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Mahendra Nath Roy*, Lovely Sarkar, Rajani Dewan

Department of Chemistry, University of North Bengal, Darjeeling 734013, India

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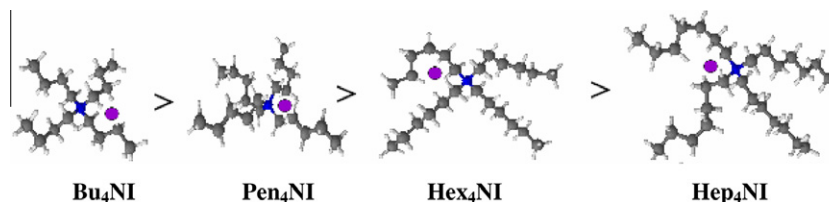
Tetraalkylammonium iodides

Triple-ion

Ion-pair

ABSTRACT

The electrolytic conductivity of the tetraalkylammonium iodides, R_4NI (R = butyl to heptyl), has been studied in (0.00, 0.25, 0.50 and 0.75) mass fraction of o-toluidine (C_7H_9N) in n-hexanol ($C_6H_{14}O$) at $T = 298.15$ K. The limiting molar conductance Λ_0 , association constants K_A and the co-sphere diameter R for ion-pair formation in 0.00 and 0.25 mass fraction of solvent mixture have been evaluated using the Fuoss-equation. However, the deviation of the conductometric curves (Λ versus $c^{1/2}$) from linearity for the electrolytes at 0.50 and 0.75 mass fraction of o-toluidine (C_7H_9N) in n-hexanol ($C_6H_{14}O$) indicates triple ion formation, and therefore the corresponding conductance data have been analyzed by the Fuoss–Kraus theory of triple ions. The observed values of the molar conductivity are explained by the ion-pairs ($M^+ + X^- \leftrightarrow MX$) and triple-ions ($2M^+ + X^- \leftrightarrow M_2X^+$, $M^+ + 2X^- \leftrightarrow MX_2^-$) formation. From the investigations, the following trend in conductance of the solvated salts has been observed:



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1. Introduction

Ion–ion and ion–solvent interactions can be studied in a better way by varying the properties such as the dielectric constant or viscosity which can be attained by using mixed solvent systems. A number of conductometric [1] and related studies of different electrolytes in non-aqueous solvents, especially mixed organic solvents, have made their optimal use in high-energy batteries [2] and for understanding organic reaction mechanisms [3]. The nature of the solvent mixtures greatly influences the ionic association of electrolytes in solution which is due to the mode of solvation of its ions [4–8]. Solvent properties such 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 conduc-

tances 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. Tetraalkylammonium salts are frequently selected as desired electrolytes in conductance studies, even though they show little or no solvation in solution due to their low surface charge density [14,15]. In continuation of our investigation on electrical conductance [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 o-toluidine in n-hexanol at $T = 298.15$ K.

2. Experimental

2.1. Materials

The solvents, o-toluidine (C_7H_9N) and n-hexanol ($C_6H_{14}O$) were purchased from Merck, India, and purified as reported earlier [16].

* Corresponding author. Tel.: +91 353 2776381.

E-mail address: mahendraroy2002@yahoo.co.in (M.N. Roy).

The mass fraction purity of the o-toluidine was ≥ 0.98 and that of n-hexanol ≥ 0.99 , respectively. The salts Bu₄NI (tetrabutylammonium iodide), Pen₄NI (tetrapentylammonium iodide), Hex₄NI (tetrahexylammonium iodide), and Hep₄NI (tetraheptylammonium iodide) of puriss grade were procured from Aldrich, Germany and used as purchased. The values of mass fraction purity obtained were $\geq 99\%$.

2.2. Apparatus and procedure

Binary solvent mixtures were prepared by mixing a required volume of o-toluidine and n-hexanol with earlier conversion of required mass of each liquid into volume at $T = 298.15$ K using exper-

TABLE 1

Physical properties of solvent mixture (o-toluidine + n-hexanol) at $T = 298.15$ K.

Mass fraction (w_1) (o- toluidine)	$\rho/\text{g} \cdot \text{cm}^{-3}$		$\eta/\text{mPa} \cdot \text{s}$		ε
	Expt.	Lit	Expt.	Lit	
0.00	0.8143	0.8161 [37]	4.590	4.590 [37]	13.30 [38,39]
0.25	0.8547		4.331		11.51
0.50	0.8780		4.118		09.72
0.75	0.9225		3.921		07.92

imental densities. A stock solution for each salt was prepared by mass and the working solutions were obtained by mass dilution. The density (ρ) was measured with an Anton Paar density-meter (DMA 4500 M) with a precision of $0.0005 \text{ g} \cdot \text{cm}^{-3}$. It was

TABLE 2

Molar conductance (Λ) and the corresponding concentration (c) for R₄NI (R= butyl, pentyl, hexyl and heptyl) in different 0.00 and 0.25 mass fraction of {o-toluidine (1) + n-hexanol(2)} at $T = 298.15$ K.

Bu ₄ NI		Pen ₄ NI		Hex ₄ NI		Hep ₄ NI	
$c \cdot 10^4/$ ($\text{mol} \cdot \text{dm}^{-3}$)	$\Lambda \cdot 10^4/$ ($\text{S} \cdot \text{m}^2 \cdot \text{mol}^{-1}$)	$c \cdot 10^4/$ ($\text{mol} \cdot \text{dm}^{-3}$)	$\Lambda \cdot 10^4/$ ($\text{S} \cdot \text{m}^2 \cdot \text{mol}^{-1}$)	$c \cdot 10^4/$ ($\text{mol} \cdot \text{dm}^{-3}$)	$\Lambda \cdot 10^4/$ ($\text{S} \cdot \text{m}^2 \cdot \text{mol}^{-1}$)	$c \cdot 10^4/$ ($\text{mol} \cdot \text{dm}^{-3}$)	$\Lambda \cdot 10^4/$ ($\text{S} \cdot \text{m}^2 \cdot \text{mol}^{-1}$)
$w_1 = 0.00$							
1.0882	7.28	1.2022	6.44	1.2081	5.60	1.2434	5.40
1.5067	6.90	1.4884	6.20	1.4957	5.37	1.5395	5.23
1.8654	6.60	1.7365	6.04	1.7450	5.18	1.7960	5.06
2.1763	6.37	1.9535	5.86	2.1556	4.96	2.0205	4.96
2.4484	6.14	2.1450	5.76	2.3267	4.86	2.2186	4.80
2.6884	5.95	2.3153	5.65	2.6175	4.69	2.3947	4.72
2.9018	5.89	2.6047	5.47	3.0538	4.44	2.6941	4.55
3.0927	5.77	3.0388	5.20	3.3654	4.36	3.1431	4.29
3.4200	5.52	3.4131	4.94	3.6953	4.14	3.4638	4.12
3.6903	5.36	3.7210	4.80	3.9886	4.00	3.8034	3.98
3.9174	5.23	3.9979	4.62	4.2283	3.92	4.1052	3.87
4.1972	5.00	4.2076	4.51	4.3906	3.80	4.3519	3.75
$w_1 = 0.25$							
1.0343	8.00	1.2924	6.71	1.2517	6.44	1.2933	6.2
1.4906	7.51	1.4191	6.60	1.4603	6.37	1.4550	6.12
1.6089	7.42	1.5317	6.48	1.6428	6.3	1.5976	6.04
2.0205	7.08	2.0678	6.10	1.8039	6.2	1.8379	5.88
2.2186	6.87	2.2155	5.95	2.1904	5.84	2.0324	5.71
2.3947	6.80	2.3346	5.88	2.3895	5.74	2.1930	5.63
2.6941	6.65	2.8417	5.57	2.5555	5.64	2.3280	5.59
3.1563	6.31	3.3260	5.35	2.7583	5.51	2.4430	5.47
3.5921	6.00	3.5698	5.23	3.0923	5.27	2.8314	5.24
3.8034	5.89	3.8034	5.16	3.6255	5.04	3.5293	4.84
4.1052	5.72	4.2130	4.89	4.3561	4.71	3.7293	4.69
4.3612	5.55	4.4627	4.85	4.5943	4.55	4.0623	4.52
1.0343	8.00	1.2924	6.71	1.2517	6.44	1.2933	6.2
$w_1 = 0.50$							
0.5280	13.16	0.4655	12.31	0.4724	11.20	0.3672	10.95
0.6537	11.60	0.5763	11.15	0.5848	10.12	0.5084	10.06
0.7627	10.44	0.6724	10.18	0.6823	9.28	0.6294	9.39
0.9421	9.01	0.8965	8.49	0.7676	8.64	0.7343	8.80
1.1440	7.60	1.0086	7.91	0.8428	8.21	0.8261	8.40
1.2480	7.06	1.1003	7.45	0.9097	7.90	0.9071	8.11
1.4990	6.09	1.2414	6.80	1.0722	7.13	0.9791	7.72
1.6343	5.86	1.3448	6.50	1.1569	6.75	1.1015	7.44
1.7559	5.59	1.4239	6.41	1.3158	6.35	1.2016	7.28
1.8866	5.51	1.4864	6.38	1.4448	6.43	1.2851	7.50
1.9515	5.59	1.6293	6.53	1.5082	6.53	1.3871	7.78
2.0020	5.80	1.7446	6.75	1.5817	6.68	1.4924	8.22
$w_1 = 0.75$							
0.2849	13.34	0.2562	12.96	0.1954	12.22	0.2056	11.47
0.3945	11.93	0.3548	11.20	0.2705	11.08	0.2847	10.56
0.4884	10.80	0.4393	10.00	0.3349	10.31	0.3525	9.79
0.5698	9.93	0.5125	8.88	0.4395	8.94	0.4112	9.14
0.6410	9.33	0.5766	8.22	0.5209	8.17	0.4626	8.62
0.8097	8.15	0.6331	7.59	0.5861	7.63	0.5080	8.10
0.9661	7.27	0.8054	6.36	0.6393	7.32	0.6168	7.20
1.0989	6.84	0.9461	5.79	0.6837	6.98	0.6729	6.94
1.2345	6.56	1.0250	5.63	0.8058	6.32	0.7592	6.59
1.3532	6.59	1.1104	6.00	0.8930	6.13	0.7931	6.61
1.4464	6.87	1.1714	6.60	0.9377	6.23	0.8224	6.74
1.4814	7.04	1.2300	7.20	1.0047	6.45	0.8910	7.11

calibrated by double-distilled water and dry air. Solvent viscosities were measured by means of a suspended Ubbelohde-type viscometer, calibrated at $T = 298.15$ K with doubly distilled water and purified methanol using density and viscosity values from the literature [17–19]. A thoroughly cleaned and thoroughly dried viscometer filled with experimental liquid was placed vertically within the glass-walled thermostat (Bose Panda Instruments Pvt. Ltd.) 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 point 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 is described elsewhere [11,20].

The conductance measurements were carried out in a Systronic 308 conductivity bridge (accuracy $\pm 0.01\%$) using a dip-type immersion conductivity cell, CD-10, having a cell constant of approximately (0.1 ± 0.001) . 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.* [21]. The conductance data were reported at a frequency of 1 kHz and were uncertain to $\pm 0.3\%$.

3. Results and discussion

The properties of the solvent mixtures are given in table 1. The concentrations and molar conductances Λ of R_4NI (R = butyl to heptyl) in different binary solvent mixtures of *o*-toluidine in *n*-hexanol are given in table 2. For the solvent mixtures, 0.00 and 0.25 mass fraction of *o*-toluidine in *n*-hexanol having relative permittivity (ϵ_r) 13.30 and 11.51, respectively, showed a linear conductance curves (Λ versus $c^{1/2}$) and extrapolation of $c^{1/2} = 0$ evaluated the starting limiting molar conductance for the electrolytes; however, as the relative permittivity, ϵ_r , dropped to 9.72 and 7.92 for the solvent mixture, 0.50 and 0.75 mass fraction of *o*-toluidine in *n*-hexanol, respectively, nonlinearity (figure 1) was observed in conductance curves.

The conductance data for the solvent mixture, 0.00 and 0.25 mass fraction of *o*-toluidine in *n*-hexanol have been analyzed using the Fuoss conductance equation [22]. So with a given set of conductivity values (c_j , $j = 1, \dots, n$), three adjustable parameters, *i.e.*, Λ_0 , K_A and R have been derived from the Fuoss equation. Here, Λ_0 is the limiting molar conductance, K_A is the observed association constant and R is the association distance, *i.e.*, the maximum centre to centre distance between the ions in the solvent separated ion-pairs. There is no precise method [23] for determining the R value but in order to treat the data in our system. The R value is assumed to be, $R = a + d$, where a is the sum of the crystallographic radii of the ions and d is the average distance corresponding to the side of a cell occupied by a solvent molecule. The distance, d is given by:

$$d/\text{cm} = 1.183 \cdot 10^{-8} [M/(\rho/g \cdot \text{cm}^{-3})]^{1/3}, \quad (1)$$

where M is the molar mass and ρ is the density of the solvent. For mixed solvents, M is replaced by the mole fraction average molar mass (M_{av}) which is given by

$$M_{av} = M_1 M_2 / (W_1 M_2 + W_2 M_1), \quad (2)$$

where W_1 is the weight fraction of the first component of molar mass M_1 . Thus, the Fuoss conductance equation may be represented as follows:

$$\Lambda = p[\Lambda_0(1 + R_K) + E_L], \quad (3)$$

$$p = 1 - \alpha(1 - \gamma), \quad (4)$$

$$\gamma = 1 - K_A c \gamma^2 f^2, \quad (5)$$

$$-\ln f = \beta k / 2(1 + kR), \quad (6)$$

$$\beta = e^2 / \epsilon k_B T, \quad (7)$$

$$K_A = K_R / (1 - \alpha) = K_R (1 + K_S), \quad (8)$$

where, Λ_0 is the limiting molar conductance, K_A is the observed association constant, R is the association distance, R_K is the relaxation field effect, E_L is the electrophoretic countercurrent, k is the radius of the ion atmosphere, ϵ is the relative permittivity of

the solvent mixture, e is the electron charge, c is the molarity of the solution, k_B is the Boltzmann constant, K_S is the association constant of the contact-pairs, K_R is the association constant of the solvent-separated pairs, γ is the fraction of solute present as unpaired ion, α is the fraction of contact pairs, f is the activity coefficient, T is the absolute temperature and β is twice the Bjerrum distance.

The computations were performed using the program suggested by Fuoss. The initial Λ_0 values for the iteration procedure are obtained from Shedlovsky extrapolation of the data [24]. Input for the program includes the number of data points, n , followed by ϵ , η (viscosity of the solvent mixture), initial Λ_0 value, T , ρ (density of the solvent mixture), mole fraction of the first component, molar mass, M_1 and M_2 along with c_j , Λ_j values where $j = 1, 2, \dots, n$ and an instruction to cover preselected range of R values.

In practice, calculations are performed by finding the values of Λ_0 and α which minimize the standard deviation, δ , whereby

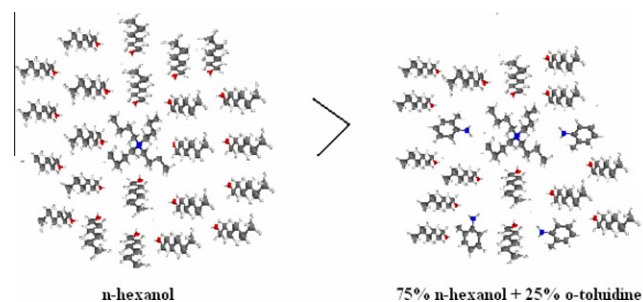
$$\delta^2 = \sum [A_{j(\text{calc})} - A_{j(\text{exp})}]^2 / n - 2 \quad (9)$$

for a sequence of R values and then plotting σ against R , the best-fit R corresponds to the minimum of the δ - R versus R curve. So, an approximate sum is made over a fairly wide range of R values using 0.1 increment to locate the minimum but no significant minimum is found in the δ - R curves, thus R values is assumed to be $R = a + d$, with terms having usual significance. Finally, the corresponding Λ_0 and K_A values are obtained which are reported in table 3 along with R and δ for the binary mixtures of the salts. ΔG° is given by the relationship [25] and given in table 1 (supplementary material),

$$\Delta G^\circ = -RT \ln K_A. \quad (10)$$

Table 3 reveals that the limiting molar conductance Λ_0 for the electrolytes in the 0.00 and 0.25 mass fraction of *o*-toluidine in *n*-hexanol increases with the increasing amount of *o*-toluidine in the mixtures.

The solvation model for the tetrabutyl ammonium ion can be shown as follows:

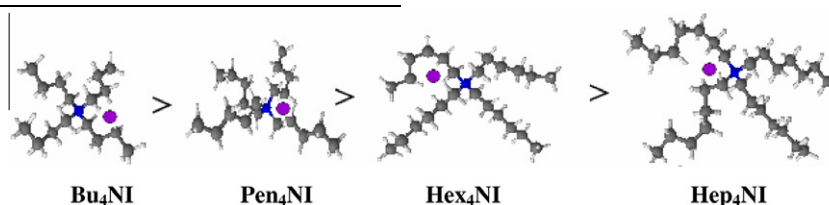


With the decrease in size of the solvated ions in case of 0.25 mass fraction of solvent mixture, the conductance of the salt increases with the increase of *o*-toluidine in the solvent mixture.

This fact is in line with the decrease of the viscosity for the solvent mixtures with increasing content of *o*-toluidine suggests concomitant increase in limiting molar conductance for the electrolytes [14,26] which is opposite to the results obtained in our recently published paper where the limiting molar conductance of the tetraalkylammonium salts decreases with the decrease in the viscosity of the solvent mixture [27].

The conductance should decrease with the decrease of the relative permittivity [27] but we obtained a reverse trend. This trend suggests predominance of solvent viscosity η over the relative permittivity ϵ_r in effecting the electrolytic conductance of the electrolytes under study in these media. In a particular solvent mixture, the limiting molar conductance Λ_0 of the electrolytes under investigation decrease as the size of the alkyl group increases, in contra-position to the conductance behaviour of the alkali metal cations, as tetraalkylammonium salts are characterized by their low surface charge density [14,15].

The trend in the conductance of the electrolytes is in the following order:



The trend in Λ_0 can be discussed through another characteristic function called the Walden product, $\Lambda_0\eta$. From tables 3 and 1 (supplementary material), it is seen that although the solvent viscosity η decreases with the increase of o-toluidine in the solvent mixture, the Walden product $\Lambda_0\eta$ increases with increasing concentration of o-toluidine of the solvent mixtures, this suggests the predominance of Λ_0 over η . The negative values of ΔG° can be explained by considering the participation of specific covalent interaction in the ion-association process. The uniformly decreasing values of ΔG° indicate a greater degree of association.

The conductance data for all the electrolytes in 0.50 and 0.75 mass fraction of o-toluidine in n-hexanol have been analyzed by the classical Fuoss–Kraus theory of triple-ion formation in the form [28,29]

$$\Lambda g(c)c^{1/2} = \frac{\Lambda_0}{(K_p)^{1/2}} + \frac{\Lambda_0^2 K_T}{(K_p)^{1/2}} \left(1 - \frac{\Lambda}{\Lambda_0}\right) c, \quad (11)$$

$$g(c) = \frac{\exp\left\{-2.303\beta'(cA)^{0.5}/\Lambda_0^{0.5}\right\}}{\left\{1 - S(cA)^{0.5}/\Lambda_0^{1.5}\right\}(1 - A/\Lambda_0)^{0.5}}, \quad (12)$$

$$\beta' = 1.8247 \times 10^6 / (\epsilon T)^{1.5}, \quad (13)$$

$$S = \alpha\Lambda_0 + \beta = \frac{0.8204 \times 10^6}{(\epsilon T)^{1.5}} \Lambda_0 + \frac{82.501}{\eta(\epsilon T)^{0.5}}. \quad (14)$$

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 conductance of the two triple ions $R_4N(l_2)^-$ and $(R_4N)_2^+I$ for R_4NI salts; $K_p \approx K_A$ and K_T are the ion pair and triple ion formation constants. To make equation (11) applicable, the symmetrical approximation of the two possible constants of triple ions equal to each other has been adopted [30] and Λ_0 values for the studied electrolytes in 0.50 and 0.75 mass fraction of o-toluidine in n-hexanol have been calculated [31]. The Λ_0^T is calculated by setting the triple ion conductance equal to $2/3\Lambda_0$ [32].

The ratio Λ_0^T/Λ_0 was thus set equal to 0.667 during linear regression analysis of equation (11). Table II (supplementary material) shows the calculated limiting molar conductance of simple ion (Λ_0), limiting molar conductance of triple ion Λ_0^T , slope and intercept of equation (11) for R_4NI (R = butyl, pentyl, hexyl, and heptyl) in 0.50 and 0.75 mass fraction of o-toluidine in n-hexanol at $T = 298.15$ K.

The linear regression analysis of equation (11) for the electrolytes with an average regression constant, $R^2 = 0.9653$, gives intercepts and slopes. These values permit the calculation of other derived parameters such as K_p and K_T listed in table 4. It is observed from figure 1 that Λ passes through a minimum as c increases. A perusal of table 4 shows that the major portion of the electrolytes exists as ion pairs and a minor portion as triple ions. The value of $\log(K_T/K_p)$ is found to be highest in Hep_4NI and lowest for Bu_4NI as given in table 4 and shown in figure 2. The result is in line with our recently published paper where the heptyl salt has the highest tendency to form triple ions [33].

At very low permittivity of the solvent, i.e., $\epsilon < 10$, electrostatic ionic interactions are very large. So the ion-pairs attract the free cations and anions ions present in the solution medium as the distance of the closest approach of the ions becomes minimum. This results in the formation of triple-ions, which acquire the charge of the respective ions in the solution [34] i.e.,

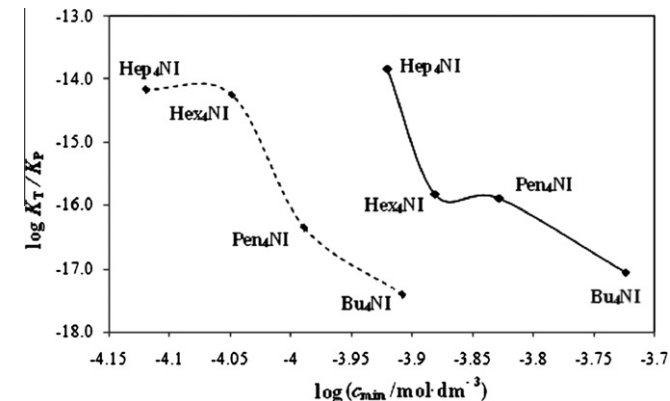


FIGURE 2. The plots of $\log K_T/K_P$ versus $\log c_{\min}$, where K_P is the ion-pair formation constant, K_T is the triple-ion formation constant and c_{\min} is the salt concentration at the minimum conductivity for the salts under investigations in 0.50 (—◆—) and 0.75 (---◇---) mass fraction of {o-toluidine (1) + n-hexanol (2)} mixtures at $T = 298.15$ K.

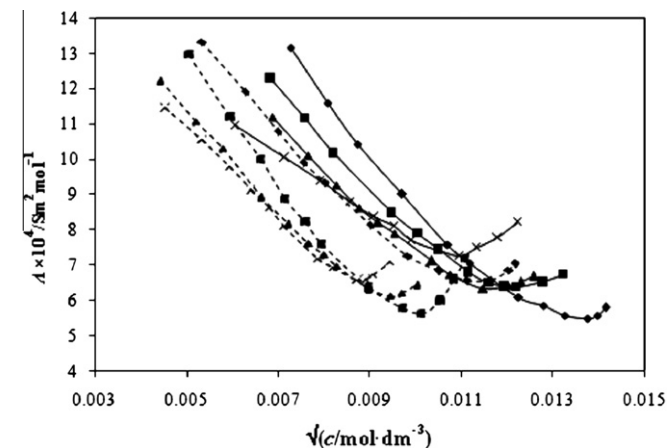


FIGURE 1. The plots of equivalent conductance (Λ) versus square root of salt concentration ($C^{1/2}$) for the salts under investigations in 0.50 and 0.75 mass fraction of {o-toluidine (1) + n-hexanol (2)} mixtures at 298.15 K: graphical points for 0.50 mass fraction of {o-toluidine (1) + n-hexanol (2)} mixtures (—◆—) Bu_4NI , (—■—) Pen_4NI , (—▲—) Hex_4NI , (—x—) Hep_4NI and graphical points for 0.75 mass fraction of {o-toluidine (1) + n-hexanol (2)} mixtures (---◇---) Bu_4NI , (---■---) Pen_4NI , (---▲---) Hex_4NI , (---x---) Hep_4NI .

TABLE 3

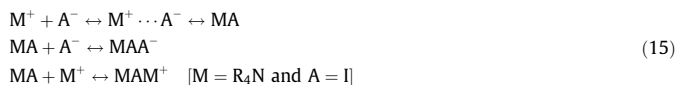
Limiting molar conductance Λ_0 , association constant K_A , co-sphere diameter R and standard deviations σ of experimental Λ for the electrolytes in 0.00 and 0.25 mass fraction of {o-toluidine(1) + n-hexanol(2)} at $T = 298.15$ K.

Salts	$\Lambda^0 \cdot 10^4 / (S \cdot m^2 \cdot mol^{-1})$	$K_A \cdot 10^{-3} / (dm^3 \cdot mol^{-1})$	R/nm	δ
$w_1 = 0.00$				
Bu_4NI	10.85	7.10	1.393	0.10
Pen_4NI	10.10	7.96	1.472	0.09
Hex_4NI	8.99	8.82	1.543	0.08
Hep_4NI	8.86	9.00	1.608	0.08
$w_1 = 0.25$				
Bu_4NI	11.51	6.59	1.378	0.09
Pen_4NI	10.18	7.09	1.457	0.04
Hex_4NI	10.07	7.49	1.527	0.10
Hep_4NI	9.88	8.08	1.592	0.09

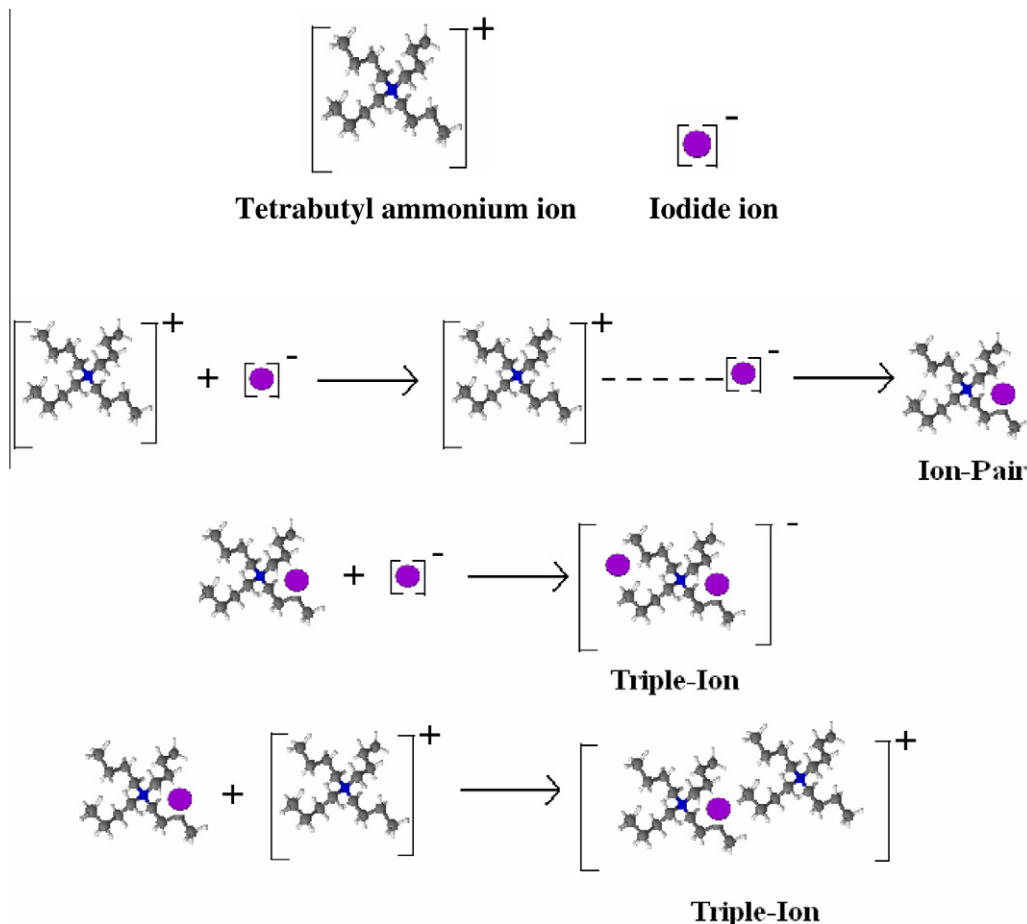
TABLE 4

Salt concentration at the minimum conductivity (c_{\min}) along with the ion-pair formation constant (K_P), triple ion formation constant (K_T) for R_4NI (R = butyl, pentyl, hexyl, and heptyl) in 0.50 and 0.75 mass fraction of {o-toluidine (1) + n-hexanol (2)} mixtures at $T = 298.15$ K.

Salts	$c_{\min} \cdot 10^4 / (mol \cdot dm^{-3})$	$\log c_{\min}$	$K_P \cdot 10^{-14} / (mol \cdot dm^{-3})^{-1}$	$K_T / (mol \cdot dm^{-3})^{-1}$	$K_T/K_P \cdot 10^{18}$	$\log K_T/K_P$
$w_1 = 0.50$						
Bu_4NI	1.8866	-3.7243	1.8163	1.5962	0.0009	-17.0561
Pen_4NI	1.4864	-3.8279	0.1741	2.2736	0.0131	-15.8841
Hex_4NI	1.3158	-3.8808	0.1687	2.5418	0.0151	-15.8220
Hep_4NI	1.2016	-3.9202	0.0025	3.6382	1.4570	-13.8365
$w_1 = 0.75$						
Bu_4NI	1.2345	-3.9085	6.3890	2.5264	0.0004	-17.4030
Pen_4NI	1.0250	-3.9893	0.6634	2.9868	0.0045	-16.3466
Hex_4NI	0.8930	-4.0491	0.0070	3.9049	0.5614	-14.2508
Hep_4NI	0.7592	-4.1197	0.0067	4.6691	0.6937	-14.1588



Schematically the triple-ion formation for 0.50 and 0.75 mass fraction of o-toluidine in n-hexanol at $T = 298.15$ K can be depicted as given below taking tetrabutylammonium bromide as an example:



of the salt in the solvent as shown in figure 3. The effect of ternary association [36] is to remove some non-conducting species MA from the solution and replace them by triple ions, which contribute to the conductance.

The picture can be well understood for the rest of the salts in a similar manner.

Furthermore, the ion-pair and triple-ion concentrations, C_p and C_T , respectively of the electrolyte are also calculated at the highest concentration of tetraalkylammonium iodides and bromides in 0.50 and 0.75 mass fraction of o-toluidine in n-hexanol using the following relations [35]:

$$\alpha = 1/(K_p^{1/2} C^{1/2}), \quad (16)$$

$$\alpha_T = (K_T/K_p^{1/2}) C^{1/2}, \quad (17)$$

$$C_p = C(1 - \alpha - 3\alpha_T), \quad (18)$$

$$C_T = (K_T/K_p^{1/2}) C^{3/2}. \quad (19)$$

Here, α and α_T are the fraction of ion-pairs and triple-ions as given in table 5, respectively. Thus, the values of C_p and C_T given in table 5 indicate that the ions are mainly present as ion-pairs even at the highest concentration of each of the salts in the solvent and a small fraction existing as triple-ions. It is observed that at the highest concentration of the electrolytes in the solvent, Bu₄NI has the minimum fraction of ion-pairs and triple-ions whereas Hep₄NI has the maximum fraction of ion-pairs and triple-ions present in 0.50 and 0.75 mass fraction of o-toluidine in n-hexanol. Furthermore, C_p is maximum for Bu₄NI, minimum for Hep₄NI and C_T is found to be highest for Hep₄NI and lowest for Bu₄NI. The ion-pair fraction (α), triple-ion fraction (α_T), ion-pair concentration (C_p) and triple-ion concentration (C_T) have been also calculated over the whole concentration range of the tetraalkylammonium halides in 0.50 and 0.75 mass fraction of o-toluidine in n-hexanol and the data are provided in table III (supplementary material). It is observed for all the salts that the amount of the triple-ions in the solution mixture increases with the increase in concentration

TABLE 5

Salt concentration at the minimum conductivity (c_{\min}), the ion pair fraction (α), triple ion fraction (α_T), ion pair concentration (c_p) and triple-ion concentration (c_T) for R₄NI (R = butyl, pentyl, hexyl, heptyl) in 0.50 and 0.75 mass fraction of {o-toluidine (1) + n-hexanol (2)} mixtures at $T = 298.15$ K.

Salts	$c_{\min} \cdot 10^4 /$ (mol · dm ⁻³)	$\alpha \cdot 10^6$	$\alpha_T \cdot 10^7$	$c_p \cdot 10^4 /$ (mol · dm ⁻³)	$c_T \cdot 10^{11} /$ (mol · dm ⁻³)
<i>w₁ = 0.50</i>					
Bu ₄ NI	1.8866	0.1708	0.0515	1.8866	0.0971
Pen ₄ NI	1.4864	0.6216	0.2101	1.4864	0.3122
Hex ₄ NI	1.3158	0.6712	0.2245	1.3158	0.2954
Hep ₄ NI	1.2016	5.7730	2.5238	1.2016	3.0327
<i>w₁ = 0.75</i>					
Bu ₄ NI	1.2345	0.1126	0.0351	1.2345	0.0434
Pen ₄ NI	1.0250	0.3835	0.1174	1.0250	0.1203
Hex ₄ NI	0.8930	4.0122	1.3992	0.8930	1.2495
Hep ₄ NI	0.7592	4.4240	1.5681	0.7592	1.1905

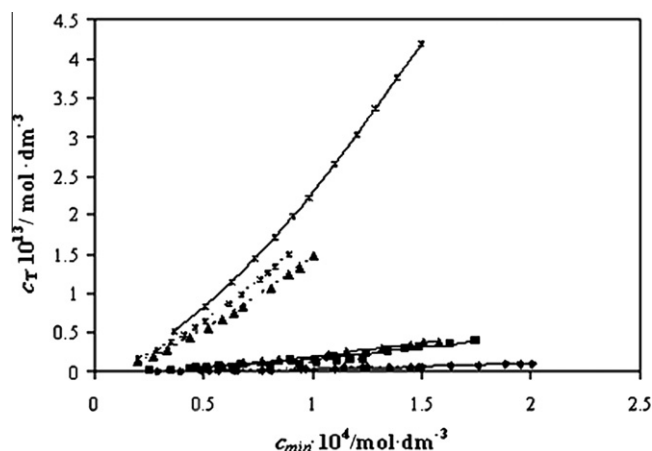


FIGURE 3. The plots of triple-ion concentrations, c_T , versus the salt concentration at the minimum conductivity, c_{min} , for the salts under investigations 0.50 and 0.75 mass fraction of {o-toluidine (1) + n-hexanol (2)} mixtures at 298.15 K. Graphical points for 0.50 mass fraction of {o-toluidine (1) + n-hexanol (2)} mixtures (—♦—) Bu_4NI , (—■—) Pen_4N , (—▲—) Hex_4NI , (—*—) Hep_4NI and graphical points for 0.70 mass fraction of {o-toluidine (1) + n-hexanol (2)} mixtures, (---♦---) Bu_4NI , (---■---) Pen_4N , (---▲---) Hex_4NI , (---*---) Hep_4NI .

4. Conclusion

It becomes clear that the tendency of the ion-pair and triple-ion formation of R_4NI depends on the size, the charge distribution of the ions and also the relative permittivity of the solvent mixtures. With increasing amount of o-toluidine *i.e.*, on decreasing relative permittivity along with decreasing viscosity of the solvent mixtures results in increase in limiting molar conductance of the electrolytes. Also in the solution mixture the amount of the triple-ions increases with the increasing concentration of the salt in the solvent for all the salts studied.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jct.2010.10.008.

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