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Ion-pair and triple-ion formation of some tetraalkylammonium iodides in n-hexanol and its binary mixtures with o-toluidine

Mahendra Nath Roy *, Lovely Sarkar, Rajani Dewan

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

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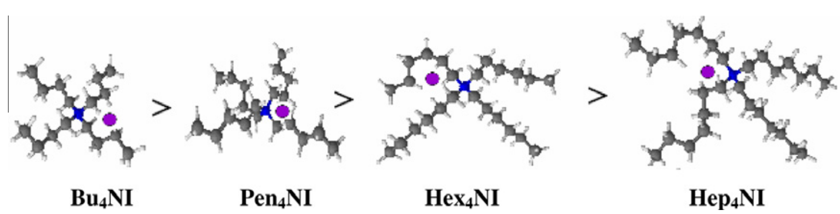
The electrolytic conductivity of the tetraalkylammonium iodides, R_4NI (R = butyl to heptyl), has been studied in (0.00, 0.25, 0.50 and 0.75) mass fraction of o-toluidine (C_7H_9N) in n-hexanol ($C_6H_{14}O$) at $T = 298.15$ K. The limiting molar conductance Λ_0, association constants K_A and the co-sphere 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:



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 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. 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).

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The mass fraction purity of the o-toluidine was ⩾0.98 and that of n-hexanol ⩾ 0.99, respectively. The salts Bu_4NI (tetrabutylammonium iodide), Pen_4NI (tetrapentylammonium iodide), Hex_4NI (tetrahexylammonium iodide), and Hep_4NI (tetraheptylammonium iodide) of puriss grade were procured from Aldrich, Germany and used as purchased. The values of mass fraction purity obtained were ⩾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 experimental 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 $g \cdot cm^{-3}$. It was

TABLE 1
Physical properties of solvent mixture (o-toluidine + n-hexanol) at T = 298.15 K.

Mass fraction (w_1) (o-toluidine)	ρ/g · cm^{-3} Expt.	ρ/g · cm^{-3} Lit	η/mPa · s Expt.	η/mPa · s Lit	ε
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

TABLE 2
Molar conductance (Λ) and the corresponding concentration (c) for R_4NI (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_4NI $c \cdot 10^4$/(mol · dm^{-3})	Bu_4NI $\Lambda \cdot 10^4$/(S · m^2 · mol^{-1})	Pen_4NI $c \cdot 10^4$/(mol · dm^{-3})	Pen_4NI $\Lambda \cdot 10^4$/(S · m^2 · mol^{-1})	Hex_4NI $c \cdot 10^4$/(mol · dm^{-3})	Hex_4NI $\Lambda \cdot 10^4$/(S · m^2 · mol^{-1})	Hep_4NI $c \cdot 10^4$/(mol · dm^{-3})	Hep_4NI $\Lambda \cdot 10^4$/(S · m^2 · 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