

Preferential Solvation of Lithium and Sodium salts Studied Viscometrically in Acetonitrile and Nitromethane Binary Mixtures at 298.15 K.

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Abstract

Viscosities of lithium perchlorate (LiClO_4), sodium perchlorate (NaClO_4), sodium tetraphenylborate (NaBPh_4), tetrabutylammonium perchlorate (Bu_4NClO_4) and tetrabutylammonium tetraphenylborate (Bu_4NBPh_4) have been measured in the range 0.002-0.2 mol 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 the viscosity was analyzed using the Jones-Dole equation. The A coefficients of the Jones-Dole equation are positive and in good agreement with the limiting theoretical values (A_∞) calculated using Falkenhagen-Vernon equation in some cases and two to three times in other cases. B-coefficients of the Jones-Dole equation are positive and large for all salts. Which were split to obtain B⁺ and B⁻ coefficients for ions. The B_± coefficients of Li⁺ and Na⁺ ions were found to be greater than the other ions in the entire solvent composition range which indicates strong solvation of the ions. Bu₄N⁺ and Ph₄B⁻ ions were found to show poor solvation due to solvophobic interactions. B-coefficient values indicate preferential solvation of Li⁺ and Na⁺ ions in the intermediate solvent composition range than in pure AN and NM. Li⁺, however, is found to be better solvated than Na⁺ in AN + NM binary mixtures at all compositions..

Keywords: : Acetonitrile; Nitromethane; Viscosity B-coefficient; Preferential Solvation

1. Introduction

In recent years, highly efficient Li⁺ rechargeable batteries are very popular because of easy handling, high performance with extensive capacity and high voltage output [1]. The electrolytic solution of high ionic conductivity, low melting point, high boiling point and high chemical and electrochemical stability can be used in Lithium ion and Li-O₂ batteries [2-3]. By using different techniques physicochemical studies of many salts in non aqueous solvents have been carried out in past [4-9] for their use in high energy batteries and for understanding organic reaction mechanism. Viscosity of solvent and electrolytic solutions taken into consideration in determining the nature and extent of solute-solvent and solvent-solvent interaction [10-12]. In all above studies focus given on solvation behavior of cations, however focus on solvation behavior of anions also given in work [13,14].

Viscometric studies of lithium perchlorate (LiClO_4), sodium perchlorate (NaClO_4), sodium tetraphenylborate (NaBPh_4), tetrabutylammonium tetraphenylborate (Bu_4NBPh_4) and tetrabutylammonium perchlorate (Bu_4NClO_4) have been carried out in Acetonitrile (AN), Nitromethane (NM) and in their binary mixtures to understand interactions in solution, to generate some new data and enhance the knowledge of electrolytic behavior which helps in selection of solvents for lithium batteries. Alkali metal ions interact with aqueous and non-aqueous solvent molecules through electrostatic forces[15-17]. So we focus on determination of solvation behavior of Li^+ and Na^+ ions in AN + NM mixture.

2. Experimental

Acetonitrile (99.7%, Rankem) was further purified as reported [18-26] and Nitromethane (99%, Hi-Media) was stored over 4 Å molecular sieves for 48 hours and then purified by vacuum distillation[18]. The purified solvents AN, and NM had ultrasonic velocity 1280.3 ms^{-1} and 1317.1 ms^{-1} , density 0.77686 kgm^{-3} and 1.1329 kgm^{-3} and viscosity 0.341 cP , 0.614 cP respectively which are in good agreement with the Literature values[18, 27, 28, 33]. Bu_4NBPh_4 and Bu_4NClO_4 were used as reference electrolytes in the present work. These salts were prepared by methods already reported [19, 29-32]. The salts Bu_4NClO_4 and $\text{Bu}_4\text{NPh}_4\text{B}$ purified by recrystallization and then stored in the vacuum desiccator over P_2O_5 and dried for 3-4 hours at 373.15 K before use [34-37]. The salts LiClO_4 (battery grade, 99.99%), NaClO_4 and NaBPh_4 were purchased from Sigma-Aldrich and used as-received. Mixtures of NM with AN were prepared by weight and their physical properties were determined. Density measurements of AN + NM binary mixtures as well as of the salt solutions were carried out using Anton Paar digital densimeter (model DSA 5000) operated in the static mode and automatically thermostated within $\pm 0.001 \text{ K}$. The densities measured had precision better than $\pm 1 \times 10^{-6} \text{ g cm}^{-3}$. The uncertainty in the solution density was found to be better than $\pm 5 \times 10^{-6} \text{ g cm}^{-3}$. An Ubbelohde suspended level viscometer was used for all viscosity measurements. The viscometer was calibrated with triply distilled water and purified AN at 298.15 K . A range of concentrations of salts were prepared by adding stock solutions of appropriate concentrations to a known quantity of solvent mixture taken in the viscometer. In all the cases, the measurements were repeated to obtain reproducible results. The overall accuracy of the viscosity measurements was found to be better than $\pm 0.1 \%$.

3. Results and Discussion

The viscosity data was analysed by using Jones-Dole equation [39]

$$\frac{\eta}{\eta_o} = 1 + AC^{1/2} + BC \quad (1)$$

where C is the molar concentration of the electrolyte and A and B are the constants, characteristics of the solvent and the electrolyte respectively. The viscosity B -coefficients of the electrolytes were evaluated by the analysis of viscosity data using equation (1). For the evaluation of coefficient B , plots of $\frac{\eta}{\eta_o} - 1 / C^{1/2}$ or $\eta_r - 1 / C^{1/2}$ vs. $C^{1/2}$ were constructed and were found to be

linear over the whole concentration range of electrolyte. The A -coefficient is a measure of ion-ion interaction and can be calculated theoretically from the limiting ionic conductances and the physical properties of the solvent using Falkenhagen-Vernon equation[40].

$$A_\eta = \frac{0.2577 \Lambda_o}{\eta_o (\epsilon_o T)^{1/2} \lambda_1^o \lambda_2^o} \left[1 - 0.6863 \left(\frac{\lambda_1^o - \lambda_2^o}{\Lambda_o} \right) \right] \quad (2)$$

where λ_1^o and λ_2^o are the limiting ionic conductance for cations and anions and η and ϵ are the viscosity and dielectric constant of the solvent respectively and T is absolute temperature. The experimental A-coefficient values are reported in Table 4 alongwith the theoretical A_{\square} coefficients calculated using Falkenhagen-Vernon equation. The agreement between the experimental and theoretical A-coefficients for most of the electrolytes in AN, NM and AN + NM mixtures has been found to be good.

Table 1: Permittivity (ϵ), density (ρ), viscosity (η^o) and ultrasonic velocity (u)

Mol % NM	ϵ	η_o / cP	$\rho_o / \text{kg m}^{-3}$	u / ms^{-1}
0	36.0	0.342	0.77686	1280.3
20	36.0	0.415	0.83101	1271.6
40	36.1	0.456	0.92352	1270.9
60	36.2	0.493	0.98911	1277.8
80	36.3	0.507	1.0602	1292.8
100	36.0	0.612	1.329	1317.1

Table 2: Viscosity B-coefficients of some salts in solvent mixture of AN + NM mixtures at 298.15 K.

Salts	$B \text{ (L mol}^{-1}\text{)}$					
	Mol% NM					
	0	20	40	60	80	100
Bu ₄ NBPh ₄	1.31	1.33	1.35	1.33	1.32	1.29
Bu ₄ NClO ₄	0.82	0.84	0.86	0.86	0.84	0.82
NaBPh ₄	1.22	1.26	1.30	1.28	1.24	1.21
LiClO ₄	0.76	0.82	0.84	0.83	0.81	0.76
NaClO ₄	0.73	0.77	0.81	0.80	0.76	0.73

4. Ionic B_+ and B. Coefficients

The ionic B_+ and B. coefficients were evaluated by splitting viscosity B coefficients into the contribution of individual ions. Gill and Sharma [12,38] based on the Bu₄NBPh₄ assumption, have suggested a method by which B-coefficients of the electrolyte in mixed solvents are splitted into the contribution of individual ions based on the following equations

$$\frac{B_{Ph_4B^-}}{B_{Bu_4N^+}} = \frac{r_{Ph_4B^-}^3}{r_{Bu_4N^+}^3} = \left(\frac{5.35}{5.00} \right)^3 \quad (3)$$

$$B_{Ph_4B^-} + B_{Bu_4N^+} = B(Bu_4NBPh_4) \quad (4)$$

using the equation (3) and (4) the viscosity B-Coefficients for Bu₄NBPh₄ and other salts are reported in Table 2. Fig. 1 shows that the B-Coefficients of all the salts pass through a maxima. Using ionic B. coefficients of ClO₄⁻ in present solvent system, B-coefficients for the other cations have been calculated and are reported in Table 3.

Table 3: Ionic B_{\pm} coefficients for some ions in AN + NM mixtures at 298.15 K.

B_{\pm} (L mol ⁻¹)						
Mol% NM						
Ions	0	20	40	60	80	100
Bu ₄ N ⁺	0.59	0.60	0.61	0.60	0.59	0.58
Ph ₄ B ⁻	0.72	0.73	0.74	0.73	0.73	0.71
ClO ₄ ⁻	0.23	0.24	0.25	0.26	0.25	0.24
Li ⁺	0.53	0.58	0.59	0.57	0.56	0.52
Na ⁺	0.50	0.53	0.56	0.54	0.51	0.49

Table 4: Experimental A coefficients (L^{1/2} mol^{-1/2}) and the corresponding theoretically calculated (A_{η}) coefficients for ions in AN + NM mixtures at 298.15 K.

Mol% NM	Bu ₄ NBPh ₄		Bu ₄ NClO ₄		NaBPh ₄		LiClO ₄		NaClO ₄	
	10 ² A _η	10 ² A	10 ² A _η	10 ² A	10 ² A _η	10 ² A	10 ² A _η	10 ² A	10 ² A _η	10 ² A
0	2.43	2.40	1.79	1.50	2.41	2.50	2.31	2.33	2.64	2.08
20	2.35	2.39	1.93	1.97	1.88	1.63	1.95	2.01	2.35	2.38
40	2.71	3.02	2.11	2.05	2.73	2.44	2.45	2.50	1.83	2.65
60	2.66	1.99	2.04	1.83	1.93	1.96	2.37	1.81	1.33	1.45
80	2.42	2.83	2.68	2.89	2.54	2.51	2.49	2.48	2.53	2.56
100	2.54	2.11	1.85	1.56	2.38	2.37	2.52	2.54	2.84	2.88

The Table 3 shows the large and positive viscosity B -coefficients for the electrolytes which is a common feature for non aqueous solvents. Fig 2 reveals that the values of ionic B_{\pm} coefficients of the cations Bu₄N⁺, Li⁺, Na⁺ and anion Ph₄B⁻ and ClO₄⁻ pass through maxima i.e. they first increase gradually on moving towards NM-rich region of the mixtures suggesting better solvation of the ions and then decrease.

5. Conclusion

The values of viscosity B -coefficients for the electrolytes and ions is large and positive which shows the greater solvation of both cations and anions. Table 3 reveals that the values of ionic B_{\pm} coefficients of the cations Bu₄N⁺, Li⁺, Na⁺ and anion Ph₄B⁻ and ClO₄⁻ first increases gradually on moving towards NM-rich region of the mixtures suggesting better solvation of the ions and then decreases. B -coefficients for Na⁺ and Li⁺ are found to be high in the entire solvent composition range. This is due to ion-solvent interactions involving electrostatic ion-dipole attraction. 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.

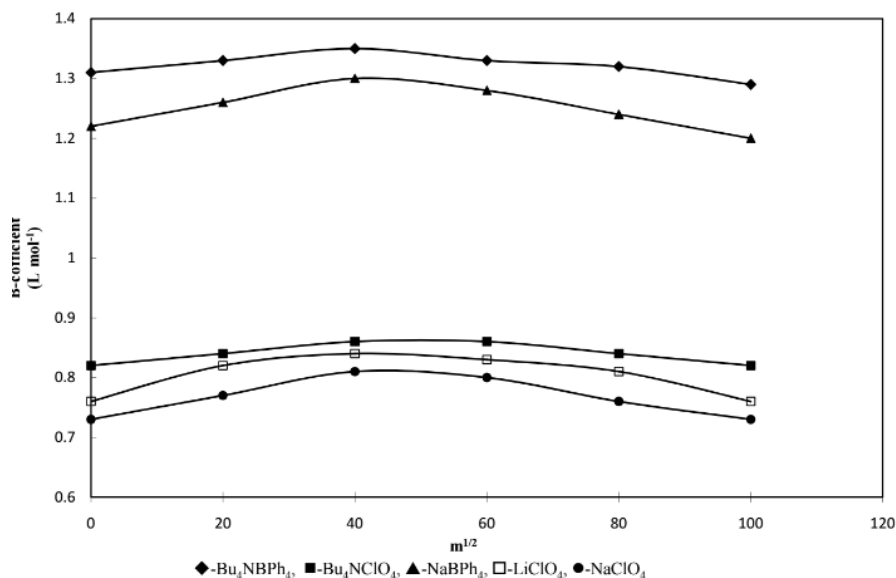


Figure 1: Plots of B-coefficients versus Mol % Nitromethane in Acetonitrile at 298.15 K

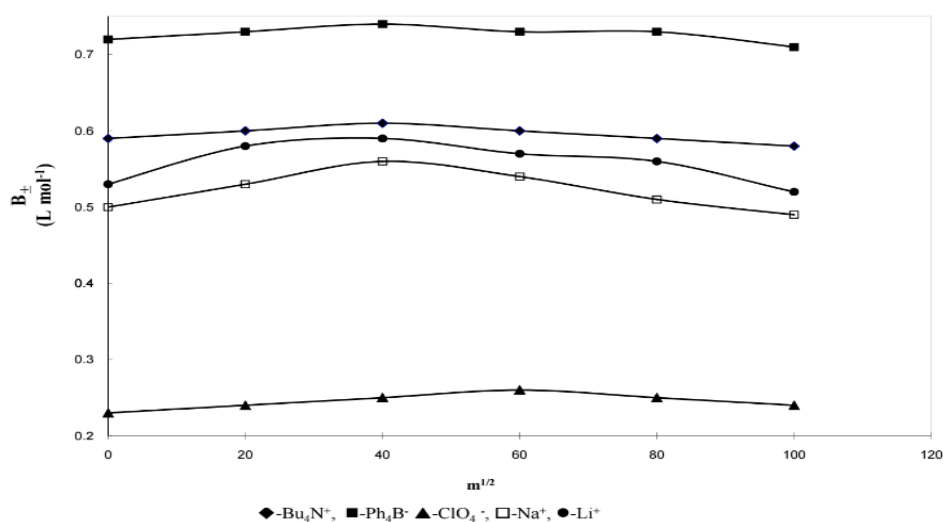


Figure 2: Plots of B_{\pm} versus Mol % Nitromethane in Acetonitrile at 298.15 K

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 mixtures at whole composition range. The B-coefficients of Bu_4N^+ and Ph_4B^- ions are not much vary with different solvent compositions and remain almost same throughout all compositions of AN + NM binary mixtures which show poor solvation of these ions. The B-coefficient 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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References

- [1] Sharon, Daniel; Hirsberg, Daniel; Afri, Michal; Chesneau, Frederick; Lavi, Ronit; Frimer, Aryeh A.; Sun, Yang-Kook; Aurbach, Doron From ACS Applied Materials & Interfaces (2015), 7(30), 16590-16600.
- [2] Skarmoutsos, Ioannis; Ponnuchamy, Veerapandian; Vetere, Valentina; Mossa, Stefano From Journal of Physical Chemistry C (2015), 119(9), 4502-4515.
- [3] Henderson, Wesley; Zhou, Qian; Weaver, Joshua From Abstracts, 42nd Middle Atlantic Regional Meeting of the American Chemical Society, College Park, MD, United States, May 21-24 (2011), MARM-486.
- [4] D. S. Gill, L. Rodehueser, P. Rubini, and J.J. Delpuech. J. Chem. Soc. Faraday Trans. 91, 2307 (1995).
- [5] D. S. Gill, U. Kamp, A. Doelle, and M. D. Zeidler, Indian J. Chem. 40A, 693 (2001).
- [6] D.Das, B. Das and D. K. Hazra, J. Sol. Chem. 31, 425 (2002).
- [7] D. S. Gill, R. Singh, H. Anand, and J.K. puri, J. Mol. Liq. 98-99, 15 (2002).
- [8] M. S. Chauhan, G. Kumar, S. Chauhan, and S. Gupta. Indian J. Chem. 43A, 734 (2004).
- [9] D. S. Gill, H. Anand, A. Kumari, and J. K. Puri, Z. Naturforsch. 59A, 615 (2004)
- [10] D. S. Gill, Z. Phy. Chemie Neue Folge, Bd. 140, (1984), 149-156.
- [11] D. S. Gill, A. Kumari, R. Gupta, Dilbag Rana, J. Mol. Liq. 133 (2007) 7-10.
- [12] D. S. Gill, A. N. Sharma, J. Chem. Soc., Faraday Trans. I. 78 (1982), 475-484.
- [13] A.Szejgis, A. Bald, M. Zurada, *Journal of Molecular Liquids* 1999, 79, 123-136.
- [14] Wypych-Stasiewicz, A. Szejgis , A. Chimielewska , A. Bald, *Journal of Molecular Liquids* 2007,130, 34-37.
- [15] J. Parker, I. D. MacLeod, D. Muir, and P. Singh, Australian J.Chem. 30. 1423 (1977).
- [16] D. S. Gill, R. Singh, and I.M. Joshi. Indian J. Chem. 39A. 579 (2000).
- [17] D. S. Gill and M. B. Sekhri, J. Chem.Soc. Faraday Trans. 1, 1982, 78, 119.
- [18] J. A. Riddick, W.B. Bunger, and T.K. Sakano, *Organic solvents, Physical Properties and Methods of Purification, Wiley Interscience, New York, 4th Ed., (1986).*
- [19] M.N. Roy, A. Banerjee, R.K. Das, *J. Chem. Therm.*, 41 (2009) 1187.
- [20] *Kratochvil and H.L. Yeager, Topics in Current Chemistry, 27 (1972) 1.*
- [21] D.S. Gill, V. Pathania, B.K. Vermani, R.P. Sharma, *Z. Phys. Chem.*, 217 (2003) 739.
- [22] D.S. Gill and M.S. Bakshi, *J. Chem. Soc., Faraday Trans., 1*, 84 (10) (1988) 3517.
- [23] D.S. Gill and M. S. Chauhan, *Z. Phys. Chems. N. F.*, 140 (1984) 149.
- [24] D.S. Gill, K. S. Arora, B. Singh, M. S. Bakshi and M. S. Chauhan, *J. Chem. Soc. Faraday Trans.*, 87 (1991) 1159.
- [25] Wypych- Stasiewicz, A. Borun, J. Benko, A. Bald, *J. Mol. Liq.* 178 (2013) 84.
- [26] Wypych- Stasiewicz, A. Borun, J. Benko, A. Bald, *J. Mol. Liq.* 190 (2014) 54.
- [27] M. V. Kaulgud, *Z. Phy. Chem. (N. F.)* 36 (1963) 365.
- [28] S. Das, D. K. Hazra, and S. C. Lihri, *J. Indian Chemical Soc.* 70 (1993) 43.
- [29] S. Gill and M. S. Chauhan, *Z. Phys. Chem. Neue Folge, Bd. S.*, 1984, 140,139.
- [30] . R. L. Kay and D. F. Evans, *J. Phys. Chem.*, 70 (1966) 2325.

- [31] D.S. Gill, *Electrochim. Acta*, 24 (1979) 701.
- [32] R. C. Paul, D. S. Gill and S. P. Narula, *Indian J. Chem.* 8 (1970) 936.
- [33] S. Gill, Vivek Pathania and Hardeep Anand, *Z. Phys chem.* 2004, 857-865.
- [34] N. Saha and B. Das, *J. Chem. Eng. Data*, 42 (1997) 227.
- [35] D.S. Gill, *J. Chem. Soc. Faraday Trans.*, 1, 77 (1981) 751.
- [36] R. M. Fuoss and L. Onsager, *J. Phys. Chem.*, 61 (1957) 668.
- [37] D.S. Gill and A. N. Sharma, *J. Chem. Soc. Faraday Trans.*, 1, 78 (1982) 465.
- [38] D' Aprano and R. M. Fuoss, *J. Solution Chem.*, 3 (1974) 45
- [39] G. Jones and M. Dole, *J. Am. Chem. Soc.*, 51 (1929) 2950.
- [40] J. Falkenhagen, E.L. Vernon, *Phys. Z.* 33 (1932) 140–144.