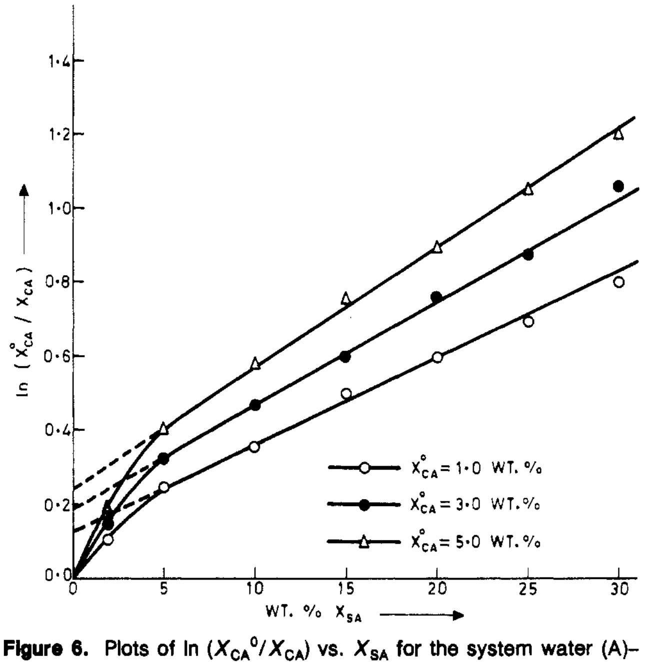

Figure 6. Plots of ln ($X_{CA}{}^0/X_{CA}$) vs. X_{SA} for the system water (A)–methyl ethyl ketone (B)–acetic acid (C)–sodium sulfate (S).

acetic acid, thereby decreasing the salting-out of acetic acid. At higher concentrations of acetic acid, more solvent is present in the aqueous phase without salt and therefore more solvent is salted-out in the presence of salt. This explains the decrease in the salting-out coefficient with the increase in acetic acid concentration in the systems having ethyl acetate and 2-ethylhexanol as solvents. On the same basis, an increase in the salting-out coefficient with the acetic acid concentration for the system having methyl ethyl ketone as solvent can be explained, since for this solvent the distribution coefficient of acetic acid is greater than 1.0.

The magnitude of the increase or decrease of the salting-out coefficient with the increase in the acetic acid concentration thus depends on three factors: (i) the magnitude of the increase of solubility of solvent with acetic acid concentration in the absence of salt; (ii) the salting-out of the solvent from the aqueous phase, and (iii) the solvent affinity for acetic acid.

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Received for review September 22, 1980. Accepted June 15, 1981.

Conductivity Studies of Uni-univalent Electrolytes in 1,1,3,3-Tetramethylurea–Water Mixtures

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The solution behavior of a series of alkali-metal salts in aqueous mixtures of the aprotic solvent of low dielectric constant 1,1,3,3-tetramethylurea (TMU) was studied by conductance techniques. All conductance data were evaluated by the procedures of the Fuoss–Onsager equation. All calculations were performed on an IBM 360/65 computer. Ionic limiting equivalent conductivities in TMU–water mixtures were obtained indirectly by using tetrabutylammonium iodide as a reference electrolyte. Stokes radii were calculated. They were much larger than the crystallographic radii, indicating that the salts studied were extensively solvated in the TMU–water mixtures.

The present work on TMU-H_2O mixtures is an attempt to obtain further information on ion–solvent interaction in these mixtures. This is a mixture of a dipolar solvent (tetramethylurea) and a protic solvent (water). The combination of two such solvents is known to produce marked changes in the chemical (*1*) and physical properties of the mixtures. It was felt that a greater understanding of reaction rates and mechanisms in nonaqueous media can be gained from fundamental electrochemical investigations which can elucidate the behavior of electrolytes in solution. Conductance studies reveal the nature of ion–solvent interactions. Although there have been a number of conductance investigations in polar aprotic solvents such as DMF (*2*), DMA (*3*), Me_2SO (*4*), and TMU (*5*), there have been no conductance studies reported for TMU-H_2O mixtures. Recently, a potentiometric study was reported for TMU-H_2O (*6*). Therefore, a conductance investigation of a series of alkali salts was undertaken to study the behavior of electrolytes in these mixtures.

Experimental Section

Solvent Preparation. Tetramethylurea (TMU) (Sigma Chemical Co.) was used after being refluxed with calcium hydride under nitrogen atmosphere and distilled at 10 mmHg. The specific conductivity of this TMU was 1.5 × 10^{-8} Ω^{-1} cm^{-1}.

Determination of Physical Properties. With 25-cm^3 Ostwald-Sprengel-type pycnometers, density measurements were determined for TMU-H_2O mixtures at 30 ± 0.001 °C. The viscosities of these mixtures were determined by using three 10-cm^3 Cannon Fenske viscometers (manufactured and calibrated by Cannon Fenske viscometers). A Townson and

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Table I. Physical Properties of TMU-H_2O Mixtures at 30 °C

properties	5 mol % TMU-H_2O	14 mol % TMU-H_2O
viscosity, g cm^{-1} s^{-1}	8.007×10^{-3}	23.31×10^{-3}
density, g cm^{-3}	1.00118	1.00635
specific conductance, Ω^{-1} cm^{-1}	88.23×10^{-6}	83.55×10^{-6}
dielectric constant	68.91	59.20

Mercer bridge-controlled thermostat bath E270 Series III assembly filled with transformer oil and maintained at 30.00 ± 0.001 °C was used in the density and viscosity determinations. Two TMU-H_2O mixtures were used in this study: 5 and 14 mol %. These solutions were all prepared by weight. Table I gives data of the physical properties of these mixtures. Dielectric constants of pure TMU and 5 and 14 mol % solutions were measured with a Dekameter DK 300 (Karl Kolb). These were done at 30 °C (Table I).

Salt Preparation and Purification. Tetrabutylammonium iodide (BDH) was recrystallized from 4:1 acetone-water mixture. Constant melting points of 146.0–147.0 °C compared favorably with literature values of 146 °C (*7*). Sodium tetraphenylborate ($NaPh_4B$) was used without further purification (Aldrich Gold Label material, 99+% pure.) Tetraethylammonium bromide (BDH) was used without further purification. Sodium chloride, potassium chloride, and potassium iodide (Analar grade) were recrystallized 3 times from conductivity water. Sodium bromide (Analar grade) was recrystallized from a 1:1 acetone–water mixture. Sodium iodide (Analar grade) was recrystallized from a 4:1 acetone–water mixture. Rubidium chloride and cesium chloride (Analar grade) were used without further purification. Conductivity water was used in the salt preparations and purifications. All salts were finely ground and dried in vacuo before use.

Apparatus. Conductimetric measurements were determined at 1591.5 Hz on a Wayne Kerr B642 autobalance universal bridge. The B642 is an autobalance transformer ratio-arm bridge for the measurement of admittance or impedance at audio frequencies, to an accuracy of 0.001%. The bridge displays capacitance and conductance simultaneously on two meters. A Townson and Mercer bridge-controlled thermostat bath E270 Series III, filled with transformer oil, was maintained at a constant temperature of 30.00 ± 0.001 °C.

Procedures. The conductance cell of 250-mL capacity was of the flask design of Daggett, Bair, and Kraus (*8*). The electrodes, ca. 2.0 cm in diameter and ca. 0.5 cm apart, were lightly platinized according to the procedure of Daggett et al. (*8*). Using the method of Fuoss, Lind, and Zwolinek (*7*), we obtained the cell constant from three independent sets of measurements. Six aqueous potassium chloride solutions ranging in concentration from 1.2×10^{-3} to 1.2×10^{-2} M were used in the determination of the cell constant. The cell constant was 0.4501 ± 0.001 cm^{-1}. Conductivity water of specific conductivity 8×10^{-7} Ω^{-1} cm^{-1} was obtained by passing distilled water through a Deeminizer ion-exchange resin and then redistilling by fractional condensation.

Ca. 200 g of the TMU-H_2O mixtures was weighed into the conductance cell which was then immersed in the oil bath and brought to temperature equilibrium. The stepwise concentration method, starting with the solvent mixture, was used in the determination of the concentration dependence of electrolyte conductance. All solution preparations were performed under normal laboratory conditions. Weighed solute samples were carefully added into the cell after the conductance of the solvent (TMU-H_2O mixture) had been obtained. All weighings were corrected to vacuum. The method of correction for the solvent conductance is very important here, since the solvent conductance is very large. A simple subtraction of the solvent conductivity (bridge reading) was used. The conductance was followed (with occasional shaking) until steady. The data given were those taken after the reading had remained steady for 5 min.

Results and Discussion

Conductivity measurements of the mixtures showed a very high increase in conductivity over either pure solvent (Table I).

The high conductivity measured can result not only from the formation of TMU–water complexes but also from the disruption of the water structure. When TMU and water were mixed, large amounts of heat were generated. This exothermic reaction is strong evidence for the existence of interactions. These interactions involve the breaking up of the polymeric water molecules and the formation of TMU–water complexes. In the water-rich region (dealt with in the present work), the net effect will be the breaking of hydrogen bonds. In this region, there are more water molecules, so that the solute (TMU) will be used up in depleting water–water hydrogen bonding. This in effect reduces the number of water–water bonds. The increase may be due to the change in the structural nature of the solvents.

The molar concentrations and the equivalent conductivities of the salts studied in tetramethylurea–water mixtures are presented in Table II. There are no dielectric-constant values for aqueous solutions of TMU in the literature. These were determined in this laboratory with a Dekameter DK 300 (Karl Kolb). With these values, the Fuoss–Onsager equation (*9*) was tested, as described in ref *5*. The calculated values are in excellent agreement with the experimental values (Table III).

Conductivity measurements of sodium tetraphenylborate were made in pure tetramethylurea for comparison with the work of Barker and Caruso (*5*). A value of $\Lambda_0 = 29.32$ at 25 °C compares very well with that of Barker and Caruso ($\Lambda_0 = 29.40$). The data for the sodium tetraphenylborate are given on Table II. The conductance values for all salts in TMU–water mixtures are given in Table IV. These Λ_0 values are obtained from the Shedlovsky y–x least-squares analysis of the original data (*10*). All conductance values listed were obtained by using values of Λ weighted by c. For all salts, the use of weighted data resulted in a better fit to the equation, as indicated by the smaller deviation $\sigma\Lambda$ for the individual conductivity values. The $\sigma\Lambda$ values varied from 0.003 to 0.010 (Table IV). Usually, limiting equivalent conductance, λ^0, can be obtained indirectly by the use of a reference electrolyte, tetrabutylammonium tetraphenylborate. The assumption was made that the limiting equivalent conductance of the tetrabutylammonium ion, shown by other workers (*11–13*) to be the same as that of the tetraphenylborate ion in methanol, is the same as that of the tetraphenylborate ion in TMU–water mixtures. On the basis of this assumption, other ionic conductances could then be evaluated from the conductances of electrolytes with common cations and anions. The tetrabutylammonium tetraphenylborate, though soluble in pure TMU, was not soluble in the TMU–water mixtures. Thus, we used the tetrabutylammonium iodide instead.

Considering the relatively normal behavior of Walden's products of tetrabutylammonium ion in almost all solvents and the large size of the iodide ion relative to the other simple anions, this choice was reasonable. The λ^0 values given in Table V were evaluated on the assumption that the simple ionic limiting conductances of Bu_4N^+ and I^- are equal.

The purpose of the present investigation is to determine relative solvation effects within an alkali-metal series; therefore, the validity of the use of tetrabutylammonium iodide is not of primary importance in this study. It is, though, satisfactory for getting relative Stokes radii. Evaluation of the validity of using any reference electrolyte in a particular solvent requires a direct measurement of transference numbers in that solvent. To determine directly ionic limiting equivalent conductivities in

Table II. Equivalent Conductivities of Salts in Tetramethylurea-Water Mixtures of 30°

10^3c	Λ	10^3c	Λ	10^3c	Λ	10^3c	Λ
			5 mol % TMU-H_2O				
KCl		NaCl		RbCl		CsCl	
1.002	79.551	1.151	68.310	0.730	82.651	0.338	82.230
2.001	77.821	2.252	67.702	1.501	82.049	1.621	84.851
2.528	77.412	3.066	67.180	2.305	81.472	3.101	83.002
3.103	77.251	5.860	66.412	3.802	80.803	4.828	82.120
4.121	76.831	6.890	66.181	5.306	80.082	7.152	81.203
5.400	76.452	8.155	65.910	6.843	79.531	8.926	80.601
6.474	76.151	10.625	65.450	9.102	78.905	10.905	80.002
7.860	75.810	11.503	65.350	10.603	78.183	13.064	79.391
9.945	75.353	12.728	65.092	12.626	77.872	18.254	78.130
$NaBPh_4$		Bu_4NI		NaBr		Et_4NBr	
0.189	36.731	0.048	65.421	0.851	65.010	0.062	72.381
0.803	36.120	0.568	56.810	2.101	64.160	0.278	67.89
2.999	35.032	0.985	51.810	2.949	63.710		
4.158	34.631	1.152	50.003	3.819	63.154	0.549	65.002
5.103	34.321	1.421	47.881	4.469	62.941	0.651	63.510
5.610	34.130	1.817	45.551	5.004	62.782	0.821	61.671
6.540	33.951	2.724	40.230	5.849	62.541	1.002	58.851
7.702	33.681	4.106	33.612	6.153	62.463	1.203	56.921
9.421	33.411			7.158	62.202	1.900	53.962
						2.968	48.344
			14 mol % TMU-H_2O				
KCl		NaCl		RbCl		CsCl	
0.501	38.001	0.502	35.473	0.294	39.701	0.596	39.501
0.856	37.831	1.363	35.012	1.004	39.282	1.005	39.184
1.993	37.532	2.612	34.463	2.010	38.904	1.813	39.003
2.336	37.462	3.952	34.004	3.249	38.432	2.504	38.642
2.910	37.351	4.655	33.791	3.984	38.241	3.102	38.580
3.850	37.192	6.722	33.252	4.780	38.052	4.585	38.131
4.961	37.022	7.822	33.001	7.421	37.511	7.536	37.522
8.324	36.614	10.304	32.492	11.970	36.772	12.484	36.730
		13.749	31.881				
$NaBPh_4$		Bu_4NI		NaBr		Et_4NBr	
0.076	21.332	0.083	22.641	0.502	31.242	0.087	30.482
0.248	21.151	0.313	22.432	1.001	31.097	0.721	29.892
0.721	21.002			1.573	30.831	1.234	29.422
1.102	20.702	0.428	22.351	2.537	30.682	1.774	29.133
1.399	20.591	0.456	22.340	3.050	30.611	2.220	29.000
1.862	20.502	0.715	22.202	3.502	30.552	2.794	28.693
2.177	20.352	1.320	21.972	4.001	30.500	4.003	28.302
2.831	20.172	2.001	21.530	4.614	30.423	4.915	27.981
			$NaBPh_4$ in Pure TMU[a]				
0.204	27.172	0.908	25.504	3.001	24.701	5.692	23.134
0.443	25.981	2.081	25.289	4.362	23.621	7.984	22.406

[a] Experiment at 25 °C.

Table III. Comparison of Experimental Λ_0 with Λ_0 Calculated from Fuoss-Onsager Equation

	Λ_0 for 5 mol % TMU-H_2O		Λ_0 for 14 mol % TMU-H_2O	
salts	exptl	theoretical	exptl	theoretical
NaCl	69.19	69.22	36.45	35.83
KCl	79.51	79.43	38.41	38.57
RbCl	84.16	83.88	40.24	40.17
CsCl	86.35	86.11	40.28	20.14
Et_4NBr	76.44	72.71	30.86	30.70
NaBr	65.72	65.78	31.42	31.77
Bu_4NI	69.28	65.72	22.86	22.83
$NaPh_4B$	37.30	37.21	21.55	21.51

TMU-H_2O mixtures and to assess the validity of the assumption $\lambda_0(TAB^+) = \lambda_0(I^-)$, we will consider transference-number measurements in this laboratory.

The order of relative anion and cationic limiting equivalent conductivities which is found in pure TMU (*5*) is the same as the order found in aqueous solutions of TMU-water mixtures. The values though are much higher in the aqueous solution than in the pure solvent TMU, indicating a lesser degree of solvation in aqueous solutions.

Table IV. Conductance Values (Λ_0) for Salts in Tetramethylurea-Water Mixtures

salts	5 mol %	$\Delta\sigma$	14 mol %	$\sigma\Lambda$
NaCl	69.19	0.001	36.45	0.001
KCl	79.51	0.001	38.41	0.001
RbCl	84.16	0.002	40.24	0.002
CsCl	86.35	0.002	40.28	0.003
Et_4NBr	76.44	0.003	30.86	0.003
NaBr	65.72	0.002	31.42	0.002
Bu_4NI	69.28	0.003	22.86	0.002
$BaPh_4B$	37.30	0.003	21.55	0.002

Table V. Ionic Equivalent Conductance (λ^0)[a]

ions	5 mol %	14 mol %
Na^+	22.13	21.57
K^+	32.47	26.29
Rb^+	37.21	28.12
Cs^+	39.31	28.16
$(C_2H_5)_4N^+$	40.99	21.02
Bu_4N^+	34.64	11.43
Cl^-	47.04	12.12
Br^-	34.45	9.85

[a] Tetrabutylammonium iodide used as the reference electrolyte.

Table VI. Stokes Radii (r_S) from Stoke's Law and Crystallographic Radii (r_X)

ions	5 mol % r_S, Å	14 mol % r_S, Å	r_X, Å
Na^+	3.39	1.63	0.95
K^+	3.15	1.34	1.33
Rb^+	2.75	1.25	1.48
Cs^+	2.60	1.25	1.69
$(C_2H_5)N^+$	2.50	1.67	1.69
Bu_4N^+	2.96	3.08	
Cl^-	2.18	2.90	1.81
Br^-	2.97	3.56	1.95

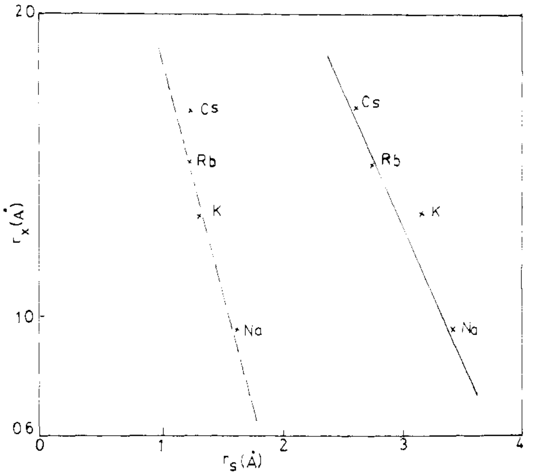

Figure 1. Plot of crystallographic radii (r_x) vs. Stokes radii (r_s) (– – –) 14 mol %; (—) 5 mol %.

It seems as though the addition of the salts further increases the long-range order of whatever structural entities that exist in the TMU–water mixtures. This will give rise to a decrease in the mobilities of the ions and thus a lower λ^0 in 14 mol % TMU–H_2O than in 5 mol % TMU–H_2O mixtures (Table V).

Procedures developed for the determination of ion-size parameters were summarized by Stern and Amis (*14*). Stokes radii can be calculated for the ions from Stokes' law

$$r_s = 0.820z/(\lambda^0\eta) \qquad (1)$$

where r_s is the Stokes ionic radius, z is the absolute magnitude of the charge of the ion, η is the viscosity of the solvent, and λ^0 is the ionic limiting equivalent conductance. Stokes radii evaluated from eq 1 are given in Table VI. Figure 1 indicates that in TMU–water mixtures, the Stokes radii of the alkali-metal cations are a linear function of the crystallographic radii of these ions, similar to that found in pure TMU (*5*).

The results indicated that the Stokes radii decreased with an increase in crystallographic radii. As expected, the cationic solvation decreased with an increase in the ionic radius in the TMU–water mixtures. Usually, if Stokes radii are greater than crystallographic radii, solvation is postulated (Table VI). Since the Stokes radii of salts in TMU–H_2O mixtures are quite large, extensive solvation of the salt in TMU–H_2O mixtures are quite large, extensive solvation of the salts is indicated. The Stokes radii though are smaller in the aqueous solutions than in pure TMU, indicating less solvation in aqueous solutions than TMU.

The values of λ^0 and r_s (Tables V and VI) show a reasonable trend for the various salts in the TMU–water mixtures. The limiting ionic conductances (Table V) of all of the ions evaluated depend on the reliability of Bu_4NI salt as a reference electrolyte.

In general, the results show that λ^0 increases with an increase in crystallographic radius, Na < K < Rb < Cs for cations. It is interesting to note that the anomalous behavior of sodium salts in TMU (*5*) was not observed in TMU–water mixtures. It is possible that, while the sodium ion may be solvated to a greater extent through nitrogen in pure TMU, it is solvated through oxygen in TMU–water mixtures.

As shown in Table IV, the $\sigma\Lambda$ values vary from 0.003 to 0.010. This indicates the accuracy of the results. The experimental results are in excellent agreement with those calculated (Table III).

From the large difference between the equivalent conductances for the TMU–H_2O mixtures and the pure solvents, TMU and water, the existence of strong interactions can be inferred. These are most likely hydrogen bonding in nature.

In conclusion, the present results of conductance studies suggest that ionic transport in TMU–H_2O mixtures is strongly governed by the ion–solvent dipole interaction. The ionic solvation determines the effective ionic radii and the mobilities of the ions in the TMU–H_2O mixtures. The Stokes radii calculated indicate the solvation of the salts in TMU–H_2O.

Since a wide range of solvation behavior has been found to exist in the TMU–water mixtures, this medium will be a convenient, useful, and interesting one for those chemical reactions whose rates are enhanced by solvation of particular ionic species in solution.

Glossary

TMU	tetramethylurea
Ω	ohm
Λ	equivalent conductance
λ	ionic conductance
η	viscosity
r_x	crystallographic radii
r_s	Stokes radii
σ	standard deviation

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Received for review October 14, 1980. Revised manuscript received April 21, 1981. Accepted June 5, 1981. We thank the Research and Publication Board of the University of the West Indies, St. Augustine, for financial support of this project.