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## Comparative Solvation Behaviour of $\text{Li}^+$ and $\text{Na}^+$ ions in Acetonitrile and Nitromethane Binary Mixtures at 298.15 K

Hardeep Anand\*, Narender Singh

Department of Chemistry, Kurukshetra University, Kurukshetra-136119, India

### ABSTRACT

Molar conductance of lithium perchlorate ( $\text{LiClO}_4$ ), sodium perchlorate ( $\text{NaClO}_4$ ), sodium tetraphenylborate ( $\text{NaBPh}_4$ ), tetrabutylammonium perchlorate ( $\text{Bu}_4\text{NClO}_4$ ) and tetrabutylammonium tetraphenylborate ( $\text{Bu}_4\text{NBPh}_4$ ) have been measured in the range 0.005-0.2 mol  $\text{kg}^{-1}$  in binary mixtures of acetonitrile (AN) and nitromethane (NM) containing 0, 10, 20, 40, 60, 80 and 100 mol% of NM in AN at 298.15 K. The experimental data of conductance has been analyzed using Shedlovsky method to evaluate limiting molar conductance ( $A_0$ ) of these electrolytes which were further split to obtain limiting ionic conductances ( $\lambda_{\pm}^0$ ) of various ions present in salts. The ionic radii ( $r_i$ ) of ions in solutions were calculated using a modified form of Stoke's law and were analyzed in the aspects of ion-solvent interactions. The solvated radii ( $r_i$ ) of  $\text{Li}^+$  and  $\text{Na}^+$  ions were found to be greater than rest of the ions in the entire solvent composition range which indicates strong solvation of the ions.  $\text{Bu}_4\text{N}^+$  and  $\text{Ph}_4\text{B}^-$  ions were found to show poor solvation due to solvophobic interaction. Solvated radii ( $r_i$ ) values indicate preferential solvation of  $\text{Li}^+$  and  $\text{Na}^+$  ions in the intermediate solvent composition range than in pure AN and NM.  $\text{Li}^+$ , however, is found to be better solvated than  $\text{Na}^+$  in  $\text{AN}^+$  NM binary mixtures at all compositions.

**Keywords:** Acetonitrile, Nitromethane, Molar conductance, Solvated radii, Preferential solvation

### INTRODUCTION

Study of solvation behavior of ions in mixed organic solvents is a subject of intensive investigation all over the world. The conductance studies of electrolytes are of great importance for obtaining information about the nature of interactions between the ions and solvent molecules, existing in the salt solutions of the solvent binary mixtures. Lithium presently is being extensively used in high energy density rechargeable batteries. This requires the selection of stable and highly polar aprotic solvents, whose polarity leads to strong intermolecular interactions, which can lead to the formation of highly conductive electrolytic solutions with lithium salts. Conductance measurements of  $\text{LiCl}$ ,  $\text{NaI}$ ,  $\text{KI}$ ,  $\text{KClO}_4$  etc in  $\text{N,N}$ -dimethylformamide, dimethylsulfoxide and hexamethylphosphotriamide gives solvation behaviour of alkali metal ions [1]. Some conductance studies of a large number of electrolytes in binary mixtures of two dipolar aprotic solvents are also available [2-5]. Since cations are highly solvated as compared to anions in dipolar aprotic solvents, therefore in all these studies, emphasis was laid down on the solvation behavior of cations. However solvation of anions studied in work [6,7], in which the conductance of ions  $\text{I}^-$ ,  $\text{Br}^-$ ,  $\text{Cl}^-$ ,  $\text{ClO}_4^-$ ,  $\text{Ph}_4\text{B}^-$ ,  $\text{Na}^+$  and  $\text{Bu}_4\text{N}^+$  was determined. Ion-solvent interaction of alkali metal salts in water and propan-1-ol were studied by conductometric studies [8]. In the present work, a comparative solvation behavior of lithium and sodium salts has been investigated. The molar conductance measurements of lithium perchlorate ( $\text{LiClO}_4$ ), sodium perchlorate ( $\text{NaClO}_4$ ), sodium tetraphenylborate ( $\text{NaBPh}_4$ ), tetrabutylammonium tetraphenylborate ( $\text{Bu}_4\text{NBPh}_4$ ) and tetrabutylammonium perchlorate ( $\text{Bu}_4\text{NClO}_4$ ) in acetonitrile (AN), nitromethane (NM) and in their binary mixtures have been carried out. The purpose of present studies is to determine the solvation behavior of  $\text{Li}^+$  and  $\text{Na}^+$  ions in  $\text{AN}^+$  NM mixtures which can help in selection of solvents for the lithium batteries.

### EXPERIMENTAL

Acetonitrile (99.7%, Rankem) was further purified as reported and Nitromethane (99%, Hi-Media) was stored over 4 Å molecular sieves for 48 hours and then purified by vacuum distillation. The purified solvents AN, and NM had ultrasonic velocity 1280.3  $\text{ms}^{-1}$  and 1317.1  $\text{ms}^{-1}$  and density 0.77686  $\text{kg}^{-3}$  and 1.1329  $\text{kg}^{-3}$  respectively which are in good agreement with the Literature values.  $\text{Bu}_4\text{NBPh}_4$  and  $\text{Bu}_4\text{NClO}_4$  were used as reference electrolytes in the present work. These salts were prepared by methods already reported [9]. The salts  $\text{LiClO}_4$ ,  $\text{NaClO}_4$ , and  $\text{NaBPh}_4$  were purified by recrystallization.

Molar conductances of the electrolytes were measured in AN, NM and their mixtures at 1000 Hz frequency at  $298.15 \pm 0.001$  K using a digital conductivity meter (Model NDC-736, Naina Electronics, New Delhi, India). The procedure of experiment were same as already reported [3,8]. The overall accuracy of the conductance measurements was found to be  $\pm 0.2$  %. The cell constant of the conductivity cell was determined by using several concentrations of KCl solutions in conductivity water and following the method reported by Fuoss and Coworkers [10].

A range of concentrations of the salts in AN<sup>+</sup> NM binary mixtures was prepared by diluting stock solutions of appropriate concentrations. The mixtures were prepared by mass and were kept in air tight stoppered glass bottles to avoid the absorption of atmospheric moisture. Solutions were prepared by mass; using an A&D company limited electronic balance (Japan, Model GR-202) with precision of  $\pm 0.01$  mg. The probable error in the molality was estimated to be less than  $\pm 1 \times 10^{-4}$ . In all cases, the measurements were repeated twice in order to obtain reproducible results [11].

## RESULTS AND DISCUSSION

Molar conductances of Bu<sub>4</sub>NBPh<sub>4</sub>, Bu<sub>4</sub>NCIO<sub>4</sub>, NaBPh<sub>4</sub>, LiClO<sub>4</sub> and NaClO<sub>4</sub> have been measured at different salt concentrations in the range of 0.005-0.2 mol dm<sup>-3</sup> in binary mixtures of AN<sup>+</sup> NM containing 10, 20, 40, 60, 80, 100 mol% of NM at 298.15 K. The limiting molar conductances ( $\Lambda_o$ ) and the ion-association constants ( $K_A$ ) reported in Tables 1 and 2 have been calculated by a least square method using a complete program involving the Shedlovsky method [12]. The Shedlovsky equation is given as:

$$\frac{1}{S\Lambda} = \frac{1}{\Lambda_o} + \frac{C\Lambda S f_{\pm}^2 K_A}{\Lambda_o^2} \quad (1)$$

Where  $f_{\pm}$  is the mean ion activity coefficient of the electrolyte and  $S$  is Onsager slope. As the precision of our conductance data is not better than  $\pm 0.2\%$ , the use of any other conductance equation which demands a precision in the conductance data much better than  $\pm 0.1\%$  was not thought worthwhile to analyze the present conductance data.  $\Lambda_o$  values already available [11-14] for some of these salts in AN are reported in parenthesis in Table 2 for comparison with the present values. A good agreement had been found between the present values and available values. Ion-association constant ( $K_A$ ) values however do not give any important information regarding ion-solvent interactions.

### Limiting ion conductances

For calculating limiting ion conductances Gill and coworkers proposed the following equations for Bu<sub>4</sub>NBPh<sub>4</sub> [14,15]:

$$\frac{\lambda_{\pm}^o(Bu_4N^+)}{\lambda_{\pm}^o(Ph_4B^-)} = \frac{5.35 - (0.0103\varepsilon + r_y)}{5.00 - (0.0103\varepsilon + r_y)} \quad (2)$$

And by using Kohlrausch's law of independent ion mobilities:

$$\lambda_{\pm}^o(Bu_4N^+) + \lambda_{\pm}^o(Ph_4B^-) = \Lambda^o(Bu_4NBPh_4) \quad (3)$$

Using equations (2) and (3) limiting ion conductance values of Bu<sub>4</sub>N<sup>+</sup> and Ph<sub>4</sub>B<sup>-</sup> in AN, NM and AN<sup>+</sup> NM mixtures have been calculated from the  $\Lambda$  data of Bu<sub>4</sub>NBPh<sub>4</sub>. The values of limiting ionic conductivity ( $\lambda^o$ ) in AN, NM and AN<sup>+</sup> NM mixtures calculated using the above equation, are given in Table 3.

### Solvated radii and preferential solvation

Gill et al.; Gill [16,17] proposed a method to calculate solvated radii for Li<sup>+</sup>, Na<sup>+</sup>, Bu<sub>4</sub>N<sup>+</sup>, Ph<sub>4</sub>B<sup>-</sup> and ClO<sub>4</sub><sup>-</sup> with the help of limiting ionic conductances from  $\Lambda_o$  values of the electrolytes in pure and mixed non-aqueous solvents using the equation:

$$r_i = \left[ Z \left| F^2 / (6\pi\eta N \lambda_i) + (0.0103\varepsilon + r_y) \right| \right] \quad (4)$$

Where,  $Z$  and  $r_i$  are the charge and actual radius of an ion in solution.  $F$  and  $N$  are Faraday's constant and Avogadro's number respectively,  $\eta$  and  $\varepsilon$  are solvent viscosity and dielectric constant of the medium respectively,  $r_y$  is an adjustable parameter reported and equal to 0.085 NM for AN and NM and their mixtures (17). The  $r_i$  values for different ions are listed in Table 3 along with their crystallographic radii ( $r_c$  for Na<sup>+</sup>=0.095; Li<sup>+</sup>=0.060; Ph<sub>4</sub>B<sup>-</sup>=0.053, Bu<sub>4</sub>N<sup>+</sup>=0.50 and ClO<sub>4</sub><sup>-</sup>=0.36 NM) [18-20]. A comparison of solvated radii with crystallographic radii of the ions suggests the preferential solvation of Li<sup>+</sup> and Na<sup>+</sup> ions upto greater extent by NM as compared to AN and in NM rich region of the mixtures. Bu<sub>4</sub>N<sup>+</sup> and Ph<sub>4</sub>B<sup>-</sup> seem to be similarly solvated in all AN<sup>+</sup> NM mixtures. The  $r_i$  values for ClO<sub>4</sub><sup>-</sup> ion show weaker solvation in mixtures than in pure solvents. Solvated radii ( $r_i$ ) values (Bu<sub>4</sub>N<sup>+</sup>=5.00 Å and Ph<sub>4</sub>B<sup>-</sup>=5.30 Å) are approximately close to their crystallographic radii (Bu<sub>4</sub>N<sup>+</sup>=5.0 Å and Ph<sub>4</sub>B<sup>-</sup>=5.35 Å) [19,20]. This shows that Bu<sub>4</sub>N<sup>+</sup> and Ph<sub>4</sub>B<sup>-</sup> ions are not solvated in the AN<sup>+</sup> NM solvent system [21-23] which is due to their large size and small charge density. In Acetonitrile, the limiting ion molar conductance for Bu<sub>4</sub>N<sup>+</sup> and Ph<sub>4</sub>B<sup>-</sup> decreases with increase in NM composition in Mixtures which indicate some special type of interactions with the solvent molecules which are hydrophobic and their magnitude increase in AN-rich region of the mixtures.

Table 1: Viscosity ( $\eta$ ), permittivity ( $\epsilon_o$ ), for AN<sup>+</sup> NM mixture at 298.15 K

Mol % NM	$\epsilon_o$	$\eta$ /cP
0	36.0	0.342
20	36.0	0.415
40	36.1	0.456
60	36.2	0.493
80	36.3	0.507
100	36.0	0.612

$\epsilon_o$  values in this table have been taken [10] and  $\eta$ /cP values were experimentally measured

**Table 2: Molar conductance ( $\Lambda_0$ ) ( $S\cdot cm^2\cdot mol^{-1}$ ) and ion-association constant ( $K_A$ ) ( $dm^3\cdot mol^{-1}$ ) values of  $LiClO_4$ ,  $NaClO_4$ ,  $NaBPh_4$ ,  $Bu_4NBPh_4$  and  $Bu_4NClO_4$  in  $AN^+$  NM mixtures at 298.15 K**

Salt	Mol % NM											
	0		20		40		60		80		100	
	$\Lambda_0$	$K_A$	$\Lambda_0$	$K_A$	$\Lambda_0$	$K_A$	$\Lambda_0$	$K_A$	$\Lambda_0$	$K_A$	$\Lambda_0$	$K_A$
$LiClO_4$	173.6	-	135.50	-	118.80	-	109.00	-	116.40	-	98.80	-
$NaClO_4$	180.4	-	137.60	17.3	122.50	6.1	112.40	-	119.80	-	101.10	-
$NaBPh_4$	136.8	-	107.83	11.9	98.04	14.8	92.31	64.6	89.23	16.6	76.15	-
$Bu_4NBPh_4$	121.2	6.7	96.58	30.9	90.76	39.4	82.40	-	80.64	-	68.24	-
$Bu_4NClO_4$	164.5	-	131.30	12.4	120.59	8.5	117.09	17.5	111.22	16.4	91.94	-

**Table 3: Limiting molar ionic conductance ( $\lambda_{\pm}^0$ ) ( $S\cdot cm^2\cdot mol^{-1}$ ) and solvated ionic radii ( $r_i$ ) (NM) for  $Li^+$  and  $Na^+$ ,  $Bu_4N^+$ ,  $Ph_4B^-$  and  $ClO_4^-$  ions in  $AN^+$  NM at 298.15 K**

Ions	$r_c$	Mol % NM											
		0		20		40		60		80		100	
		$\lambda_{\pm}^0$	$r_i$	$\lambda_{\pm}^0$	$r_i$	$\lambda_{\pm}^0$	$r_i$	$\lambda_{\pm}^0$	$r_i$	$\lambda_{\pm}^0$	$r_i$	$\lambda_{\pm}^0$	$r_i$
$Li^+$	(0.06)	71.90	0.46	54.30	0.49	44.70	0.53	44.70	0.50	46.90	0.47	42.30	0.44
$Na^+$	(0.095)	78.70	0.43	56.40	0.48	48.40	0.50	48.10	0.47	50.30	0.45	44.60	0.42
$Bu_4N^+$	(0.50)	63.80	0.50	50.15	0.52	46.49	0.51	42.79	0.51	37.72	0.51	35.44	0.50
$Ph_4B^-$	(0.53)	57.40	0.54	46.43	0.55	44.27	0.53	39.61	0.55	34.92	0.54	32.80	0.53
$ClO_4^-$	(0.36)	101.70	0.36	81.20	0.37	74.10	0.37	64.30	0.38	69.50	0.36	56.50	0.36

$r_c$  is the crystallographic radii of ions

## CONCLUSION

The solvated radii ( $r_i$ ) for  $Na^+$  and  $Li^+$  are found to be much higher as compared to their crystallographic radii in the entire solvent composition range. This is due to ion-solvent interactions involving electrostatic ion-dipole attraction [24,25]. The values become even higher with an increase in AN as well as NM compositions in the binary mixtures of  $AN^+$  NM system, indicating that the extent of solvation of  $Li^+$  and  $Na^+$  ions also increases. The solvation of these ions, therefore, has been found to pass through a maximum.  $Li^+$  has been found to have higher solvation than  $Na^+$  in  $AN^+$  NM binary mixture at whole composition range. The solvated radii of  $Bu_4N^+$  and  $Ph_4B^-$  ions are nearly equal to their crystallographic radii and remain almost same at all compositions of  $AN^+$  NM binary mixtures. The  $r_i$  values for  $Li^+$  and  $Na^+$  are found to be higher in the entire solvent composition range which indicates strong solvation of these ions. Studies reveal that  $Li^+$ , however, has higher solvation than  $Na^+$  in  $AN^+$  NM mixtures at all compositions.

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