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Effect of Salt on the Distribution of Acetic Acid between Water and Organic Solvent

Dahyabhai J. Shah[†] **and Krishna K. Tiwari***

Department of Chemical Technology, University of Bombay, Matunga, Bombay 400 019, India

Equilibrium distribution data for three important systems, water–ethyl acetate–acetic acid–sodium sulfate, water–2-ethylhexanol–acetic acid–sodium sulfate, and water–methyl ethyl ketone–acetic acid–sodium sulfate, at 30 °C are presented. Empirical correlations are obtained to represent these experimental data. With an increase in the salt concentration, the distribution coefficient of acetic acid increases, showing the "salting-out" effect. With the solvents ethyl acetate and 2-ethylhexanol the salting-out coefficient decreases with an increase in the acetic acid concentration, while with the solvent methyl ethyl ketone the salting-out coefficient increases with an increase in the acetic acid concentration. This change in salting-out coefficient with acetic acid concentration is explained on the basis of solvent solubility, salting-out of the solvent, and the solvent affinity for the acetic acid.

The distribution data for the water–acetic acid–solvent system are available in the literature for many organic solvents (*1–3*). However, very often, in practice, the aqueous streams contain salts such as sodium sulfate. The effect of salt on the distribution of acetic acid between water and an organic solvent has thus a direct engineering application.

Swabb and Mongan (*4*) have studied the salt effect in the system water–isopropyl ether–acetic acid–sodium sulfate. McAteer et al. (*5*) have studied the water–methyl isobutyl ketone–acetic acid–sulfuric acid system. The effect of lithium chloride, sodium chloride, and potassium chloride on the water–acetic acid–benzene system has been studied by Eisen and Joffe (*6*). the effect of magnesium chloride on the same system has been studied by Desai and Eisen (*7*). However, data are not available for the salt effect with such useful solvents as ethyl acetate, 2-ethylhexanol, and methyl ethyl ketone. In the present work, therefore, the effect of sodium sulfate on the distribution of acetic acid between water and each of the above-mentioned solvents was studied.

Theory

When salt is added to an aqueous solution of a nonelectrolyte, the activity coefficient of the nonelectrolyte changes. the increase in the activity coefficient is termed "salting-out" while the decrease in the activity coefficient is termed "salting-in". The above phenomena may be explained on the basis of various theories such as the hydration theory, the electrostatic theory, and the internal pressure concept.

According to the hydration theory (*8*), salting-out results owing to the effective removal of water molecules from their role as solvent. This is due to the preferential orientation of water molecules around salt ions. The number of water molecules so bound by each salt ion is called the hydration number of the ion. Although this theory has considerable success when applied to the aqueous solutions of nonpolar nonelectrolytes, it fails to explain the wide variation in the hydration numbers obtained from the salting-out effect with different nonelectrolytes.

The electrostatic theories explain the salt effects on the basis of the alteration in the dielectric constant of the solution. Debye and McAulay (*9*), Debye (*10*), and Butler (*11*) have derived equations for the activity coefficient of nonelectrolytes in dilute salt solutions. These equations predict that salting-out will occur if the dielectric constant of the nonelectrolyte solution is less than that of water, and salting-in if the reverse is true. The theories predict that the logarithm of the activity coefficient of the nonelectrolyte is a linear function of the ionic strength.

According to the internal pressure concept proposed by Tammann (*12*) and applied by McDevit and Long (*13*), the contraction in total volume upon the addition of salt to water can be thought of as a compression of the solvent. This compression makes it more difficult for the introduction of a molecule of nonelectrolyte, and this results in salting-out. An increase in total volume upon the addition of a salt would produce the counter effect known as salting-in.

Semiquantitative expressions derived on the basis of the above theories have very limited applicability. However, several empirical correlations have been found to be suitable for the prediction of the salt effect on the liquid–liquid equilibria. Setschenow (*14*) has proposed the following empirical correlation for the salt effect on the distribution of a solute between two relatively immiscible solvents:

$$\ln (X_{CA}{}^0/X_{CA}) = k_s X_{SA} \qquad (1)$$

where X_{CA} and $X_{CA}{}^0$ are the aqueous-phase solute concentrations with and without salt in equilibrium with the same solvent-phase solute concentration, respectively, and X_{SA} is the aqueous-phase salt concentration. Swabb and Mongen (*4*) and McAteer et al. (*5*) have used the above correlation to present their data.

Long and McDevit (*15*) have suggested the use of the following equation which is derived on the basis of thermodynamic considerations:

$$\ln (X_{CA}{}^0/X_{CA}) = k_s X_{SA} + k_c(X_{CA} - X_{CA}{}^0) \qquad (2)$$

This equation becomes identical with that proposed by Setschenow when either k_c or $(X_{CA} - X_{CA}{}^0)$ is negligible.

Eisen and Joffe (*6*) have shown that the following correlation proposed by Hand for a ternary system

$$\log \frac{X_{CB}}{X_{BB}} = \log A_0 + B_0 \log \frac{X_{CA}}{X_{AA}} \qquad (3)$$

can be used for quaternary systems containing salt. X_{CA} and X_{AA} are the solute and water concentrations, respectively, in the water-rich phase, while X_{CB} and X_{BB} are the solute and solvent concentrations, respectively, in the solvent-rich phase. They have expressed the constants log A_0 and B_0 as linear functions of the salt concentration:

$$\log A_0 = a + bX_{SA} \qquad (4)$$

$$B_0 = c + dX_{SA} \qquad (5)$$

where *a*, *b*, *c*, and *d* are constants which depend on the nature of the solute, the nature of the salt, and the temperature. But these are independent of the salt concentration. It has been shown that a quaternary system which obeys the above

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[†] Present Address: Shri Bhagubhai Mafatlal Polytechnic Vile Parle (W), Bombay 400 056, India.

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Table I. Equilibrium Distribution of Acetic Acid at 30 °C for the System Water (A)-Ethyl Acetate (B)-Acetic Acid (C)-Sodium Sulfate (S)

total amt of acetic acid, g		equilibrium concn (salt free basis), g/100 g					
2.5	X_{SA}	0.00	5.05	10.20	15.40	20.95	26.40
	X_{CA}	2.97	2.84	2.66	2.38	2.20	2.10
	X_{CB}	2.60	2.83	3.01	3.25	3.52	3.68
5.0	X_{SA}	0.00	5.35	11.17	16.85	22.95	
	X_{CA}	5.45	5.05	4.65	4.31	3.83	
	X_{CB}	5.20	5.55	5.88	6.33	6.77	
10.0	X_{SA}	0.00	5.83	12.50	19.20	25.80	
	X_{CA}	10.20	9.32	8.33	7.30	6.29	
	X_{CB}	10.45	11.20	11.86	12.40	13.02	
15.0	X_{SA}	0.00	7.37	15.85	23.7		
	X_{CA}	15.10	13.11	11.27	9.33		
	X_{CB}	16.60	17.40	18.10	18.60		

Table II. Equilibrium Distribution of Acetic Acid at 30 °C for the System Water (A)-2-Ethylhexanol (B)-Acetic Acid (C)-Sodium Sulfate (S)

total amt of acetic acid, g		equilibrium concn (salt free basis), g/100 g						
2.5	X_{SA}	0.00	5.19	10.43	15.80	21.14	26.90	32.40
	X_{CA}	3.30	3.20	2.97	2.78	2.65	2.51	2.28
	X_{CB}	2.02	2.15	2.38	2.55	2.75	2.90	3.11
5.0	X_{SA}	0.00	5.29	10.70	16.08	21.75	27.40	33.00
	X_{CA}	6.64	6.41	5.99	5.74	5.39	5.01	4.70
	X_{CB}	3.95	4.28	4.57	4.96	5.32	5.73	6.11
10.0	X_{SA}	0.00	5.49	11.12	16.75	22.60	28.40	34.60
	X_{CA}	13.54	12.99	12.25	11.59	10.90	10.12	9.47
	X_{CB}	7.84	8.40	9.13	9.80	10.43	11.17	11.80
15.0	X_{SA}	0.00	5.84	11.90	17.90	24.20		
	X_{CA}	20.47	19.54	18.70	17.60	16.60		
	X_{CB}	11.83	12.85	13.64	14.48	15.39		

Table III. Equilibrium Distribution of Acetic Acid at 30 °C for the System Water (A)-Methyl Ethyl Ketone (B)-Acetic Acid (C)-Sodium Sulfate (S)

total amt of acetic acid, g		equilibrium concn (salt free basis), g/100 g				
2.0	X_{SA}	0.00	5.01	10.61	22.32	33.58
	X_{CA}	1.99	1.62	1.44	1.17	0.83
	X_{CB}	2.65	2.90	3.03	3.20	3.50
3.0	X_{SA}	0.00	5.02	10.73	22.74	34.42
	X_{CA}	3.00	2.50	2.15	1.57	1.16
	X_{CB}	3.92	4.27	4.52	4.89	5.16
4.0	X_{SA}	0.00	5.25	11.32	23.83	35.55
	X_{CA}	4.17	3.32	2.81	2.05	1.49
	X_{CB}	5.16	5.74	6.05	6.56	7.07
5.0	X_{SA}	0.00	5.48	11.73	24.44	36.43
	X_{CA}	5.52	4.10	3.37	2.46	1.87
	X_{CB}	6.42	7.08	7.47	8.03	8.60

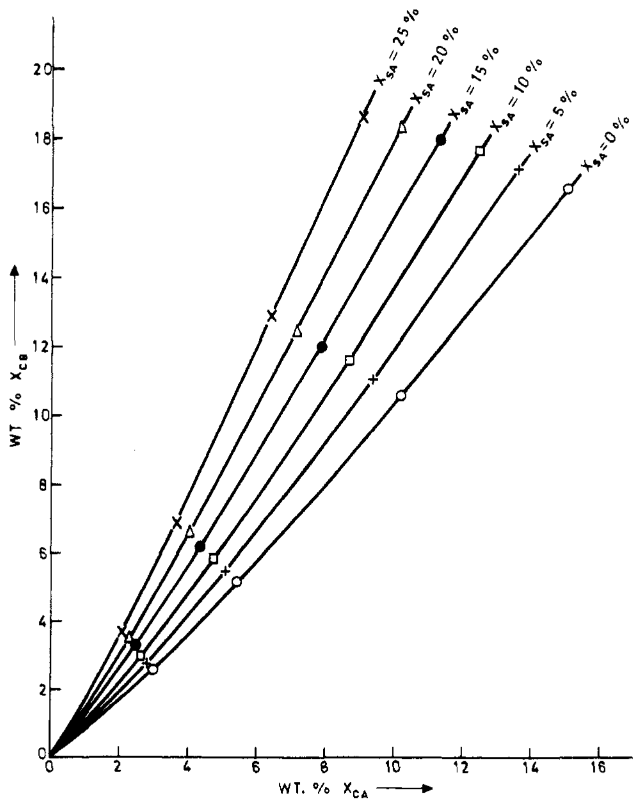

Figure 1. Equilibrium distribution curves for the system water (A)-ethyl acetate (B)-acetic acid (C)-sodium sulfate (S) at 30 °C.

equation will not obey the Setschenow equation.

Experimental Section

An aqueous solution (50 mL) containing a known amount of acetic acid, 50 mL of solvent, and a known amount of sodium sulfate were taken in a 250-mL stoppered separatory funnel kept in a constant-temperature water bath maintained at 30 °C. The mixture was shaken intermittently for 2 min after every 10 min. This procedure was performed for 2 h although the time required for the attainment of equilibrium was much less than 2 h. In addition, ~1 h was allowed for the phase separation. The phases were then withdrawn, their volumes were measured, and they were analyzed for acetic acid concentration. The analysis was done by taking 10 mL of the phase, weighing it, and titrating against a standard sodium hydroxide solution using phenolphthalein as an indicator. When ethyl acetate was employed as a solvent, standard barium hydroxide solution was used for the titration.

The solubility of sodium sulfate in the organic phase under consideration was found to be negligible as compared to the salt concentration in the aqueous phases. Therefore, the amount of sodium sulfate initially taken was assumed to be present in the aqueous phase only. The variation in acetic acid concentration leads to substantial changes in the mutual solubilities, and hence it was not possible to maintain the concentration of sodium sulfate at a constant value. However, at a fixed total acetic acid content in the system, the acetic acid concentrations in both phases are continuous functions of the salt concentration in the aqueous phase. Therefore, the equilibrium distribution data are obtained by varying the salt concentration at various fixed acetic acid contents. The range of the acetic acid concentrations covered is in the two-phase region of the ternary systems in the absence of salt. The solubility of salt in the aqueous phase was found to decrease with an increase in the acetic acid concentration. Therefore, with ethyl acetate and 2-ethylhexanol as solvents, the distribution data with 15 wt % acetic acid content could not be obtained at higher salt concentrations.

Results and Discussion

The equilibrium concentrations of acetic acid in the aqueous and organic phases obtained at various acetic acid contents are given in Tables I-III. The equilibrium concentrations of acetic acid at various fixed salt concentrations in the aqueous phase, viz., 5%, 10%, 15%, 20%, and 25% (and also 30% in the case of methyl ethyl ketone as solvent) were obtained from the above data by graphical interpolation. These are presented graphically in Figures 1-3.

When ethyl acetate was employed as a solvent, the plots of ln (X_{CA}^0/X_{CA}) vs. X_{SA} for the system water-ethyl acetate-acetic

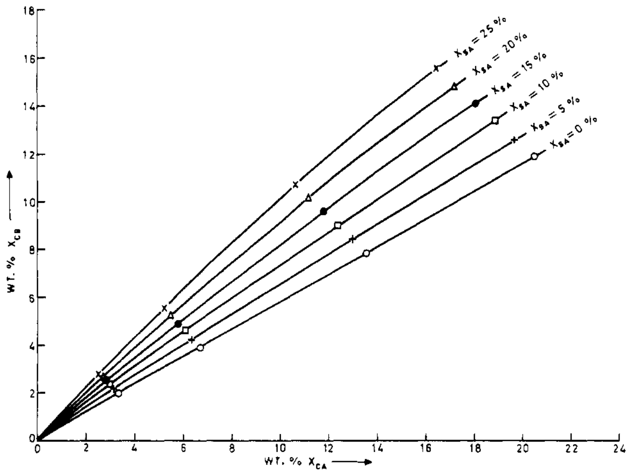

Figure 2. Equilibrium distribution curves for the system water (A)-2-ethylhexanol (B)-acetic acid (C)-sodium sulfate (S) at 30 °C.

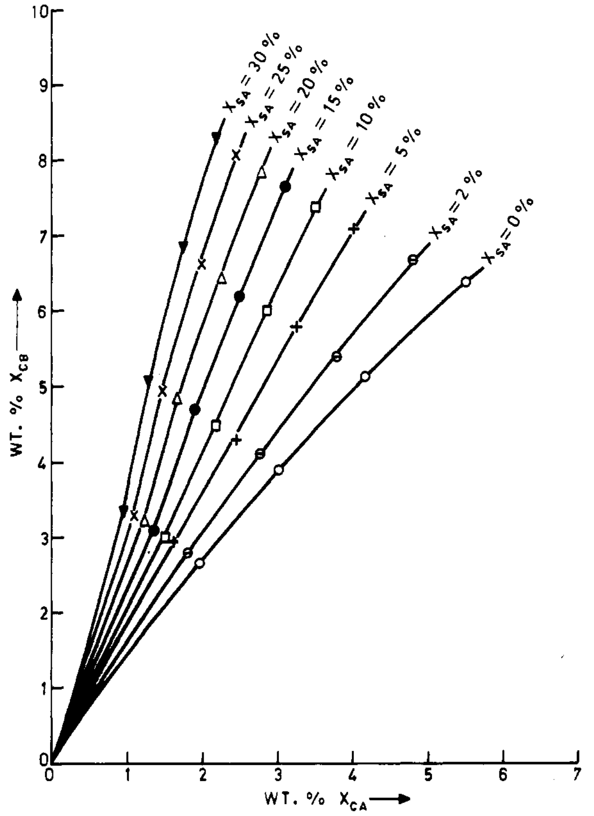

Figure 3. Equilibrium distribution curves for the system water (A)-methyl ethyl ketone (B)-acetic acid (C)-sodium sulfate (S) at 30 °C.

acid-sodium sulfate are as shown in Figure 4. The value of the slope of the line gives the salting-out coefficient. The coefficient is found to decrease slightly with an increase in $X_{CA}{}^0$ from 2.5 to 15.0. The data for this system can be represented up to 20 wt % salt concentration by the following equation:

$$\ln (X_{CA}{}^0/X_{CA}) = [2.57 \times 10^{-2} - (1.1 \times 10^{-4})X_{CA}{}^0]X_{SA} \quad (6)$$

Similarly for the system where 2-ethylhexanol is the solvent, the plots of ln $(X_{CA}{}^0/X_{CA})$ vs. X_{SA} are straight lines as shown in Figure 5. The slope of the lines depends on the value of $X_{CA}{}^0$. The data for this system can be represented satisfactorily by the following equation:

$$\ln (X_{CA}{}^0/X_{CA}) = [2.63 \times 10^{-2} - (2.6 \times 10^{-4})X_{CA}{}^0]X_{SA} \quad (7)$$

For the system containing methyl ethyl ketone as the solvent, the plots of ln $(X_{CA}{}^0/X_{CA})$ vs. X_{SA}, as shown in Figure 6, are straight lines in the region above 5 wt % salt concentration. The following equation correlates the data for the system quite satisfactorily in the salt concentration range above 5 wt %:

$$\ln (X_{CA}{}^0/X_{CA}) = [2.1 \times 10^{-2} + (2.3 \times 10^{-3})X_{CA}{}^0]X_{SA} + [9 \times 10^{-2} + (3 \times 10^{-2})X_{CA}{}^0] \quad (8)$$

When salt is added to the systems discussed above, it decreases the solvent solubility in the aqueous phase. Thus, the aqueous phase gets modified in its affinity for acetic acid for two reasons, viz., the presence of salt and the salting-out of solvent. For solvents like ethyl acetate and 2-ethylhexanol, the value of the distribution coefficient less than 1.0 implies that, as compared to water, these solvents have less affinity for acetic acid. In such cases, the salting-out of solvent from the aqueous phase will increase the aqueous-phase affinity for

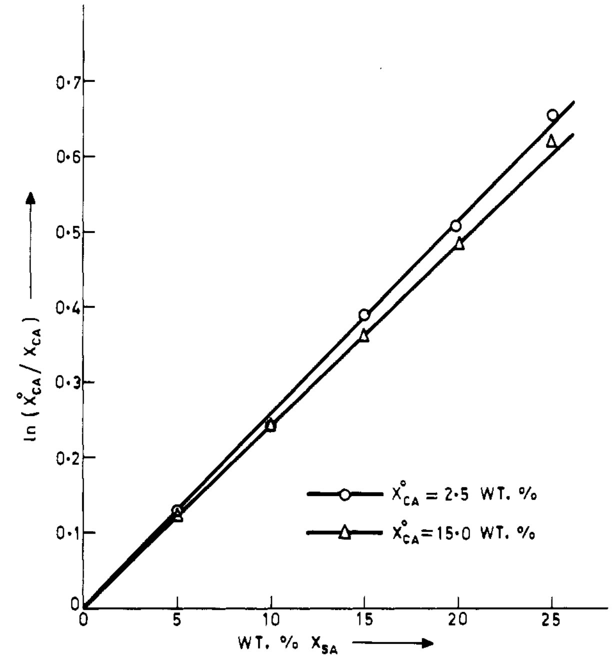

Figure 4. Plots of ln $(X_{CA}{}^0/X_{CA})$ vs. X_{SA} for the system water (A)-ethyl acetate (B)-acetic acid (C)-sodium sulfate (S).

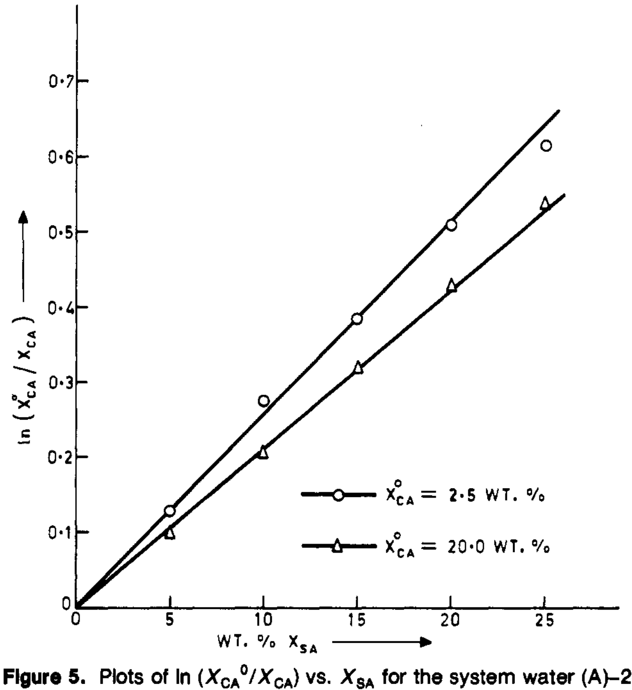

Figure 5. Plots of ln $(X_{CA}{}^0/X_{CA})$ vs. X_{SA} for the system water (A)-2-ethylhexanol (B)-acetic acid (C)-sodium sulfate (S).

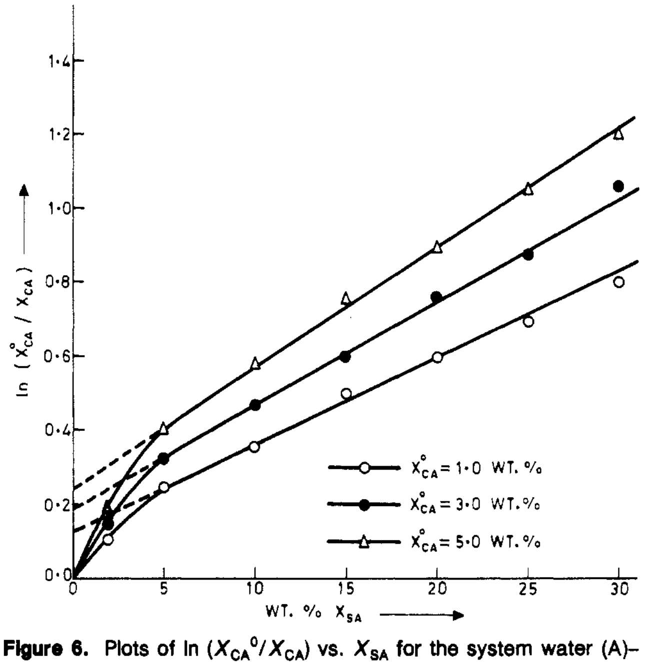

Figure 6. Plots of ln ($X_{CA}{}^{0}/X_{CA}$) vs. X_{SA} for the system water (A)–methyl ethyl ketone (B)–acetic acid (C)–sodium sulfate (S).

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

Chigosim W. Okpala and Dow M. Maharajh*

Department of Chemistry, University of the West Indies, St. Augustine, Trinidad, West Indies

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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