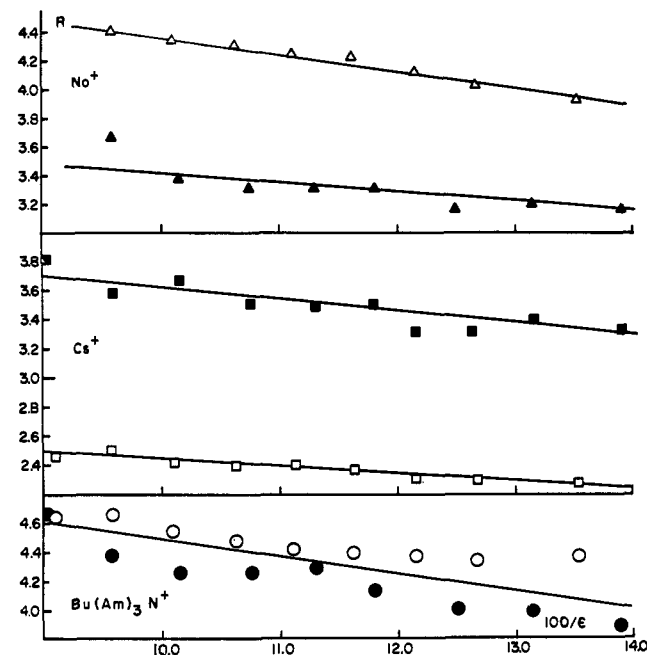


Figure 4. Stokes radii vs.  $1/\epsilon$ : nonshaded points, THF; shaded points, DME.

ordinated (specifically solvated) with the solvent, both in THF and DME. Probably four molecules of THF and only two of DME participate in the coordination, and this makes the  $\text{Na}^+$  ion larger in THF than in DME in accord with our observations.

A reverse relation is found for the  $\text{Cs}^+$  ion. Its radius in THF, about  $2.3\text{--}2.5 \text{ \AA}$ . only, is smaller than that found in DME, about  $3.4\text{--}3.7 \text{ \AA}$ . It seems that

Cs<sup>+</sup> ion is not coordinated with THF since in this solvent its Stokes radius is only slightly greater than that of a bare Cs<sup>+</sup>. However, DME being a better solvating agent coordinates even with the large Cs<sup>+</sup> ion making its Stokes radius substantially larger than that of Cs<sup>+</sup> in THF. The greater solvating power of DME arises from the presence of two O atoms in its molecule. This reduces the number of solvating entities which have to be immobilized in the solvation shell and favors the entropy of solvation.

It should be stressed that the observed changes in Stokes radii are large, and hence our conclusions are not affected by the  $\pm 10$ – $15\%$  uncertainties arising from experimental errors. The ability of DME to solvate Cs<sup>+</sup> ions, while THF is incapable to do it, is reflected in the respective  $K_{\text{dis}}$ . This constant is 20 times greater for Cs<sup>+</sup>,BPh<sub>4</sub><sup>-</sup> in DME than in THF.

Having assessed the solvating power of DME and THF for the free ions, we may turn our attention to their ability to solvate the respective ion pairs. Much insight may be gained by comparing the experimental results with those calculated on the basis of the simple "sphere in continuum" model. We propose to calculate the dissociation constant from the Fuoss equation<sup>7</sup>

$$K_{\text{dis}} = (3000/4\pi a^3 N) \exp(-e^2/ae\epsilon kT)$$

leading to Ramsey's expression<sup>8</sup>

$$\Delta H = (Ne^2/\epsilon a)(1 + d \ln \epsilon/d \ln T)$$

for the heat of dissociation if  $a$ , the distance separating the ions, is assumed to be temperature independent. The results are summarized in Table VII.

Table VII. The Thermodynamic Constants of Ionic Dissociation of Tetraphenylboride Salts in DME and THF Calculated at 25°

		$-\Delta H$ , kcal./mole	Log $K_{\text{dis}}$
Bu(Am) <sub>3</sub> N <sup>+</sup> ,BPh <sub>4</sub> <sup>-</sup>			
$a = 7.8 \text{ \AA}$ .	THF calcd.	0.95	-4.25
	obsd.	1.3	-4.25
	DME calcd.	1.65	-4.30
	obsd.	2.3	-4.45
$\frac{\Delta H(\text{DME})}{\Delta H(\text{THF})} =$		calcd. 1.75	
	obsd.	1.75	
Cs <sup>+</sup> , BPh <sub>4</sub> <sup>-</sup>			
$a = 5.6 \text{ \AA}$ .	THF calcd.	1.30	-5.65
	obsd.	1.55	-5.80
	DME calcd.	2.3	-5.70
	obsd.	3.5	-4.55
Na <sup>+</sup> , BPh <sub>4</sub> <sup>-</sup>			
$a = 7.5 \text{ \AA}$ .	THF calcd.	1.0	-4.45
	obsd.	1.3	-4.06
$a = 7.3 \text{ \AA}$ .	DME calcd.	1.7	-4.70
	obsd.	1.8	-4.27
$\frac{\Delta H(\text{DME})}{\Delta H(\text{THF})} =$		calcd. 1.7	
	obsd.	1.4	

<sup>a</sup> The experimental uncertainty of  $\pm 10\%$  in  $K_{\text{dis}}$  may lead to a maximum error in  $\Delta H$  of  $\pm 0.3$  kcal./mole. Even this large error cannot invalidate our main conclusions. We feel, however, that the reported  $\Delta H$  values are reliable within  $\pm 0.2$  kcal./mole.

Both the agreements and the disagreements between the calculated and observed values, as revealed by

(7) R. M. Fuoss, *J. Am. Chem. Soc.*, **80**, 5059 (1958).

(8) J. T. Denison and J. B. Ramsey, *ibid.*, **77**, 2615 (1955).

Table VII, are interesting and significant. For the Bu(Am)<sub>3</sub>N<sup>+</sup>,BPh<sub>4</sub><sup>-</sup> a common distance  $a = 7.8 \text{ \AA}$ . separating the ions in the pair accounts well for the observed  $K_{\text{dis}}$  and reasonably well for the respective  $\Delta H$  values. It is interesting that Ramsey's equation leads to a perfect agreement between the observed and calculated ratios,  $\Delta H(\text{DME})/\Delta H(\text{THF})$ . This might indicate that the somewhat greater  $-\Delta H$  observed, when compared to the calculated, may result from a slight increase in the temperature dependence of the "effective" dielectric constant of the medium surrounding the ion pair. On the whole, one concludes that the "sphere in continuum" model accounts satisfactorily for the behavior of this salt in both solvents: the Bu(Am)<sub>3</sub>N<sup>+</sup> ion seems not to be coordinated with the solvent neither when associated into the ion pair nor when existing as free dissociated ion; *i.e.*, we deal here with contact ion pairs which dissociate into ions not coordinated with solvent.

The situation is more complex for Na<sup>+</sup>,BPh<sub>4</sub><sup>-</sup>. It is obvious that any reasonable agreement between the theory and the experiment demands  $a$  to be substantially larger than that expected for a contact ion pair. Hence, it seems that in both solvents, DME and THF, a large fraction of Na<sup>+</sup>,BPh<sub>4</sub><sup>-</sup> exists as solvent-separated ion pairs. Our choice of  $a$ , given in Table VII, is somewhat arbitrary and based on the assumption that *all* Na<sup>+</sup>, BPh<sub>4</sub><sup>-</sup> are in the form of solvent-separated ion pairs. The chosen values serve more to emphasize the qualitative aspect of the problem and not to test quantitatively the theory. We postulate that the pair arises from the association of a solvent-coordinated Na<sup>+</sup> cation and a noncoordinated BPh<sub>4</sub><sup>-</sup> anion. Now, the Stokes radii give estimates for the dimensions of the ions, and these may be used to calculate  $a$ . However, the best value of  $a$  for Bu(Am)<sub>3</sub>N<sup>+</sup>,BPh<sub>4</sub><sup>-</sup> is lower by about 10% than that calculated from Stokes radii. This is reasonable since one anticipates some compression in the process of ion-pair formation. Therefore, the value  $a = 7.5 \text{ \AA}$ . for Na<sup>+</sup>,BPh<sub>4</sub><sup>-</sup> in THF was calculated by decreasing the Stokes radii by about 10%. The  $a$  value in DME should be smaller than that in THF, since the respective Stokes radius is smaller. However, such a value, *i.e.*, 6.8, would be too small and we have chosen the value of 7.3 as a reasonable compromise. It may be seen that the agreement between the theory and the experiment is less satisfactory for Na<sup>+</sup>,BPh<sub>4</sub><sup>-</sup> than for Bu(Am)<sub>3</sub>N<sup>+</sup>,BPh<sub>4</sub><sup>-</sup>. This reflects the weakness of our assumption that the sodium ion in the pair is completely coordinated in DME or THF. Apparently, only a fraction of Na<sup>+</sup>,BPh<sub>4</sub><sup>-</sup> pairs are solvent separated, and that is larger in DME than in THF. Again, this is a reasonable conclusion indicating a higher solvating power for DME than for THF, in spite of the slightly lower dielectric constant of the former.

The large difference in the solvating power of DME and THF is most strikingly manifested in the behavior of Cs<sup>+</sup>,BPh<sub>4</sub><sup>-</sup> in these two solvents. It has been pointed out at the beginning of our discussion that the relatively large, free Cs<sup>+</sup> ion is solvated by DME but not by THF. Therefore one expects Cs<sup>+</sup>,BPh<sub>4</sub><sup>-</sup> to be a contact ion pair in THF, and subsequently  $a$  was calculated by adding the Stokes radius of BPh<sub>4</sub><sup>-</sup>, decreased again by 10%, to the radius of a bare

Cs<sup>+</sup> ion (1.7 Å). On this basis one obtains a good agreement between the observed and calculated values for  $K_{\text{dis}}$  and  $\Delta H$  of Cs<sup>+</sup>,BPh<sub>4</sub><sup>-</sup> in THF. On the other hand, no value of  $a$  can give an agreement between the observed and calculated  $K_{\text{dis}}$  and  $\Delta H$  for Cs<sup>+</sup>,BPh<sub>4</sub><sup>-</sup> in DME. For example, if we assume, as we did in Table VII, that Cs<sup>+</sup>,BPh<sub>4</sub><sup>-</sup> forms a contact ion pair in DME, and therefore that  $a$  is the same in both solvents, then the calculated  $K_{\text{dis}}$  is  $\sim 20$  times too low and the calculated  $\Delta H$  is less negative by 1.2 kcal./mole than the observed value. The improvement of the calculated  $K_{\text{dis}}$  may be achieved by increasing the chosen value for  $a$ , but then the disagreement between the calculated and observed  $\Delta H$  becomes even larger.

The difficulty is caused by the ability of DME to coordinate with a free Cs<sup>+</sup> ion and by its apparently poor affinity for the Cs<sup>+</sup> ion in a Cs<sup>+</sup>,BPh<sub>4</sub><sup>-</sup> ion pair. Thus, the observed  $-\Delta H$  is larger, since the coordination of DME with the *dissociated* bare Cs<sup>+</sup> adds to the exothermicity of the process; and by the same token,  $K_{\text{dis}}$  increases since  $\Delta G$  of the coordination is negative.

Finally we should emphasize that the free energy of coordination is only a small fraction of that arising from the transfer of an ion from vacuum into a medium having a dielectric constant greater than unity. For example, the transfer of a bare Cs<sup>+</sup> ion into THF or DME evolves about 80 kcal./mole (there are some problems as to what values for  $R$  and  $\epsilon$  should be used in the Born equation  $-\Delta G = (Ne^2/2R)(1 - 1/\epsilon)$ ; see, e.g., ref. 9). However, these terms are automatically taken into account in the equations of Fuoss or of Ramsey. One may wonder, therefore, whether the observed discrepancies are real. It is our feeling that they are, and the differences in behavior of the investigated salts in DME and THF seem to us illuminating and showing the role of solvent coordination (specific solvation).

### The Behavior of Ion Pairs at Low Temperatures

Inspection of Figures 1 and 2 shows that the exothermicity of ion-pair dissociation is drastically reduced at lower temperatures. This behavior was observed for all the systems investigated in this laboratory (see, e.g., ref. 10 and 11). The decrease in the exo-

(9) R. H. Stokes, *J. Am. Chem. Soc.*, **86**, 979, 982, 2333 (1964).

thermicity of the dissociation at lower temperatures is expected on the basis of Ramsey's equation, since  $-\Delta H$  is proportional to  $1/\epsilon$ , and  $\epsilon$  increases with decreasing temperature. The observed decrease, however, is greater than calculated, particularly for Cs<sup>+</sup>, BPh<sub>4</sub><sup>-</sup> in DME. Apparently the contact ion pairs become solvated at lower temperatures and this leads to a substantial decrease of  $-\Delta H$  (see ref. 10 in which spectroscopic evidence is reported to demonstrate the change in the state of solvation of Na<sup>+</sup> and Li<sup>+</sup> salts of fluorenyl<sup>-</sup>).

### Recapitulation

DME and THF are in many respects similar solvents, as shown by the data listed in Tables I and II. They are unable to coordinate with the bulky Bu(Am)<sub>3</sub>N<sup>+</sup> and BPh<sub>4</sub><sup>-</sup> ions and therefore the simple model of "sphere in continuum" accounts well for the behavior of Bu(Am)<sub>3</sub>N<sup>+</sup>,BPh<sub>4</sub><sup>-</sup> in both solvents. The model still applies to Na<sup>+</sup>,BPh<sub>4</sub><sup>-</sup>, although less satisfactorily, if one assumes that the Na<sup>+</sup> ions are fully coordinated with the solvent in DME and in THF. The coordination takes place whether the cation is free or forms an ion pair, some discrepancies indicating, however, that not all the ion pairs are fully coordinated with the solvent. Finally, large differences are observed in the behavior of Cs<sup>+</sup>,BPh<sub>4</sub><sup>-</sup> in DME and THF. These may be rationalized by assuming a coordination of Cs<sup>+</sup> ion with the solvent in DME but lack of it in THF. Of course, in THF a Cs<sup>+</sup> ion is not coordinated with the solvent when it forms an ion pair, and most of the ion pairs seem not to be coordinated with the solvent even in DME.

Thus, DME is still a solvating agent for medium size ions when THF loses this capacity. This probably results from the need of involving four THF molecules in the solvation shell, whereas two DME molecules suffice under the same conditions. This point was fully appreciated by other workers.<sup>12</sup>

*Acknowledgment.* We wish to thank the National Science Foundation for the financial support of this investigation.

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(11) R. C. Roberts and M. Szwarc, *ibid.*, **87**, 5542 (1965).

(12) (a) A. I. Shatenstein, E. S. Petrov, and M. I. Belusova, "Organic Reactivity," Vol. 1, Tartu State University, Estonia, U.S.S.R., p. 191; (b) J. F. Garst and E. R. Zabolotny, *J. Am. Chem. Soc.*, **87**, 495 (1965); (c) F. Cafasso and B. R. Sundheim, *J. Chem. Phys.*, **31**, 809 (1959).