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Articles

Ion-Pair and Triple-Ion Formation by Some Tetraalkylammonium Iodides in Binary Mixtures of 1,4-Dioxane + Tetrahydrofuran

Mahendra Nath Roy,*[†] Prasanna Pradhan,[†] Rajesh Kumar Das,[†] Biswajit Sinha,[†] and Prabir Kumar Guha[‡]

Department of Chemistry, University of North Bengal, Darjeeling-734013, India, and Department of Chemistry,
Siliguri College, Darjeeling-734001, India

Electrical conductances of tetraalkylammonium iodides, R_4NI (R = pentyl to heptyl) have been measured at 298.15 K in low-permittivity mixtures of 1,4-dioxane ($\varepsilon = 2.21$) and tetrahydrofuran ($\varepsilon = 7.58$). Minima in the conductometric curves (Λ versus $\sqrt{c}$) were observed for electrolyte concentrations dependent upon both the electrolyte and the binary solvent mixture. The conductance data have been analyzed by the Fuoss−Kraus theory of triple ions. A numerical evaluation of ion-pair and triple-ion formation constants (K_P and K_T) was made, and the results have been discussed in terms of a molecular scale model.

Introduction

Progress in battery technology using the lithium electrolytes in etheral solution[1] has occurred largely in the past decade. Recently, there has been a renewed interest[2] in the study of association or dimerization of electrolytes in a media of low permittivity. In a media of low permitttivity, salts are generally so associated that the states of the ionic species in solutions are difficult to elucidate. A number of conductometric[3] and related studies of different electrolytes in nonaqueous solvents, especially mixed solvents, have been made for their optimal use in high-energy batteries[4] and for understanding organic reaction mechanisms.[5] Ionic association of salts in solution depends upon the mode of solvation of its ions,[6–10] which in turn depends on the nature of the solvent or solvent mixtures. 1,4-Dioxane and tetrahydrofuran are polar aprotic solvents of low permittivity, each with great present-day synthetic and industrial importance. They are frequently used in electrical conductance studies[3,4,11,12] and in high-energy batteries.[3,4,11,12] Tetraalkylammonium salts are characterized by their low surface charge density, and they show little or no solvation in solution.[11,12] Hence, in this paper, we reported the electrical conductances of some tetraalkylammonium iodides, R_4NI (R = pentyl to heptyl), in low-permittivity mixtures where mass fractions of 1,4-dioxane in tetrahydrofuran are 10, 20, and 30, respectively.

Experimental Section

Materials. 1,4-Dioxane and tetrahydrofuran were purchased from Merck, India, and purified as reported earlier.[13,14] The salts Pen_4NI, Hex_4NI, and $Hept_4NI$ of puriss grade were purchased from Aldrich, Germany, and purified by dissolving in mixed alcohol medium and recrystallized from solvent ether medium.[15] After filtration, the salts were dried in an oven for a few hours.

Apparatus and Procedure. Binary solvent mixtures were prepared by mixing a required volume of 1,4-dioxane and tetrahydrofuran with earlier conversion of required mass of each liquid into volume at 298.15 K using literature densities.[16] A stock solution for each salt was prepared by mass, and the working solutions were obtained by mass dilution. The conversion of molality into molarity was accomplished using density values. The uncertainty of molarity of different salt solutions is evaluated to $\pm$ 0.0001 $mol \cdot dm^{-3}$.

>The values of relative permittivity (ϵ) of the solvent mixtures were assumed to be an average of those of the pure liquids and calculated using the procedure as described by Rohdewald and Moldner.[17]

Table 1. Density ρ, Viscosity η, and Dielectric Constant ε, for 1,4-Dioxane (1) + Tetrahydrofuran (2) at T = 298.15 K

	$\rho \cdot 10^{-3}/(kg \cdot m^{-3})$		$\eta/(mPa \cdot s)$		
solvent mixture	exptl	lit.	exptl	lit.	ε
$w_1 = 0.00$	0.8807	0.8807[16]	0.463	0.4630[16]	7.58[11]
$w_1 = 0.10$	0.8941	−	0.490	−	7.04[a]
$w_1 = 0.20$	0.9071	−	0.510	−	6.51[a]
$w_1 = 0.30$	0.9190	−	0.530	−	5.96[a]
$w_1 = 1.00$	1.0305	1.0305[16]	1.200	1.2000[16]	2.21[11]

[a] Calculated using the scheme given in ref 17.

Densities were measured with an Ostwald−Sprengel-type pycnometer having a bulb volume of about 25 cm^3 and an internal diameter of the capillary of about 0.1 cm. The pycnometer was calibrated at 298.15 K with doubly distilled water and benzene.[18] The pycnometer with experimental liquid was equilibrated in a glass-walled thermostatted water bath maintained at $\pm$ 0.01 K of the desired temperature. The pycnometer was then removed from the thermostat, properly dried, and weighed in an electronic balance with a precision of $\pm$ 0.01 mg. Adequate precautions were taken to avoid evaporation losses during the time of measurements. An average of triplicate measurements was taken into account. The uncertainty of density values is $\pm$ $3 \cdot 10^{-4}$ $g \cdot cm^{-3}$. The viscosity was measured by means of a suspended Ubbelohde-type viscometer, calibrated at 298.15 K with doubly distilled water and purified methanol using density and viscosity values from the literature.[19–21]

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* Corresponding author. Tel.: +91-353-2699425. Fax: +91-353-2699001. E-mail: mahendraroy2002@yahoo.co.in.
[†] University of North Bengal.
[‡] Siliguri College.

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Table 2. Concentrations c and Molar Conductances Λ of R_4NI (R = Pentyl to Heptyl) in Different Binary Solvent Mixtures of 1,4-Dioxane (1) and Tetrahydrofuran (2) at T = 298.15 K

Pen_4NI		Hex_4NI		$Hept_4NI$	
$\frac{c \cdot 10^4}{mol \cdot dm^{-3}}$	$\frac{\Lambda}{S \cdot cm^2 \cdot mol^{-1}}$	$\frac{c \cdot 10^4}{mol \cdot dm^{-3}}$	$\frac{\Lambda}{S \cdot cm^2 \cdot mol^{-1}}$	$\frac{c \cdot 10^4}{mol \cdot dm^{-3}}$	$\frac{\Lambda}{S \cdot cm^2 \cdot mol^{-1}}$
		$w_1 = 0.10$			
0.8046	7.02	0.6367	8.12	0.3419	12.27
0.8138	6.86	0.6469	8.04	0.3754	11.64
0.8294	6.60	0.6541	7.98	0.4052	11.13
0.8385	6.46	0.6631	7.91	0.4319	10.77
0.8549	6.26	0.6696	7.88	0.4559	10.48
0.8674	6.46	0.6754	7.89	0.4776	10.52
0.8702	6.52	0.6806	7.93	0.4973	10.84
0.8726	6.59	0.6851	7.98	0.5153	11.33
		$w_1 = 0.20$			
0.4957	4.94	0.5460	3.98	0.6037	6.38
0.5016	4.83	0.5518	3.94	0.6142	4.94
0.5077	4.74	0.5598	3.88	0.6288	3.03
0.5122	4.76	0.5646	3.85	0.6376	1.94
0.5197	4.90	0.5694	3.83	0.6456	1.00
0.5229	4.98	0.5736	3.84	0.6541	0.55
0.4788	5.21	0.5764	3.86	0.6625	1.63
0.4839	5.12	0.5808	3.90	0.6672	2.53
		$w_1 = 0.30$			
0.2156	2.77	0.3125	4.97	0.5589	2.74
0.2564	2.70	0.3247	3.71	0.5675	2.30
0.2906	2.64	0.3420	2.13	0.5749	1.92
0.3481	2.56	0.3536	1.13	0.5813	1.63
0.3827	2.53	0.3657	0.35	0.5869	1.49
0.3986	2.53	0.3758	1.23	0.5917	1.62
0.4124	2.55	0.3819	2.13	0.5962	1.86
0.4274	2.58	0.3868	2.96	0.6001	2.09
0.4406	2.62				
0.4508	2.65				

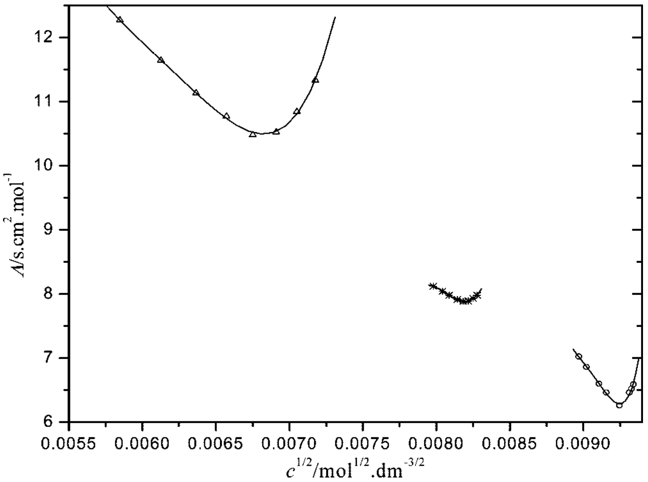

Figure 1. Plots of molar conductance (Λ) versus square root of salt concentration ($c^{1/2}$) at T = 298.15 K in w_1 = 0.10 of 1,4-dioxane (1) + tetrahydrofuran (2). ○, Pen_4NI; * Hex_4NI; Δ, $Hept_4NI$.

A thoroughly cleaned and perfectly dried viscometer filled with experimental liquid was placed vertically in the glass-walled thermostat maintained to ± 0.01 K. After attainment of thermal equilibrium, efflux times of flow were recorded with a stopwatch correct to ± 0.1 s. At least three repetitions of each data reproducible to ± 0.1 s were taken to average the flow times. The uncertainty of viscosity values is ± 0.003 mPa·s. The details of the methods and measurement techniques have been described elsewhere.[13,14] The conductance measurements were carried out in a systronic 308 conductivity bridge (accuracy ± 0.01 %) using a dip-type immersion conductivity cell, CD-10, having a cell constant of 0.1 ± 10 %. Measurements were made in a water bath maintained within $T = (298.15 \pm 0.01)$ K, and the cell was calibrated by Lind et al.[22] The conductance data were reported at a frequency of 1 KHz and were uncertain to ± 0.3 %.

Results and Dscussion

The physical properties of the binary solvent mixtures at 298.15 K are listed in Table 1. The concentrations and molar conductances Λ of R_4NI (R = pentyl to heptyl) in different binary solvent mixtures of 1,4-dioxane and tetrahydrofuran are given in Table 2.

Figures 1 to 3 represent the plots of molar conductance Λ versus square root of salt concentration $\sqrt{c}$ for the salts under investigations at 298.15 K in different binary mixtures of 1,4-dioxane and tetrahydrofuran. A minimum has been found for all the electrolytes suggesting the possible formation of triple-ions in these solutions. Fuoss and Krauss as early as 1933 introduced the concept of triple-ion formation from univalent electrolytes to explain the minima in the relation between the equivalent conductance and the concentration of tetraisoamylammonium nitrate in 1,4-dioxane + water mixtures (ε < 12). A result of the classical Fuoss−Kraus theory[23] of triple-ion formation can be presented by the eq[24,25]

$$\Lambda g(c)\sqrt{c} = \frac{\Lambda_0}{\sqrt{K_P}} + \frac{\Lambda_0^T K_T}{\sqrt{K_P}}\left(1 - \frac{\Lambda}{\Lambda_0}\right)c \qquad (1)$$

where $g(c)$ is a factor that lumps together all the intrinsic interaction terms and is defined by and $\beta' = 1.8247 \cdot 10^6/(\varepsilon T)^{3/2}$ is the Debye−Huckel term of the activity coefficient, $f = \exp[-(2.303/\Lambda_0^{1/2})\beta'(c\Lambda^{1/2})]$, and S is the Onsager conductance term of the conductance equation $\Lambda = \Lambda_0 - S(c\Lambda/\Lambda_0)$,[2] defined by

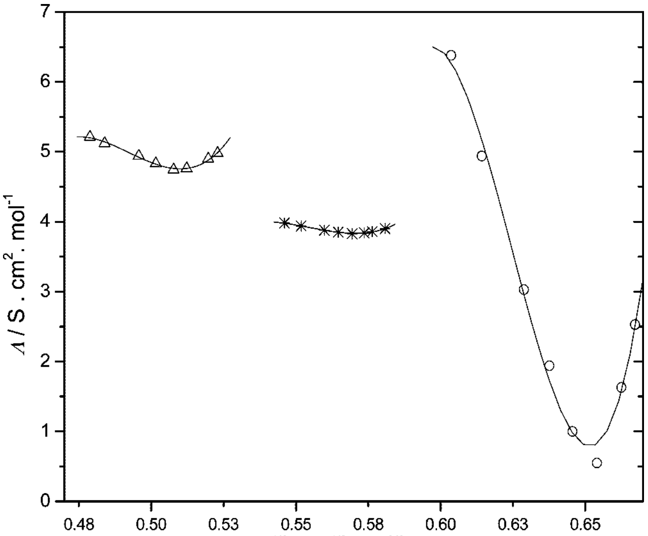

Figure 2. Plots of molar conductance (Λ) versus square root of salt concentration ($c^{1/2}$) at T = 298.15 K in w_1 = 0.20 of 1,4-dioxane (1) + tetrahydrofuran (2). ○, Pen_4NI; *, Hex_4NI; Δ, Hept_4NI.

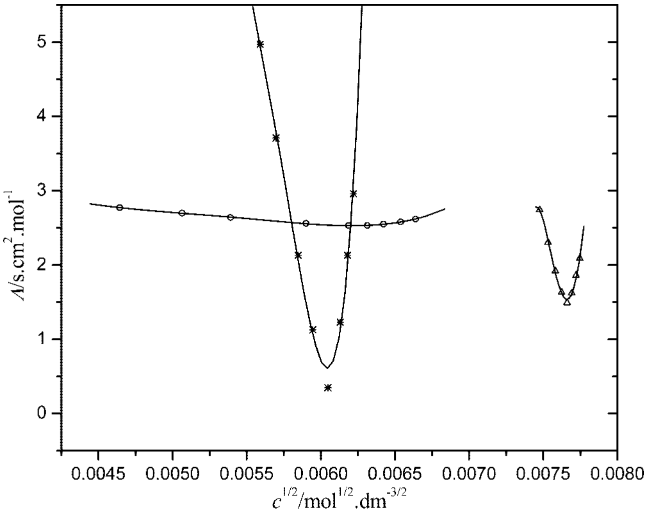

Figure 3. Plots of molar conductance (Λ) versus square root of salt concentration ($\sqrt{c}$) at T = 298.15 K in w_1 = 0.30 of 1,4-dioxane (1) + tetrahydrofuran (2). ○, Pen_4NI; *, Hex_4NI; Δ, Hept_4NI.

$$S = \alpha\Lambda_0 + \beta = \frac{0.8204 \cdot 10^6}{(\varepsilon T)^{3/2}}\Lambda_0 + \frac{82.501}{\eta(\varepsilon T)^{1/2}}$$

where the units of Λ_0 and η are $\text{S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$ and poise, respectively. Also, Λ_0 is the sum of the molar conductance of the simple ions at infinite dilution and Λ_0^{T} is the sum of the conductances of the two triple ions $\text{R}_4\text{N}(\text{I}_2)^-$ and $(\text{R}_4\text{N})^+{}_2$ I for R_4NI salts. K_P and K_T are the ion-pair and triple-ion formation constants. To make eq 1 applicable, the symmetrical approximation of the two possible constants of triple ions equal to each other has been adopted[2] and Λ_0 values for the studied electrolytes have been calculated following the scheme as suggested by Krumgalz.[12]

The calculated values have been listed in Table 3. Linear regression analysis of eq 1 gives the intercept and slope, and the values have been listed in Table 3. The K_T and K_P, calculated from the slopes and intercepts, are listed in Table 4. A perusal of Table 4 shows that the major portion of the electrolytes exists as ion pairs with only a negligible portion as triple ions. The observed difference in K_P and K_T values can be explained by the molecular scale model[26,27]

Table 3. Calculated Limiting Molar Conductance Λ_0, Slope, and Intercepts of Equation 1 for R_4NI (R = Pentyl to Heptyl) in Different Binary Solvent Mixtures of 1,4-Dioxane (1) and Tetrahydrofuran (2) at T = 298.15 K

solvent mixture	Λ_0 / $\text{S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$	slope	intercept
$w_1 = 0.10$		Pen_4NI	
	199.21	0.0064 (± 0.0003)	−0.011 (± 0.002)
		Hex_4NI	
	195.57	0.0346 (± 0.0002)	−0.029 (± 0.003)
		Hept_4NI	
	193.34	0.0974 (± 0.0001)	−0.050 (± 0.001)
$w_1 = 0.20$		Pen_4NI	
	192.20	0.1315 (± 0.0002)	−0.108 (±0.001)
		Hex_4NI	
	188.68	0.2975 (± 0.0002)	−0.225 (± 0.002)
		Hept_4NI	
	186.53	1.4633(±0.0001)	−0.837 (± 0.002)
$w_1 = 0.30$		Pen_4NI	
	185.92	5.1354 (± 0.0003)	−1.042 (± 0.002)
		Hex_4NI	
	182.52	0.3102 (± 0.0001)	−0.173 (± 0.003)
		Hept_4NI	
	180.44	0.5852 (± 0.0004)	−0.585 (± 0.006)

Table 4. Maximum Concentration c, Ion-Pair Formation Constant K_P, Triple-Ion Formation Constant K_T, Ion-Pair Concentration c_P, and Triple-Ion Concentration c_T for R_4NI (R = Pentyl to Heptyl) in Different Binary Solvent Mixtures of 1,4-Dioxane (1) and Tetrahydrofuran (2) at T = 298.15 K

salt	$c^a \cdot 10^4$ / $\text{mol}\cdot\text{dm}^{-3}$	$K_P \cdot 10^5$ / $\text{mol}^{-1}\cdot\text{dm}^3$	K_T / $\text{mol}^{-1}\cdot\text{dm}^3$	$c_P \cdot 10^5$ / $\text{mol}\cdot\text{dm}^{-3}$	$c_T \cdot 10^{10}$ / $\text{mol}\cdot\text{dm}^{-3}$
			$w_1 = 0.10$		
Pen_4NI	0.8726	3316.37	0.883	8.71	0.40
Hex_4NI	0.6851	450.34	1.783	6.72	1.51
Hept_4NI	0.5153	132.90	2.753	4.95	2.81
			$w_1 = 0.20$		
Pen_4NI	0.4839	31.55	1.823	4.81	3.98
Hex_4NI	0.5805	7.03	1.983	4.92	6.16
Hept_4NI	0.6672	0.50	2.622	3.85	13.40
			$w_1 = 0.30$		
Pen_4NI	0.4508	0.32	7.389	3.50	4.25
Hex_4NI	0.3868	11.12	2.688	3.25	6.64
Hept_4NI	0.6001	1.26	1.728	3.77	23.50

[a] Maximum concentrations at which calculations have been performed.

$$\begin{aligned} &\text{M}^+ + \text{A}^- \leftrightarrow \text{M}^+ \ldots \text{A}^- \leftrightarrow \text{MA} \\ &\text{MA} + \text{A}^- \leftrightarrow \text{MAA}^- \\ &\text{MA} + \text{M}^+ \leftrightarrow \text{MAM}^+ \quad [\text{M} = \text{R}_4\text{N and A} = \text{I}] \end{aligned} \tag{2}$$

It is likely possible that association of R_4N^+ cations with solvent components shifts the above equilibrium toward the left, thus decreasing K_P values and increasing K_T values. The ion-pair and triple-ion concentrations (c_P and c_T, respectively) of the electrolytes at the highest electrolyte concentration have been derived using eqs [25–27] 3 to 6 and are listed in Table 4.

$$\alpha = (K_P c)^{-1/2} \tag{3}$$

$$\alpha_T = \frac{K_T}{K_P^{0.5}} c^{1/2} \tag{4}$$

$$c_P = c(1 - \alpha - 3\alpha_T) \tag{5}$$

$$c_T = \frac{K_T}{K_P^{1/2}} c^{3/2} \tag{6}$$

It was observed that dielectric constants of the binary solvent mixtures decreased as the amount of 1,4-dioxane increased in the solvent mixtures. The concomitant increase in K_T and C_T values suggests that R_4N^+ cations are preferably more solvated by 1,4-dioxane than by tetrahydrofuran. On the contrary, the steric hindrance caused by the CH_2- group adjacent to the ethereal group of the cyclic ethers may cause solvation hindrance favoring the anion I^- as a competitor for the first coordination shell of R_4N^+ cations. This may shift the above equilibrium toward right increasing K_P values.

Table 4 shows that for a particular solvent mixture, i. e., for a particular value of dielectric constant of the solvent mixture, K_P values are in the order $Pen_4NI > Hex_4NI > Hept_4NI$, and that of K_T values is $Pen_4NI < Hex_4NI < Hept_4NI$. This suggests that smaller R_4N^+ cations tend to remain more as ion-pairs than larger ones, which in turn has greater capacity to form triple ions. This also supports our earlier view of preferential solvation[10] of R_4N^+ cations by 1,4-dioxane in the electrolyte solutions.

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