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Ion Pair and Triple Ion Formation by Some Tetraalkylammonium Iodides in Binary Mixtures of Carbon Tetrachloride + Nitrobenzene[†]

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Electrical conductances of tetraalkylammonium iodides, R_4NI (R = butyl to heptyl), in different mass % (20 to 80) of carbon tetrachloride (CCl_4) + nitrobenzene ($PhNO_2$) have been measured at 298.15 K. Limiting molar conductances Λ_0, association constants K_A, and cosphere diameter R for ion pair formation in the mixed solvent mixtures have been evaluated using the Lee−Wheaton conductivity equation. However, the deviation of the conductometric curves (Λ versus $\sqrt{c}$) from linearity for the electrolytes in 80 mass % of CCl_4 + $PhNO_2$ indicated triple ion formation, and therefore corresponding conductance data have been analyzed by the Fuoss−Kraus theory of triple ions. Limiting ionic molar conductances $\lambda_0^{\pm}$ have been calculated by the reference electrolyte method along with a numerical evaluation of ion pair and triple ion formation constants ($K_P \approx K_A$and K_T); the results have been discussed in terms of solvent properties and configurational theory.

Introduction

Mixed solvents enable the variation of properties such as dielectric constant or viscosity, and therefore the ion−ion and ion−solvent interactions can be better studied. Furthermore, different quantities strongly influenced by solvent properties can be derived from concentration dependence of the electrolyte conductivity. Consequently, a number of conductometric[1] and related studies of different electrolytes in nonaqueous solvents, especially mixed organic solvents, have been made for their optimal use in high-energy batteries[2] and for understanding organic reaction mechanisms.[3] Ionic association of electrolytes in solution depends upon the mode of solvation of its ions,[4−8] which in turn depends on the nature of the solvent or solvent mixtures. Such solvent properties as viscosity and the relative permittivity have been taken into consideration as these properties help in determining the extent of ion association and the solvent−solvent interactions. Thus, extensive studies on electrical conductances in various mixed organic solvents have been performed in recent years[9−13] to examine the nature and magnitude of ion−ion and ion−solvent interactions. Also, tetraalkylammonium salts are characterized by their low surface charge density, and they show little or no solvation in solution.[14,15] As such, they are frequently selected as desired electrolytes in conductance studies. In continuation of our investigation on electrical conductances,[8,10,11] the present work deals with the conductance measurements of some tetraalkylammonium iodides, R_4NI (R = butyl to heptyl), in binary mixtures of CCl_4—a nonpolar aprotic liquid—and $PhNO_2$—a polar aprotic liquid—at 298.15 K.

Experimental Section

Materials. CCl_4 (carbon tetrachloride, CAS: 56-23-5) and $PhNO_2$ (nitrobenzene, CAS: 98-95-3) were purchased from Merck, India, and purified as reported earlier.[16] The mole percent purities for the liquids used as checked by GC (HP6890) using an FID detector were better than 99. The salts Bu_4NI (*N*,*N*,*N*-tributyl-1-butanaminium iodide, CAS: 311-28-4), Pen_4NI (*N*,*N*,*N*-tripentyl-1-pentanaminium iodide, CAS: 2498-20-6), Hex_4NI (*N*,*N*,*N*-trihexyl-1-hexanaminium iodide, CAS: 2138-24-1), and $Hept_4NI$ (*N*,*N*,*N*-triheptyl-1-heptanaminium iodide, CAS: 3535-83-9) of puriss grade were purchased from Aldrich, Germany, and purified by dissolving in mixed alcohol medium and recrystallized from solvent ether medium.[17] After filtration, the salts were dried in a oven for a few hours.

Table 1. Density ρ, Viscosity η, and Dielectric Constant ε for CCl_4 (1) + $PhNO_2$ (2) at T = 298.15 K

	$(\rho\cdot10^{-3})/(\mathrm{kg\cdot m^{-3}})$		$(\eta)/(\mathrm{mPa\cdot s})$		
solvent mixture	exptl	lit.	exptl	lit.	ε_r
$w_1 = 0.00$	1.1982	1.1985^{40} 1.1983^{41}	1.686	1.686^{41}	34.69^{18}
$w_1 = 0.20$	1.2614		1.613		29.66^{a}
$w_1 = 0.40$	1.3314		1.411		23.90^{a}
$w_1 = 0.60$	1.4067		1.224		17.45^{a}
$w_1 = 0.80$	1.4910		1.099		10.22^{a}
$w_1 = 1.00$	1.5843	1.5844^{41}	0.902	0.9017^{41}	2.25^{41}

[a] Obtained by interpolation of literature data from ref 18.

Apparatus and Procedure. Binary solvent mixtures were prepared by mixing a required volume of CCl_4 and $PhNO_2$ with earlier conversion of required mass of each liquid into volume at 298.15 K using experimental densities. A stock solution for each salt was prepared by mass, and the working solutions were obtained by mass dilution. The uncertainty of molarity of different salt solutions is evaluated to ± 0.0001 $\mathrm{mol\cdot dm^{-3}}$.

The values of relative permittivity ε_r of the solvent mixtures were obtained by interpolation of the solvent permittivity data from the literature[18] by cubic spline fitting. The physical properties of the binary solvent mixtures at 298.15 K are listed in Table 1. 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

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water and benzene.[19] The pycnometer with experimental liquid was equilibrated in a glass-walled thermostatted water bath maintained at ± 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 ± 0.01 mg. Adequate precautions were taken to avoid evaporation losses during the time of measurements. An average of triplicate measurement was taken into account. The uncertainty of density values is $\pm 3 \cdot 10^{-4}$ $g \cdot cm^{-3}$. Solvent viscosities were 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.[20−22] 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 had been described elsewhere.[11,23] 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 approximately (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 the method proposed by Lind et al.[24] The conductance data were reported at a frequency of 1 kHz and were uncertain to ± 0.3 %.

Results and Discussion

The concentrations and molar conductances Λ of R_4NI (R = butyl to heptyl) in different binary solvent mixtures of CCl_4 and $PhNO_2$ are given in Table 2.

For the solvent mixtures in the range of moderate relative permittivity ($\varepsilon_r = 29.66$ to 17.45), the conductance curves (Λ versus $\sqrt{c}$) were linear, and extrapolation of $\sqrt{c} = 0$ evaluated the starting limiting molar conductances for the electrolytes; however, as the relative permittivity ε_r droped to 10.22 for the solvent mixture containing 80 mass % of CCl_4 in $PhNO_2$, nonlinearity (Figure 1) was observed in conductance curves. Thus the conductance data, in the solvent mixtures ($w_1 = 0.20$ to 0.60) wherein higher clusters other than ion pair formation was not expected, were analyzed by the Lee−Wheaton conductance equation[25] in the form

$$\Lambda = \alpha_i\left\{\Lambda_0[1 + C_1\beta\kappa + C_2(\beta\kappa)^2 + C_3(\beta\kappa)^3] - \frac{\rho\kappa}{1 + \kappa R}\left[1 + C_4\beta\kappa + C_5(\beta\kappa)^2 + \frac{\kappa R}{12}\right]\right\} \quad (1)$$

The mass action law association[26] is

$$K_A = (1 - \alpha_i)\gamma_A/\alpha_i^2 c_i \gamma_\pm^2 \quad (2)$$

and the equation for the mean ionic activity coefficient

$$\gamma_\pm = \exp\left[-\frac{q\kappa}{1 + \kappa R}\right] \quad (3)$$

where C_1 to C_5 are least-squares fitting coefficients as described by Pethybridge and Taba;[25] Λ_0 is the limiting molar conductivity; K_A is the association constant; α_i is the dissociation degree; q is the Bjerrum parameter; γ is the activity coefficient; and $\beta = 2q$. The distance parameter R is the least distance that two free ions can approach before they merge into an ion pair. The Debye parameter κ, the Bjerrum parameter q, and ρ[25] are defined by the expressions

$$\kappa = 16000\pi N_A q c_i \alpha_i \quad (4)$$

$$q = \frac{e^2}{8\varepsilon_0\varepsilon_r kT} \quad (5)$$

$$\rho = \frac{Fe}{299.79 \cdot 3\pi\eta} \quad (6)$$

where the symbols have their usual significance.[27]

Equation 1 was resolved by an iterative procedure. For a definite R value, the initial values of Λ_0 and K_A were obtained by the Kraus−Bray method.[28] The parameters Λ_0 and K_A were made to approach gradually their best values by a sequence of alternating linearization and least-squares optimizations by the Gauss−Siedel method[29] until satisfying the criterion for convergence. The best value of a parameter is the one when eq 1 is best fitted to the experimental data corresponding to minimum standard deviation σ_Λ for a sequence of predetermined R values, and standard deviation σ_Λ was calculated by the following equation

$$\sigma_\Lambda^2 = \sum_{i=1}^{n} \frac{[\Lambda_i(\text{calcd}) - \Lambda_i(\text{obsd})]^2}{n - m} \quad (7)$$

where n is the number of experimental points and m is the number of fitting parameters. The conductance data were analyzed by fixing the distance of closest approach R with two-parameter fit ($m = 2$). As for the electrolytes studied in the solvent mixtures ($w_1 = 0.20$ to 0.60), no significant minima were observed in the σ_Λ versus R curves, and the R values were arbitrarily preset at the center to center distance of the solvent-separated pair[8]

$$R = a + d \quad (8)$$

where a is the sum of the crystallographic radii of the cation and anion and d is the average distance corresponding to the side of a cell occupied by a solvent molecule. The definitions of d and related terms have already been described in the literature.[8] R was generally varied by a step of 0.1 Å, and the iterative process was continued with eq 1.

Table 3 reveals that the limiting molar conductances Λ_0 for the electrolytes decrease with the increase of CCl_4 content in the solvent mixtures. This fact is in line with the decrease of the relative permittivity ε_r of the solvent mixtures.[14,30] Although the decreasing trend of viscosity for the solvent mixtures with increasing content of CCl_4 suggests concomitant increase in limiting molar conductances[14,30] for the electrolytes, we observed an opposite trend. This trend suggests predominance of relative permittivity ε_r over the solvent viscosity η_0 in effecting the electrolytic conductances of the electrolytes under study in these media. In a particular solvent mixture, the limiting molar conductances Λ_0 of the electrolytes under investigation decrease as the size of the alkyl group increases, in contraposition to the conductance behavior of the alkali metal cations, as tetraalkylammonium salts are characterized by their low surface charge density.[14,15]

The decreasing trend of Walden products $\Lambda_0\eta_0$ in Table 3 is mainly in accordance with the concomitant decrease of both the solvent viscosity and limiting molar conductance of the electrolytes. The ionic conductances $\lambda_0^\pm$ for the various R_4N^+ cations (R = butyl to hexyl) in different solvent mixtures ($w_1 = 0.20$ to 0.60) were calculated using tetrabutylammonium tetraphenyl borate (Bu_4NBPh_4) as a reference electrolyte following the scheme as suggested by B. Das et al.[31] We calculated its limiting molar conductances $\lambda_0^\pm$ in our solvent compositions by interpolation of conductance data from the literature[18] using

Table 2. Concentrations c and Molar Conductances Λ of R_4NI (R = Butyl to Heptyl) in Different Binary Solvent Mixtures of CCl_4 (1) + $PhNO_2$ (2) at T = 298.15 K

Bu_4NI		Pen_4NI		Hex_4NI		$Hept_4NI$	
$(c\cdot10^4)$ $(\mathrm{mol\cdot dm^{-3}})$	(Λ) $(\mathrm{S\cdot cm^2\cdot mol^{-1}})$	$(c\cdot10^4)$ $(\mathrm{mol\cdot dm^{-3}})$	(Λ) $(\mathrm{S\cdot cm^2\cdot mol^{-1}})$	$(c\cdot10^4)$ $(\mathrm{mol\cdot dm^{-3}})$	(Λ) $(\mathrm{S\cdot cm^2\cdot mol^{-1}})$	$(c\cdot10^4)$ $(\mathrm{mol\cdot dm^{-3}})$	(Λ) $(\mathrm{S\cdot cm^2\cdot mol^{-1}})$
			$w_1 = 0.20$				
8.3	39.50	8.3	38.60	8.4	36.38	8.3	35.20
15.3	37.00	15.3	36.00	15.3	34.66	15.3	33.20
21.2	35.80	21.2	34.90	21.2	33.14	21.2	32.33
26.2	34.68	26.2	34.20	26.3	32.14	26.2	31.22
30.6	34.00	30.6	33.00	30.64	31.66	30.6	30.72
34.4	33.50	34.4	33.00	34.5	30.50	34.4	30.20
37.8	32.80	37.8	31.70	37.8	30.30	37.8	29.89
40.8	32.10	40.8	31.30	40.8	29.80	40.8	29.30
45.9	31.70	43.5	30.60	43.5	29.40	45.9	29.00
50.1	30.50	48.1	29.70	46.0	29.37	50.1	28.40
53.6	30.00	51.9	29.27	50.1	28.92	53.6	28.19
57.8	29.40	55.1	28.66	51.9	28.49	56.5	27.70
61.2	29.20	57.8	28.52	55.1	28.29	59.0	27.62
64.0	28.59	61.2	28.08	57.9	27.82	61.2	27.28
66.3	28.34	64.0	27.80	60.2	27.23	63.1	27.25
68.3	28.26	66.3	27.58	63.2	27.22	65.6	27.00
69.9	28.01	68.3	27.37	65.7	27.11	67.6	26.76
71.4	28.00	70.5	27.23	67.1	26.98	69.4	26.51
72.3	27.80	72.3	26.96	69.5	26.62	70.9	26.36
73.8	27.76	74.2	26.95	71.5	26.44	72.7	26.28
			$w_1 = 0.40$				
4.4	38.80	4.4	36.89	4.4	35.50	4.6	34.61
8.1	37.00	6.3	36.00	6.3	35.25	6.6	33.82
11.3	35.80	8.1	35.20	8.0	34.18	8.4	32.71
13.9	34.56	9.7	34.56	9.7	33.86	10.1	32.31
16.3	33.37	11.2	34.00	11.1	33.39	11.6	31.84
18.3	32.83	13.9	32.90	12.8	32.47	13.1	31.35
20.1	32.30	16.2	32.34	13.8	32.10	14.4	30.91
23.1	31.50	18.2	31.43	14.9	32.04	15.7	30.54
25.6	30.43	20.0	30.70	17.1	31.23	17.9	29.82
27.6	30.19	21.6	30.50	19.0	30.86	19.9	29.66
29.3	29.81	23.0	30.14	20.7	30.30	21.6	29.16
31.4	29.32	24.3	29.38	22.2	29.75	23.2	28.61
33.1	28.97	26.5	29.30	23.5	29.21	24.6	28.60
34.4	28.44	28.4	29.06	24.7	29.16	25.9	28.24
35.6	28.36	29.9	28.68	25.8	28.77	27.0	27.99
36.9	27.91	31.2	28.22	27.7	28.41	29.0	27.54
37.9	27.66	32.9	27.94	29.3	27.64	30.7	27.37
39.0	27.40	34.3	27.69	30.7	27.73	32.1	26.95
39.9	27.29	35.5	27.35	31.9	27.48	33.4	26.81
40.7	27.29	36.7	26.94	33.4	26.93	34.5	26.40
			$w_1 = 0.60$				
1.7	36.41	1.7	34.60	1.7	33.30	1.7	32.30
2.5	34.82	2.4	33.05	2.4	32.51	2.4	31.60
3.2	34.12	3.1	32.50	3.1	31.40	3.1	30.80
3.8	32.94	3.8	31.40	3.7	30.48	3.8	30.05
4.4	32.12	4.3	30.70	4.3	30.20	4.3	29.73
4.9	31.31	4.9	30.00	4.8	29.70	4.9	28.93
5.4	30.94	5.4	29.50	5.3	29.00	5.4	28.67
5.9	30.44	5.8	29.10	5.8	28.60	5.8	28.11
6.3	29.80	6.3	28.90	6.2	28.40	6.3	28.00
7.1	29.21	6.7	28.50	6.6	28.00	6.7	27.70
7.8	28.20	7.0	27.96	7.4	27.56	7.0	27.20
8.4	27.66	7.7	27.70	7.7	27.14	7.7	26.87
8.9	27.18	8.3	26.94	8.3	26.71	8.4	26.33
9.5	26.81	8.9	26.63	8.9	26.30	8.9	25.94
9.9	26.50	9.4	26.08	9.3	25.88	9.4	25.74
10.7	25.86	9.8	25.71	9.8	25.80	10.2	24.96
11.4	25.42	10.6	25.40	10.6	25.26	11.3	24.02
11.9	25.31	11.3	24.60	11.2	24.87	11.8	23.82
12.6	24.62	11.8	24.51	11.8	24.46	12.3	23.54
13.2	24.54	12.3	24.29	12.2	24.24	12.9	23.29
			$w_1 = 0.80$				
1.7	4.07	1.7	3.72	1.7	3.72	1.7	3.64
2.4	3.57	2.4	3.27	2.4	3.20	2.4	3.38
3.1	3.26	3.1	2.96	3.1	2.95	3.1	3.09
3.8	3.03	3.8	2.71	3.8	2.75	3.8	2.90
4.3	2.93	4.3	2.49	4.3	2.61	4.3	2.72
4.9	2.81	4.9	2.36	4.9	2.50	4.9	2.63
5.4	2.72	5.4	2.25	5.4	2.40	5.4	2.51
5.8	2.59	5.8	2.16	5.8	2.31	5.8	2.43
6.3	2.55	6.3	2.10	6.3	2.28	6.3	2.36
7.0	2.45	7.0	2.00	7.0	2.21	6.7	2.29
7.7	2.33	7.7	1.87	7.7	2.13	7.0	2.23

Table 2. (Continued)

Bu_4NI		Pen_4NI		Hex_4NI		$Hept_4NI$	
$(c\cdot10^4)$ (mol·dm^{-3})	(Λ) (S·cm^2·mol^{-1})	$(c\cdot10^4)$ (mol·dm^{-3})	(Λ) (S·cm^2·mol^{-1})	$(c\cdot10^4)$ (mol·dm^{-3})	(Λ) (S·cm^2·mol^{-1})	$(c\cdot10^4)$ (mol·dm^{-3})	(Λ) (S·cm^2·mol^{-1})
8.4	2.26	8.3	1.82	8.4	2.05	7.7	2.17
8.9	2.19	8.9	1.74	8.9	1.98	8.4	2.08
9.4	2.15	9.4	1.72	9.4	1.95	8.9	2.02
10.2	2.05	9.8	1.68	10.2	1.87	9.4	1.97
10.9	2.01	10.6	1.66	10.9	1.81	9.8	1.94
11.6	1.94			11.6	1.77	10.6	1.87
12.1	1.90			12.1	1.75	11.3	1.82
12.7	1.86			12.5	1.70	11.8	1.78
13.3	1.82			13.1	1.66	12.3	1.75

cubic spline fitting. The $\lambda_0^{\pm}$ values were in turn utilized for the calculation of Stokes' radii r_s according to the classical expression[32]

$$r_s = \frac{F^2}{6\pi N_A \lambda_0^{\pm} \eta_0} \tag{9}$$

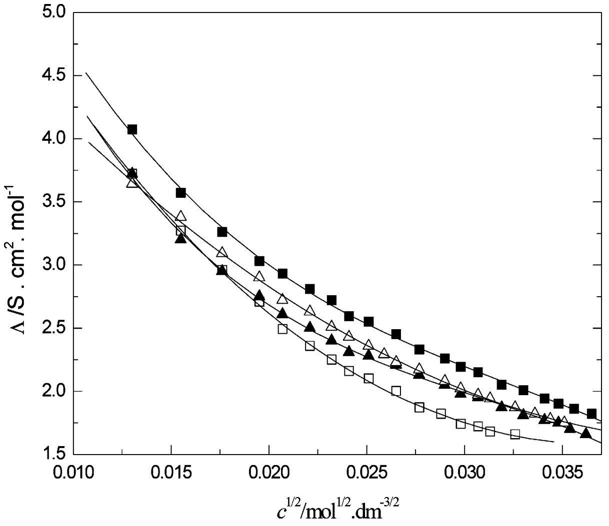

Figure 1. Plots of molar conductance, Λ, versus square root of salt concentration, $c^{1/2}$, in $w_1 = 0.80$ of CCl_4 (1) + $PhNO_2$ (2) at $T = 298.15$ K. ■, Bu_4NI; □, Pen_4NI; ▲, Hex_4NI; △, $Hept_4N$.

Table 3. Limiting Molar Conductance Λ_0, Association Constant K_A, Cosphere Diameter R, and Standard Deviations σ of Experimental Λ from Equation 1 and Walden Products for the Electrolytes in Different Binary Solvent Mixtures of CCl_4 (1) + $PhNO_2$ (2) at T = 298.15 K

w_1	Λ_0 (S·cm^2·mol^{-1})	K_A	R Å	$\Lambda_0\eta_0$ (S·cm^2·mol^{-1}·mPa·s)	σ
			Bu_4NI		
0.20	46.23	159.9	12.0	74.57	0.24
0.40	45.71	301.1	12.4	64.49	0.22
0.60	44.94	330.5	12.7	54.99	0.25
			Pen_4NI		
0.20	42.53	90.9	11.9	69.77	0.21
0.40	42.35	246.1	13.4	59.75	0.26
0.60	41.51	1075.3	12.6	50.79	0.26
			Hex_4NI		
0.20	41.74	126.5	11.9	67.33	0.23
0.40	41.31	231.9	12.3	58.28	0.25
0.60	39.01	816.2	12.6	47.74	0.24
			$Hept_4NI$		
0.20	39.59	99.6	11.9	63.86	0.12
0.40	39.30	195.8	12.3	55.44	0.14
0.60	38.51	851.9	12.6	47.13	0.16

Table 4. Limiting Ionic Conductance $\lambda_0^{\pm}$, Ionic Walden Product $\lambda_0^{\pm}\eta_0$, Stokes' Radii r_s, and Crystallographic Radii r_c at T = 298.15 K

ion	$\lambda_0^{\pm}$ (S·cm^2·mol^{-1})	$\lambda_0^{\pm}\eta_0$ (S·cm^2·mol^{-1}·mPa·s)	r_s Å	r_c[a] Å
		$w_1 = 0.20$		
Bu_4N^+	13.38	21.58	3.79	4.94
Pen_4N^+	9.68	15.61	5.25	5.29
Hex_4N^+	8.89	14.34	5.71	5.60
$Hept_4N^+$	8.74	10.87	7.53	5.88
I^-	32.85	52.99	1.76	2.16
		$w_1 = 0.40$		
Bu_4N^+	14.97	21.12	3.93	4.94
Pen_4N^+	11.61	16.38	5.09	5.29
Hex_4N^+	10.57	14.91	5.60	5.60
$Hept_4N^+$	8.56	12.08	6.95	5.88
I^-	30.74	43.37	1.87	2.16
		$w_1 = 0.60$		
Bu_4N^+	15.83	18.82	4.15	4.94
Pen_4N^+	12.40	15.18	5.26	5.29
Hex_4N^+	9.90	12.16	6.56	5.60
$Hept_4N^+$	9.40	11.50	6.89	5.88
I^-	29.11	35.62	2.32	2.16

[a] r_c values are taken from ref 14.

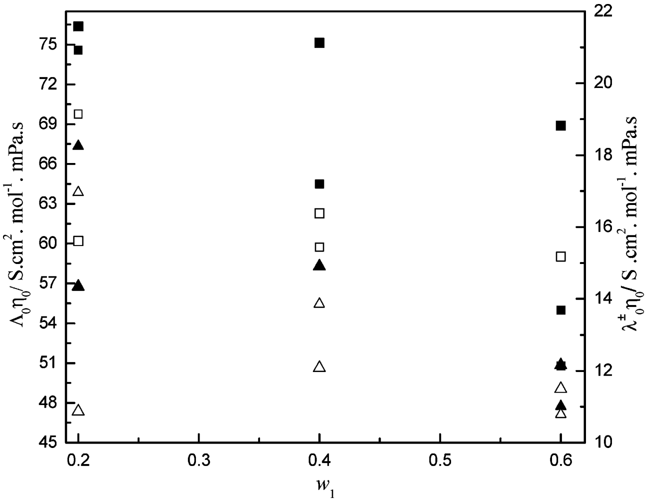

Figure 2. Plots of Walden products, $\Lambda_0\eta_0$, for electrolytes and ionic Walden products, $\lambda_0^{\pm}\eta_0$, versus w_1 of CCl_4 (1) + $PhNO_2$ (2) mixtures at T = 298.15 K. ■, Bu_4NI or Bu_4N^+; □, Pen_4NI or Pen_4N^+; ▲, Hex_4NI or Hex_4N^+; △, $Hept_4N$ or $Hept_4N^+$.

Ionic Walden products $\lambda_0^{\pm}\eta_0$, Stokes' radii r_s, and crystallographic radii r_c are presented in Table 4. The trends in ionic Walden products $\lambda_0^{\pm}\eta_0$ and Walden products $\Lambda_0\eta_0$ for all the electrolytes in the solvent mixtures (w_1 = 0.20 to 0.60) are depicted in Figure 2. It shows that Walden products $\Lambda_0\eta_0$ for all electrolytes decrease almost linearly as the CCl_4 content increases in the solvent mixtures, but the trend in ionic Walden products $\lambda_0^{\pm}\eta_0$ for R_4N^+ ions is rather irregular. However, the I^- ion shows a similar trend with the electrolytes in this regard.

Table 5. Calculated Limiting Molar Conductance Λ_0, Slope and Intercepts of Equation 10, 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 = Butyl to Heptyl) in 80 Mass % of CCl_4 (1) + $PhNO_2$ (2) at T = 298.15 K

Λ_0 $(S \cdot cm^2 \cdot mol^{-1})$	slope	intercept $\cdot 10^2$	$c^a \cdot 10^4$ $(mol \cdot dm^{-3})$	$K_P \cdot 10^5$	K_T	$c_P \cdot 10^3$	$c_T \cdot 10^6$
			Bu_4NI				
50.04	9.069	6.164	13.3	6.6	220.6	1.24	13.1
	(± 0.003)	(± 0.002)					
			Pen_4NI				
46.22	5.824	5.265	10.6	7.7	165.8	1.01	6.5
	(± 0.002)	(± 0.003)					
			Hex_4NI				
43.44	7.121	5.408	13.1	6.4	194.4	1.23	11.5
	(± 0.004)	(± 0.001)					
			$Hept_4NI$				
42.88	15.422	5.235	12.3	6.7	441.7	1.12	23.3
	(± 0.001)	(± 0.001)					

[a] Maximum concentrations used in calculations.

Thus, it seems that the I^- ion plays a predominating role in characterizing the conductance behavior of the electrolytes under study in these media. The position of the curves in Figure 2, $\Lambda_0\eta_0$ or $\lambda_0^{\pm}\eta_0$ versus w_1, suggests a relationship $Bu_4N^+ < Pen_4N^+ < Hex_4N^+ < Hept_4N^+$ for Stokes' radius just similar to their ionic radii order. For tetraalkylammonium ions, the Stokes' radii are either lower or comparable to their crystallographic radii r_c, particularly for smaller ions. This suggests that these ions are comparatively less solvated than alkali metal ions due to their intrinsic low surface charge density.

The conductance data for all the electrolytes in 80 mass % of CCl_4 in $PhNO_2$ ($\varepsilon_r = 10.22$) were analyzed by the classical Fuoss−Kraus theory of triple ion formation in the form[33,34]

$$\Lambda g(c)\sqrt{c} = \frac{\Lambda_0}{\sqrt{K_P}} + \frac{\Lambda_0^T K_T}{\sqrt{K_P}}\left(1 - \frac{\Lambda}{\Lambda_0}\right)c \tag{10}$$

where $g(c)$ is a factor that lumps together all the intrinsic interaction terms and is defined by

$$g(c) = \frac{\exp\{-(2.303/\Lambda_0^{1/2})\beta(c\Lambda^{1/2})\}}{\{1 - (S/\Lambda_0^{3/2})(c\Lambda)^{1/2}\}(1 - \Lambda/\Lambda_0)^{1/2}} \tag{11}$$

$$\beta = 1.8247 \cdot 10^6/(\varepsilon T)^{3/2} \tag{12}$$

$$S = \alpha\Lambda_0 + \beta = \frac{0.8204 \cdot 10^6}{(\varepsilon T)^{3/2}}\Lambda_0 + \frac{82.501}{\eta(\varepsilon T)^{1/2}} \tag{13}$$

In the above equations, Λ_0 is the sum of the molar conductance of the simple ions at infinite dilution; Λ_0^T is the sum of the conductances of the two triple ions $R_4N(I_2)^-$ and $(R_4N)_2^+I$ for R_4NI salts; and $K_P \approx K_A$ and K_T are the ion pair and triple ion formation constants. To make eq 10 applicable, the symmetrical approximation of the two possible constants of triple ions equal to each other has been adopted, and Λ_0 values for the studied electrolytes in 80 mass % of CCl_4 in $PhNO_2$ have been calculated using respective Λ_0 and η_0 values in 60 mass % of CCl_4 in $PhNO_2$ according to the Walden rule.[14,30] Λ_0^T is calculated by setting the triple ion conductance equal to $2/3\Lambda_0$.[35] The ratio Λ_0^T/Λ_0 was thus set equal to 0.667 during linear regression analysis of eq 10.

Table 6. Interionic Distance Parameter a_{IP} and Interionic Distance for Triple Ion a_{TI} in 80 mass % of CCl_4 in $PhNO_2$ at T = 298.15 K

electrolyte	a_{IP}/Å	a_{TI}/Å	$1.5a_{IP}$/Å
Bu_4NI	3.01	3.95	4.51
Pen_4NI	2.99	4.32	4.48
Hex_4NI	3.02	3.92	4.53
$Hept_4NI$	3.01	3.62	4.51

Linear regression analysis of eq 10 for the electrolytes with an average regression constant, $R^2 = 0.9653$, gives intercepts and slopes. These permit the calculation of other derived parameters such as K_P and K_T listed in Table 5. A perusal of Table 5 shows that the major portion of the electrolytes exists as ion pairs with a minor portion as triple ions. Using the K_P values, the interionic distance parameter a_{IP} has been calculated with the aid of the Bjerrum's theory of ionic association[36] in the form

$$K_P = \frac{4\pi N_A}{1000}\left[\frac{e^2}{\varepsilon_r kT}\right]^3 Q(b) \tag{14}$$

$$Q(b) = \int_2^b y^{-4}\exp(y)\mathrm{d}y \tag{15}$$

$$b = \frac{e^2}{a_{IP}\varepsilon_r kT} \tag{16}$$

The a_{IP} values obtained are given in Table 6. The $Q(b)$ and b values have been calculated by the literature procedure.[36] Table 6 reveals that a_{IP} values are almost similar for all the electrolytes though the actual ionic sizes varied by (0.28 to 0.35) Å. This may be due to easy penetration by the I^- ion to some extent into the void spaces between the alkyl chains, as suggested by Abbott and Schiffrin.[37] Thus, an increase in chain length for tetraalkylammonium ions does not affect the distance of closest approach between the two ions. The a_{IP} are much less in comparison with the crystallographic radii (r_c) suggesting probable contact ion pairs for the iodides in solution.[14] This will cause a decrease in the degree of freedom for the cations in the ion pair resulting in their loss of configurational entropy of the contact pair. Generally, K_P values do not change significantly for quaternary ammonium ions with the alkyl chain consisting of more than 3 carbon atoms. The small changes in the K_P may thus be related to entropic contributions. The interionic distance a_{TI} for the triple ion can be calculated using the expressions[33]

$$K_T = \frac{2\pi N_A a_{TI}^3}{1000} I(b_3) \tag{17}$$

$$b_3 = \frac{e^2}{a_{TI}\varepsilon_r kT} \tag{18}$$

$I(b_3)$ is a double integral tabulated in the literature[33] for a range of values of b_3. Since $I(b_3)$ is a function of a_{TI}, a_{TI} values have been calculated by an iterative computer program. The a_{TI} values (Table 6) for the electrolytes are greater than the corresponding a_{IP} values but are much less than the expected theoretical value $1.5a_{IP}$. This is probably due to repulsive forces between the two anions or cations in the triple ions $R_4N(I_2)^-$ and $(R_4N)_2^+I$ as suggested by Hazra et al.[38]

A perusal of Table 5 shows that the major portion of the electrolytes exists as ion pairs with a minor portion as triple ions. The tendency of triple ion formation can be judged from the K_T/K_P ratios, which are highest for Hept$_4$NI. These ratios suggest that strong association between the ions is due to the Coulombic interactions as well as to covalent forces in the solution. At very low permittivity of the solvent ($\varepsilon_r < 15$),[30] electrostatic interactions are very strong permitting the ion pair to attract free anions/cations from solution bulk and from triple ions[33,38] which acquire the charge of the combining ion, i.e.

$$\begin{aligned}&M^+ + A^- \leftrightarrow M^+ ... A^- \leftrightarrow MA\\&MA + A^- \leftrightarrow AMA^-\\&MA + M^+ \leftrightarrow MAM^+ \qquad [M = R_4N \text{ and } A = I]\end{aligned} \tag{19}$$

The effect of ternary association[39] thus removes some nonconducting species MA from solution and replaces them by triple ions which increase the conductance manifested by nonlinearity observed in conductance curves for the electrolytes in 80 mass % of CCl_4 in $PhNO_2$.

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[38] 20 to 23 and are listed in Table 5.

$$\alpha = (K_P c)^{-1/2} \tag{20}$$

$$\alpha_T = \frac{K_T}{K_P^{0.5}} c^{1/2} \tag{21}$$

$$c_P = c(1 - \alpha - 3\alpha_T) \tag{22}$$

$$c_T = \frac{K_T}{K_P^{1/2}} c^{3/2} \tag{23}$$

While the highest c_P value was found for Bu$_4$NI, the highest c_T value was found for Hept$_4$NI.

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