Solvation and Chemical Equilibrium Studies of Alkali Metal Salts in 1,1,3,3-Tetramethylurea

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Abstract: The solvation behavior of a series of alkali metal salts in a relatively new, aprotic solvent of low dielectric constant, 1,1,3,3-tetramethylurea (TMU), was studied by conductance techniques. All conductance data were evaluated both by the procedures of Fuoss and Shedlovsky and by the Fuoss–Onsager equations for associated and unassociated electrolytes. Alkali metal tetraphenylborides, sodium and potassium perchlorate, and potassium thiocyanate are unassociated electrolytes in tetramethylurea; rubidium and cesium perchlorate, lithium and sodium bromide and nitrate, and sodium thiocyanate are associated electrolytes in TMU. Higher limiting equivalent conductivities for sodium salts than for corresponding potassium salts revealed an anomalous solvation behavior of the sodium ion in TMU. Continually increasing conductances of alkali metal iodide-TMU solutions indicated slow attainment of equilibrium in these solutions. Ionic limiting equivalent conductivities in TMU were obtained indirectly by using triisoamylbutylammonium tetraphenylboride as a reference electrolyte. Stokes radii, much larger than crystallographic radii, indicated that the salts studied were extensively solvated in tetramethylurea.

Increasing use of nonaqueous solvents as media for organic and inorganic reactions has led to numerous investigations of solvent effects on the rates and mechanisms of reactions in solution. The addition of certain N,N-disubstituted amides and sulfur oxides [among them dimethylformamide (DMF), dimethylacetamide (DMA), tetramethylurea (TMU), and dimethyl sulfoxide (DMSO)] significantly increased the rates of alkylation of sodiomalonic esters with alkyl halides in benzene.[1] The unusual rate acceleration was attributed to specific solvation of the sodium ion by these solvents. The investigation by Lüttringhaus and Dirkson of tetramethylurea as a solvent for numerous organic reactions revealed that TMU provides "remarkable solvation of alkali metal ions."[2]

Greater understanding of reaction rates and mechanisms in nonaqueous media can be gained from fundamental electrochemical investigations which elucidate the behavior of electrolytes in solution. Conductance studies reveal the nature of ion–solvent interactions directly from experimental measurements. Although there have been a number of conductance investigations in polar, aprotic solvents such as DMF,[3,4] DMA,[5] and DMSO[6] there have been no conductance studies reported for TMU. Tetramethylurea promises to be of considerable importance as a reaction medium since it has a wide liquid range of −1–176.5° and since it is an excellent solvent for many organic, inorganic, and polymeric compounds. Therefore, a conductance investigation of a series of alkali metal salts was undertaken in order to study the behavior of electrolytes in this solvent.

Experimental Section

Solvent Purification. Tetramethylurea (TMU), obtained from Ott Chemical Co., was purified by vacuum distillation at about 1 mm. Approximately 2.5 l. of solvent was refluxed over granular barium oxide at 38–40° for 14–16 hr; about 2 l. of solvent was collected over a period of 30–40 hr. Purified solvent was stored and dispensed under nitrogen. The specific conductivity of freshly distilled TMU was 2×10^{-8} ohm^{-1} cm^{-1}; the conductivity increased to about 8×10^{-8} ohm^{-1} cm^{-1} after storage under nitrogen for a period of 3–4 weeks. Karl Fischer titrations, standardized with water in methanol solutions (Sargent Chemical Co.), indicated that unpurified TMU had a water content of 0.77%. Purified TMU which had been stored for several weeks contained less than 0.01%. The intense water absorptions from 3575 to 3400 cm^{-1} in the infrared spectrum of unpurified TMU were absent in the spectrum of purified solvent.

Determination of Physical Properties. With 10-cm^3 modified Ostwald–Sprengel-type pycnometers a density of 0.9619 ± 0.0001 g/ml was determined for TMU at 25°. A viscosity of 1.401 ± 0.003 cP was determined at 25° with sizes 25 and 50 Cannon Fenske viscometers (manufactured and calibrated by Cannon Instrument Co.). With viscometers of the chosen sizes flow times were sufficiently large that kinetic energy corrections were assumed to be negligible. A Sargent S-84805 thermostatic bath assembly filled with water and maintained at 25.00 ± 0.01° was used in the density and viscosity determinations. A dielectric constant of 23.45 ± 0.06 (1 MHz) was determined for TMU at 25° by previously described techniques.[7]

Salt Preparation and Purification. Triisoamylbutylammonium tetraphenylboride and triisoamylbutylammonium iodide were synthesized and purified by the procedures of Coplan and Fuoss.[8] Upon repeated recrystallizations constant melting points of 122.0–122.5° for the iodide and 272–275° for the tetraphenylboride compared favorably with literature values of 119° and 274–275°, respectively.[8] Triisoamylbutylammonium perchlorate was prepared by the addition of an approximately 1.5 *M* solution of perchloric acid to a methanol–water mixture of triisoamylbutylammonium iodide. After repeated recrystallizations from water it had a melting point of 102–103° as compared with a melting point of 94–96° reported for the compound prepared by reacting silver perchlorate with triisoamylbutylammonium iodide.[9] All melting points were taken with a Mel-Temp capillary melting point apparatus (Laboratory Devices). Potassium, rubidium, and cesium tetraphenylborides were prepared by mixing aqueous equimolar solutions of potassium chloride (Baker Analyzed reagent), rubidium or cesium iodide (Alfa Inorganics, Optronic grade), and sodium tetraphenylboride (Baker Analyzed reagent). The potassium, rubidium, and cesium tetraphenylborides were dissolved in purified tetramethyl-

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urea and reprecipitated with water. Rubidium and cesium perchlorates were prepared by the addition of an approximately 1.5 *M* perchloric acid solution to an aqueous solution of rubidium or cesium bromide (Alfa Inorganics, Optronic grade). The rubidium and cesium perchlorates were washed well with water to remove excess acid. Sodium bromide (Baker Analyzed reagent) and sodium perchlorate (Fisher reagent) were recrystallized from an acetone–ether mixture. Lithium bromide (Alfa Inorganics, Optronic grade), sodium tetraphenylboride, potassium thiocyanate, potassium perchlorate, lithium nitrate, and sodium nitrate (Baker Analyzed reagent) were used without further purification. Conductivity water was used in the salt preparations and purifications. All salts were finely ground and dried *in vacuo* prior to use.

Apparatus. Resistances were measured at 2000 Hz on a Model 4666 Leeds and Northrup Dyke-Jones bridge. The bridge input signal was obtained from a Hewlett-Packard Model 200-C oscillator. The bridge balance was determined with a General Radio Co. Model 1232-A tuned amplifier and null detector. Periodic resistance measurements made also at 500 and 1000 Hz revealed that the resistances were frequency independent. Series resistances for solvent and dilute solutions were calculated from measured parallel resistances shunted with 30,000 ohms. For moderately dilute solutions, measured series resistances were found to be the same as series resistances calculated from measured parallel resistances. A Sargent S-84805 thermostatic bath assembly equipped with a Lauda thermoregulator and filled with light mineral oil was maintained at a constant temperature of 25.00 ± 0.02°.

Procedures. The conductance cells of 300-ml capacity were of the flask design of Daggett, Bair, and Kraus.[10] The electrodes, about 1.8 cm in diameter and approximately 0.5 cm apart, were lightly platinized (6 C/cm^2) according to the procedures of Jones and Bollinger.[11] Using the method of Lind, Zwolenik, and Fuoss[12] the cell constants were obtained from three independent sets of measurements. Twelve aqueous potassium chloride solutions ranging in concentration from 1.4×10^{-4} to 1.4×10^{-3} *M* were used in the determination of each cell constant. The cell constants, 0.1837 ± 0.0001 and 0.2110 ± 0.0001 cm^{-1}, were independent of concentration in the range considered. Conductivity water of specific conductivity 6×10^{-7} ohm^{-1} cm^{-1} was obtained by passing laboratory distilled water through a Deeminizer ion-exchange resin (Crystalab Inc.).

Approximately 100 ml of TMU was dispensed and weighed into the conductance cells which then were immersed in the oil bath and brought to temperature equilibrium. Two separate stock solutions were prepared by weight. In determining the molar concentrations of the salt solutions the assumption was made that the densities of the solutions were the same as that of the solvent. All solution preparations were performed under normal laboratory conditions since TMU and most salts used were not appreciably hygroscopic. Brief exposures to the atmosphere had a negligible effect on the solvent conductivity. After measuring the resistance of the solvent successive amounts of stock solution were dispensed into each cell from a weight buret. Thus there were two independent sets of measurements for each salt studied. All weighings were corrected to vacuum. In all conductance experiments a solvent correction was applied to the solution resistances by subtracting the specific conductivity of the solvent from the conductivity of the solution. Generally the specific conductance of the solvent was well below 1% of the conductivity of the most dilute solution. Above the concentration $C_{\max}$, in which $C_{\max} = 3.2 \times 10^{-7}D^3$, or above the concentration at which $\kappa a = 0.2$ the laws of dilute solutions for electrolytes no longer are valid;[13] therefore, the highest concentration used was below these upper limits. Resistance readings were taken on freshly shaken solvent and solutions in order to minimize the Soret effect[14] and the "shaking effects."[15] Constant resistance readings were obtained readily for all TMU solutions except those containing sodium salts. Generally the resistances of the TMU salt solutions remained constant overnight.

Results and Discussion

The molar concentrations and the equivalent conductivities of the salts studied in tetramethylurea are presented in Table I.

All conductance data were evaluated both by the procedures of Fuoss and Shedlovsky[16] and by the Fuoss–Onsager equations[13,17] for associated and unassociated electrolytes. All calculations were performed on an IBM 360/65 computer by using least-squares analyses to evaluate the conductance parameters.

The Shedlovsky treatments yielded values of Λ_0 and K_A from least-squares analyses of the functions Λ_0' *vs.* C and y *vs.* x. The symbols have their usual meaning

$$\Lambda_0' = (\Lambda + \beta C^{1/2})/(1 - \alpha C^{1/2})$$

$$1/\Lambda S_z = 1/\Lambda_0 + C\Lambda S_z f^2 K_A/\Lambda_0^2$$

in which $x = C\Lambda S_z f^2$ and $y = 1/\Lambda S_z$.

All salts were considered both as unassociated and as associated electrolytes in the Fuoss–Onsager evaluation of the conductance data. For unassociated electrolytes the conductance is expressed by eq 1 and for associated electrolytes by eq 2.

$$\Lambda = \Lambda_0 - SC^{1/2} + EC \log C + JC \qquad (1)$$

$$\Lambda = \Lambda_0 - S(C\gamma)^{1/2} + EC\gamma \log C\gamma + JC\gamma - K_A C\gamma \Lambda f^2 \qquad (2)$$

The symbols in eq 1 and 2 have their usual meaning: $S = \alpha\Lambda_0 + \beta$, $E = E_1\Lambda_0 - E_2$. The coefficients α, β, E_1, and E_2, which are functions of the physical properties of the solvent, are 1.403, 70.42, 19.82, and 145.7, respectively, for TMU at 25°. The viscosity term $F\Lambda_0C$ omitted from eq 1 and 2 was considered negligible since F was assumed to be small for the salts studied. The values of Λ_0 and K_A would remain unchanged and the value of a would be slightly higher if this viscosity correction associated with the J term were included. The initial Λ_0 values used in the Fuoss–Onsager equations were those obtained from the Shedlovsky y–x least-squares analyses of original data. The conductance values obtained from the Fuoss–Onsager equations are listed in Table II for each of the independent sets of measurements. All conductance values listed were obtained using values of Λ weighted by C or $C\gamma$. For all salts the use of weighted data resulted in a better fit to the equations as indicated by the smaller standard deviation $\sigma\Lambda$ for the individual conductivity values. The tetraphenylboride salts, sodium perchlorate, potassium perchlorate, and potassium thiocyanate are unassociated in TMU. Evaluation of these salts by eq 2 led to negative association constants and to degrees of dissociation greater than unity. Results for rubidium perchlorate and cesium perchlorate as both unassociated and associated electrolytes are presented in Table II so that a comparison between the two methods of evaluation can be made. Hawes and Kay have indicated[18] that if an electrolyte is associated and if it is evaluated as an unassociated electrolyte, then a low a value and poor precision will result. If the electrolyte is associated and if it is evaluated as

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Table I. Equivalent Conductivities of Salts in Tetramethylurea at 25° [a,b]

$C \times 10^4$	Λ	$C \times 10^4$	Λ	$C \times 10^4$	Λ	$C \times 10^4$	Λ	$C \times 10^4$	Λ		
$NaBPh_4$		$KBPh_4$		$RbBPh_4$		$CsBPh_4$		TABBPh$_4$			
a		a		a		a		a			
0.1916	28.82	0.2185	28.49	0.2817	28.69	0.2236	29.64	0.4046	26.72		
1.056	28.22	0.4812	28.21	0.6428	28.38	0.4932	29.37	1.422	26.15		
1.959	27.82	1.820	27.44	2.984	27.26	0.9077	29.08	2.616	25.70		
3.400	27.35	3.173	26.97	6.323	26.48	2.028	28.55	4.495	25.18		
5.917	26.75	5.255	26.46	11.15	25.75	7.125	27.25	7.028	24.69		
9.111	26.21	8.016	25.96	15.55	25.25	10.55	26.72	9.296	24.35		
11.62	25.87	14.86	25.09	17.98	25.03	14.32	26.26	11.00	24.12		
b		b		b		b		b			
0.6636	28.42	0.2570	28.52	0.9939	28.18	0.5111	29.49	0.3518	26.68		
1.220	28.10	0.5327	28.29	2.348	27.52	1.081	29.09	0.7974	26.40		
2.421	27.62	1.970	27.47	4.794	26.81	2.352	28.50	2.670	25.62		
4.280	27.07	6.996	26.14	8.680	26.10	4.682	27.82	4.505	25.15		
7.111	26.48	10.30	25.62	13.57	25.47	7.402	27.26	10.09	24.20		
10.65	25.95	13.47	25.24	17.73	25.05	10.52	26.79	12.27	23.93		
11.92	25.79	15.72	25.00	23.69	24.57	13.43	26.41	13.75	23.77		
$NaClO_4$		$KClO_4$		$RbClO_4$		$CsClO_4$		TABClO$_4$			
a		a		a		a		a			
1.103	42.94	0.9392	42.47	0.8163	43.11	0.8810	43.78	0.1464	41.83		
3.101	41.91	1.711	42.02	1.550	42.59	1.794	43.21	0.5603	41.32		
7.278	40.57	3.198	41.32	3.613	41.54	2.404	42.87	1.096	40.84		
10.02	39.95	5.784	40.44	6.339	40.58	4.559	41.94	3.646	39.42		
14.20	39.17	11.71	39.06	14.45	38.75	8.151	40.80	5.492	38.68		
21.73	38.10	18.80	37.92	19.22	38.00	11.58	39.98	8.094	37.85		
30.10	37.20	23.26	37.32	21.82	37.64	15.27	39.25	11.79	36.91		
b		b		b		b		b			
1.243	42.89	0.8643	42.52	1.514	42.66	0.8544	43.84	0.5879	41.31		
3.240	41.89	1.554	42.14	2.432	42.15	1.483	43.43	1.101	40.85		
4.968	41.26	3.038	41.43	7.230	40.38	2.322	42.94	2.110	40.17		
7.578	40.52	5.089	40.71	16.48	38.44	4.876	41.84	3.844	39.32		
10.26	39.93	9.876	39.49	21.10	37.77	9.449	40.48	5.975	38.50		
14.39	39.17	15.13	38.52	28.70	36.85	13.71	39.55	8.691	37.66		
28.88	37.34	19.84	37.80	30.98	36.60	18.63	38.69	12.47	36.74		
NaSCN		KSCN		LiBr		NaBr		$LiNO_3$		$NaNO_3$	
a		a		a		a		a		a	
1.763	46.46	6.569	44.67	1.260	42.66	0.7160	44.26	2.303	43.36	2.126	39.72
4.368	44.81	9.686	43.75	2.845	41.76	2.418	41.58	5.101	41.16	3.850	36.18
5.641	44.13	13.15	42.95	4.379	41.08	6.175	37.94	7.650	39.62	5.751	33.45
7.027	43.46	16.63	42.22	5.027	40.83	10.67	35.09	10.42	38.25	7.582	31.45
9.642	42.38	21.08	41.47	7.997	39.88	16.20	32.63	14.34	36.67	9.407	29.88
13.79	41.02	29.26	40.35	14.29	38.40	22.06	30.69	18.46	35.32	12.03	28.05
20.10	39.28	38.50	39.31	20.24	37.35	27.67	29.23	23.54	33.95	14.28	26.78
b		b		b		b		b		b	
3.455	45.47	4.575	45.41	2.375	42.12	0.4822	44.58	3.249	42.58	1.870	40.54
6.782	43.72	7.480	44.38	5.028	40.96	2.385	41.50	5.535	40.90	3.780	36.38
8.776	42.85	10.33	43.60	6.972	40.28	6.007	38.01	9.618	38.67	5.376	34.01
10.86	42.07	13.37	42.87	8.684	39.78	10.77	35.02	13.26	37.11	7.478	31.63
14.95	40.76	17.35	42.10	12.21	38.93	15.90	32.74	18.59	35.33	9.650	29.74
22.40	38.91	25.52	40.84	16.31	38.11	21.77	30.78	25.69	33.47	11.93	28.16
30.98	37.22	32.53	39.95	29.64	36.17	29.69	28.77	35.80	31.46	14.22	26.85

[a] a and b designate independent series of measurements. [b] TAB = triisoamylbutylammonium, BPh_4 = tetraphenylboride.

associated, then a high *a* value and a positive value of K_A of greater magnitude than the standard deviation result. These trends are evident from the data presented for the two perchlorate salts. Triisoamylbutylammonium perchlorate, sodium thiocyanate, the bromides, and the nitrates are associated electrolytes in TMU. The two independent sets of measurements for each salt were combined and treated as one set of data. The averaged conductance values for all salts are presented in Table III.

Typical $\Lambda_0'-C$ plots and $y-x$ plots are indicated in Figures 1 and 2. The Shedlovsky function Λ_0' is almost linear in concentration for unassociated electrolytes.[19] Both Shedlovsky treatments yielded the same values for the limiting equivalent conductivities of the tetraphenylboride salts. In the $\Lambda_0'-C$ plots (Figure 1) the increasing curvature within the salt series NaBr > NaSCN > $NaClO_4$ indicates increasing association within the series; in the $y-x$ plots (Figure 2) the increasing slope of the straight line indicates increasing association. From the $y-x$ treatment of data it is to be expected that unreliable association constants will be obtained for those salts having K_A values less than 100.[20] Within the associated electrolyte series NaSCN < $LiNO_3$ < NaBr < $NaNO_3$ the $y-x$ method of analysis resulted in K_A values of 118, 232, 388, and 1220, respectively. As indicated in Table III the Fuoss–Onsager evaluation of data gave association constant values of 67.2, 167, 316, and 1120 for the same salt series. The relative differences between K_A

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(19) Reference 13, p 197.

(20) Reference 13, p 232.

Table II. Conductance Values of the Fuoss-Onsager Equation for Salts in Tetramethylurea[a]

Salt	$\sigma\Lambda$	Λ_0	a_J	K_A	S	E	J
$NaBPh_4$	0.003	29.40 ± 0.009	6.35 ± 0.06		111.7	437.1	1516
	0.002	29.36 ± 0.004	6.33 ± 0.03		111.6	436.3	1511
$KBPh_4$	0.004	28.96 ± 0.009	6.31 ± 0.05		111.1	428.3	1488
	0.006	29.04 ± 0.020	5.97 ± 0.10		111.1	429.8	1438
$RbBPh_4$	0.006	29.24 ± 0.016	6.19 ± 0.07		111.4	433.7	1482
	0.008	29.29 ± 0.020	5.95 ± 0.07		111.5	434.8	1445
$CsBPh_4$	0.002	30.19 ± 0.006	6.19 ± 0.04		112.8	452.6	1528
	0.005	30.27 ± 0.012	6.06 ± 0.07		112.9	454.2	1512
$TABBPh_4$	0.003	27.45 ± 0.008	6.49 ± 0.06		108.9	398.3	1439
	0.004	27.40 ± 0.012	6.47 ± 0.07		108.9	397.4	1434
$NaClO_4$	0.007	44.50 ± 0.017	4.67 ± 0.03		132.9	736.2	1859
	0.007	44.53 ± 0.015	4.65 ± 0.03		132.9	736.8	1854
$KClO_4$	0.009	43.93 ± 0.022	4.59 ± 0.05		132.1	724.9	1814
	0.012	43.97 ± 0.028	4.63 ± 0.07		132.1	725.7	1828
$RbClO_4$	0.008	44.34 ± 0.024	4.17 ± 0.05		132.6	733.0	1718
	0.007	44.39 ± 0.021	4.14 ± 0.03		132.7	734.0	1713
	0.003	44.44 ± 0.017	5.22 ± 0.19	15.9 ± 2.6	132.8	735.0	1996
	0.006	44.46 ± 0.039	4.46 ± 0.20	6.2 ± 3.5	132.8	735.3	1803
$CsClO_4$	0.005	45.18 ± 0.013	3.81 ± 0.04		133.8	749.7	1647
	0.006	45.20 ± 0.016	3.81 ± 0.04		133.8	750.1	1649
	0.004	45.23 ± 0.023	4.46 ± 0.37	9.3 ± 4.7	133.9	750.6	1833
	0.003	45.26 ± 0.015	4.47 ± 0.19	10.2 ± 2.5	133.9	751.2	1837
$TABClO_4$	0.003	42.42 ± 0.016	4.54 ± 0.35	27.0 ± 4.2	129.9	694.9	1741
	0.003	42.45 ± 0.016	5.37 ± 0.39	38.3 ± 4.3	130.0	695.7	1945
NaSCN	0.010	48.96 ± 0.067	2.91 ± 0.39	51.2 ± 7.9	139.1	824.6	1479
	0.008	49.20 ± 0.064	3.60 ± 0.23	64.8 ± 5.0	139.5	829.4	1725
KSCN	0.006	48.76 ± 0.015	3.77 ± 0.02		138.8	820.7	1765
	0.008	48.77 ± 0.021	3.77 ± 0.03		138.9	820.8	1766
LiBr	0.003	44.36 ± 0.017	4.26 ± 0.18	15.0 ± 2.6	132.7	733.5	1746
	0.006	44.50 ± 0.035	4.30 ± 0.19	16.1 ± 3.4	132.9	736.1	1760
NaBr	0.005	46.32 ± 0.034	4.96 ± 0.18	325 ± 4	135.4	772.3	2011
	0.006	46.08 ± 0.039	4.40 ± 0.17	307 ± 4	135.1	767.6	1849
$LiNO_3$	0.004	46.98 ± 0.031	4.14 ± 0.18	167 ± 3	136.3	785.3	1812
	0.003	47.01 ± 0.021	3.97 ± 0.07	164 ± 2	136.4	785.9	1762
$NaNO_3$	0.005	48.36 ± 0.061	7.43 ± 0.68	1120 ± 10	138.3	812.6	2723
	0.007	48.57 ± 0.079	7.39 ± 0.90	1130 ± 20	138.6	816.8	2726

[a] No viscosity correction applied.

values decrease as the association constant values increase. Values of the limiting equivalent conductivity for the perchlorates and tetraphenylborides determined from the Shedlovsky y-x functions were about 0.4% lower than those listed in Table III; the Shedlovsky Λ_0 values for the nitrates were about 0.6% higher than those calculated from the Fuoss-Onsager equation for associated electrolytes.

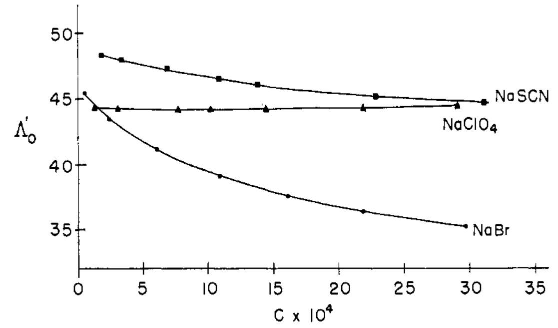

Figure 1. Shedlovsky Λ_0'-C plots for NaBr, NaSCN, and $NaClO_4$ in tetramethylurea.

Correlations between the properties of the electrolyte and solvent and the extent of association are limited. The association behavior of alkali metal salts in acetonitrile was found to depend upon the degree of solvation of the cations and the size of the anions.[21] As the crystallographic radii of the cations increased there was a slight increase in the association of the alkali metal perchlorates. The association constant decreased as the crystallographic radii of the anions increased. Table III reveals that, in general, these are the trends observed for association behavior of electrolytes in tetramethylurea.

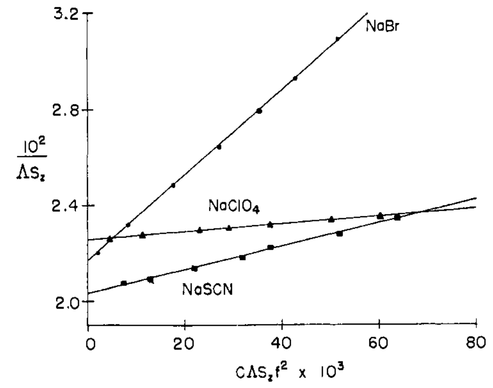

Figure 2. Shedlovsky y-x plots for NaBr, NaSCN, and $NaClO_4$ in tetramethylurea.

Since the alkali metal iodides are very soluble in tetramethylurea, conductance investigations of these salts were attempted in order to determine their be-

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[21] R. L. Kay, B. J. Hales, and G. P. Cunningham, *J. Phys. Chem.*, 71, 3925 (1967).

Table III. Average Conductance Values of the Fuoss-Onsager Equations for Salts in Tetramethylurea

Salt	Λ_0	a_J	K_A
$NaBPh_4$	29.39	6.31	
$KBPh_4$	28.99	6.17	
$RbBPh_4$	29.27	6.01	
$CsBPh_4$	30.24	6.07	
$TABBPh_4$	27.45	6.33	
$NaClO_4$	44.52	4.65	
$KClO_4$	43.96	4.57	
$RbClO_4$	44.42	4.57	7.2
$CsClO_4$	45.24	4.49	10.2
$TABClO_4$	42.43	4.86	31.6
NaSCN	49.12	3.79	67.2
KSCN	48.77	3.77	
LiBr	44.44	4.46	18.0
NaBr	46.20	4.67	316
$LiNO_3$	47.00	4.14	167
$NaNO_3$	48.46	7.31	1120

Table IV. Ionic Limiting Equivalent Conductivities in Tetramethylurea at 25° [a]

Cation	λ_0^+	Anion	λ_0^-
Li^+	14.13	SCN^-	33.44
Na^+	15.74	NO_3^-	32.80
K^+	15.26	Br^-	30.38
Rb^+	15.63	ClO_4^-	28.71
Cs^+	16.52	BPh_4^-	13.72
TAB^+	13.72		

[a] $TABBPh_4$ used as reference electrolyte.

havior in solution. However, the conductance of freshly prepared iodide solutions initially decreased and then continually increased with time as the solutions aged. The increase in conductance for a 1–48-hr period was accompanied by a solution color change from colorless through light yellow to an intense dark yellow. Similar conductance–time effects observed for the hydrogen halides in acetonitrile have been attributed to slow attainment of ionization equilibrium due to solvent–solute interactions.[22] Conductance–time effects observed for solutions of iodine and iodine monohalides in acetonitrile[23] and of iodine in pyridine[24] also have been attributed to solvent–solute interactions. Initial reactions between solvent and solute produce nonconducting addition compounds which slowly form conducting ionic complexes by charge-transfer processes. Since tetramethylurea forms addition compounds with hydrogen halides[2] and charge-transfer complexes with iodine,[25] simple electrolyte behavior is not to be expected for alkali metal iodides in TMU. Kinetic investigations which should be possible for iodide salts in tetramethylurea by conductance techniques are being considered in this laboratory.

Ionic limiting equivalent conductivities were obtained indirectly by using triisoamylbutylammonium tetraphenylboride as a reference electrolyte. The assumption was made that the limiting equivalent conductivity of the triisoamylbutylammonium ion, shown by Coplan and Fuoss to be equal to that of the tetraphenylboride ion in methanol,[8] is the same as that of the tetraphenylboride ion in tetramethylurea. Considering $\lambda_0(TAB^+) = \lambda_0(BPh_4^-)$ in TMU, the set of ionic limiting equivalent conductivities presented in Table IV was obtained. Addition of cationic and anionic limiting equivalent conductivities from Table IV, which reproduces any salt limiting equivalent conductivity in Table III within 0.2%, indicates the reliability of the data. The purpose of the present investigation is the determination of relative solvation effects within an alkali metal salt series; therefore, the validity of the use of $TABBPh_4$ as a reference electrolyte in TMU is not of primary concern in this study. Evaluation of the validity of using any reference electrolyte in a particular solvent requires a direct measurement of transference numbers in that solvent. Although there have been an increasing number of accurate conductance studies in many nonaqueous solvents, there have been very few transference number measurements in these solvents. Transference numbers have been determined in formamide[26] and in several substituted amides (methylformamide,[27] dimethylformamide,[3] and methylacetamide[28]), but there have been few correlations between these investigations and conductance studies in these solvents. To determine directly ionic limiting equivalent conductivities in TMU and to assess the validity of the assumption $\lambda_0(TAB^+) = \lambda_0(BPh_4^-)$ in TMU, transference number measurements will be considered in this laboratory.

As expected, the limiting equivalent conductivities of the cations increase as the crystallographic radii increase. As the crystallographic radii increase the effective size of the cations decreases owing to decreasing solvation. The high limiting equivalent conductivity of the sodium ion in TMU is to be noted. The same anomalous behavior of the sodium ion has been observed in conductance studies in dimethylacetamide (D = 37.78),[5] dimethylpropionamide (D = 33.1),[29] and dimethylbutyramide (D = 28.0).[30] In these solvents the sodium salts had a Λ_0 value about 0.5 unit higher than that for the corresponding potassium salts. This same difference has been found between sodium and potassium salts in TMU. The assumption was made[30] that owing to the size and the structure of the solvent molecules, steric factors may contribute significantly to the anomalous solvation behavior of the sodium ion in the three substituted amides. If a general structure $R—C(=O)—N(CH_3)_2$ is used to represent the amides and tetramethylurea, it is seen that when R = CH_3, C_3H_7, C_4H_9, and $N(CH_3)_2$ the unusual solvation behavior of the sodium ion is observed. In these media solvation probably occurs through the oxygen atom, although nitrogen may participate to a slight degree. Possibly, owing to the crystallographic size and the charge density of the sodium ion, solvation through nitrogen occurs to a greater extent for this ion than for other alkali metal ions studied. Sodium ion solvated through nitrogen may be of smaller effective size and therefore more highly conducting than sodium ion solvated through oxygen. Extending this amide series, dimethylformamide (R = H) can form a

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(22) (a) G. J. Janz and S. S. Danyluk, *J. Amer. Chem. Soc.*, **81**, 3846 (1959); (b) *ibid.*, **81**, 3850 (1959); (c) *ibid.*, **81**, 3854 (1959).

(23) (a) R. E. Buckley and J. F. Mills, *ibid.*, **76**, 4845 (1954); (b) A. I. Popov and N. E. Skelly, *ibid.*, **77**, 3722 (1955); (c) A. I. Popov and W. A. Deskin, *ibid.*, **80**, 2976 (1958).

(24) L. F. Audrieth and E. J. Birr, *ibid.*, **55**, 668 (1933).

(25) R. P. Lang, *J. Phys. Chem.*, **72**, 2129 (1968).

(26) (a) J. M. Notley and M. Spiro, *ibid.*, **70**, 1502 (1966); (b) R. Gopal and D. N. Bhatnagar, *ibid.*, **68**, 3892 (1964).

(27) R. Gopal and D. N. Bhatnagar, *ibid.*, **70**, 3007 (1966).

(28) R. Gopal and D. N. Bhatnagar, *ibid.*, **69**, 2382 (1965).

(29) E. D. Wilhoit and P. G. Sears, *Trans. Ky. Acad. Sci.*, **17**, 123 (1956).

(30) H. M. Smiley and P. G. Sears, *ibid.*, **19**, 62 (1958).

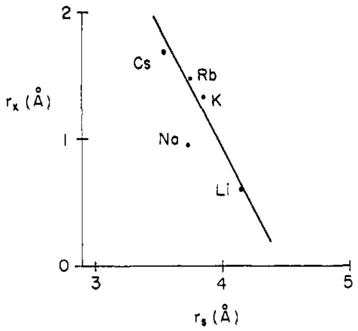

Figure 3. Crystallographic radii *vs.* Stokes radii of alkali metal ions in tetramethylurea.

larger solvation sphere around the sodium ion since the oxygen atoms of the solvent molecules are more accessible to the sodium ions. In DMF (D = 36.71) there is no anomalous behavior of the sodium ion; potassium salts are more conducting than corresponding sodium salts.[3,4] Reversals in the order of the limiting equivalent conductivities of lithium and sodium salts have been noted in the polar, aprotic solvents hydrocyanic acid[31] and sulfolane.[32]

The order of relative anionic limiting equivalent conductivities which is to be expected[33] in TMU is the same as the order found in other polar nonaqueous solvents such as dimethylacetamide,[5] dimethylformamide,[3,4] sulfolane,[32] acetone,[34] nitrobenzene,[35] and nitromethane.[36]

Many procedures, summarized by Stern and Amis,[37] have been developed for the determination of ion-size parameters. A size parameter for a salt in solution can be obtained by adding the Stokes radii of cation and anion comprising the salt. Therefore, Stokes radii were calculated for the ions from

$$r_s = 0.820z/\eta_0\lambda_0$$

in which r_s is the Stokes ionic radius, z is the absolute magnitude of the charge of the ion, η_0 is the viscosity of TMU in poise, and λ_0 is the ionic limiting equivalent conductivity. Figure 3 indicates that, with the exception of the sodium ion, in TMU the Stokes radii of the alkali metal cations are a linear function of the crystallographic radii of these ions. Data from Tables III and V indicate that for all salts (except $NaNO_3$ which is very associated and which has an accompanying large uncertainty in the Fuoss–Onsager a value) the sum of the Stokes cationic and anionic radii is greater than the Fuoss–Onsager ion-size parameter a. Table V reveals that the sum of the Stokes ionic radii of any alkali metal salt is much greater than the sum of its crystallographic radii. Since the Stokes radii of salts in TMU are quite large, extensive solvation of the salts is indicated.

Table V. Crystallographic Radii (r_x) and Stokes Radii (r_s) of Ions in Tetramethylurea

	r_x, Å	r_s, Å
Li^+	0.60[a]	4.14
Na^+	0.95[a]	3.72
K^+	1.33[a]	3.84
Rb^+	1.48[a]	3.74
Cs^+	1.69[a]	3.54
TAB^+		4.27
SCN^-		1.75
NO_3^-	2.64[b]	1.78
Br^-	1.95[a]	1.93
ClO_4^-	2.92[b]	2.04
BPh_4^-		4.27

[a] L. Pauling, "Nature of the Chemical Bond," 2nd ed, Cornell University Press, Ithaca, N. Y., 1948. [b] E. R. Nightingale, Jr., *J. Phys. Chem.*, 63, 1381 (1959).

Since many electrolytes are readily soluble in tetramethylurea and since a wide range of solvation behavior has been found to exist in this solvent, TMU will be a useful solvent for those chemical reactions whose rates are enhanced by solvation of particular ionic species in solution.

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