Compressibility Studies of Solvation Behaviour of Lithium and Sodium Ions in Nitromethane + Dimethylsulfoxide Binary Mixtures at 298.15 K

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The isentropic compressibilities (K_s) and apparent molal isentropic compressibilities ($K_{s,\phi}$) of lithium perchlorate (LiClO$_4$), sodium perchlorate (NaClO$_4$), sodium tetraphenylborate (NaBPh$_4$), tetrabutylammonium tetraphenylborate (Bu$_4$NBPh$_4$) and tetrabutylammonium perchlorate (Bu$_4$NClO$_4$), have been calculated from measured ultrasonic velocity (u) and density (ρ) of these salts in the concentration range 0.001 to 0.60 mol Kg^{-1} in the mixed binary solutions of nitromethane (NM) and dimethyl sulfoxide (DMSO) containing 0, 20, 40, 60, 80 and 100 mol% of DMSO in NM at 298.15 K. Limiting values of apparent molal isentropic compressibilities ($K_{s,\phi}^{\circ}$) for various salts were evaluated and split into the contributions ($K_{s,\phi}^{\circ}$)$_\pm$ of the individual ions. Exceptionally large and negative ($K_{s,\phi}^{\circ}$)$_\pm$ values were obtained whose variation with solvent composition shows strong solvation of both Li$^+$ and Na$^+$ in NM + DMSO mixtures at all compositions of the mixed binary solutions. Solvation of Li$^+$ and Na$^+$ increases as mol% of DMSO in NM increases. Solvation exhibited by Li$^+$, however, is much stronger than Na$^+$ in all compositions of the mixtures. Solvation exhibited by ClO$_4^-$ in NM + DMSO mixtures is weak which perchlorate ion shows by having some interactions with DMSO in the DMSO-rich compositions of the mixtures. The large and positive values for Bu$_4$N$^+$ and Ph$_4$B$^-$ are indicative of some special type of interactions, mainly solvophobic with the solvent molecules.

Keywords: Compressibility, Solvation, Lithium perchlorate, Sodium perchlorate, Dimethyl sulfoxide, Nitromethane.

INTRODUCTION

The interactions among solute-solvent components of salt solutions have been the area of interest for the past few years. For better understanding of the strength and nature of solute-solvent interactions and ionic association and dissociation of salts, a lot of studies were carried out by measuring conductivity, ultrasonic velocity and density of the solutions containing electrolytes in solvents and their binary mixtures [1-3]. From ultrasonic velocity and density data, limiting ionic apparent molal isentropic compressibilities were determined whose signs and values gives prediction about strength and nature of the ion-solvent interactions [4-10]. Many studies of transport properties, which are important and are of great interest in the research related to potentially interesting electrolytes for lithium and sodium batteries, are available now a days [11-14]. Solvation properties of electrolytes have applications in understan-

ding lithium high-energy density battery behaviour and increased attention in both academic and industrial studies [15-17].

Solvation characteristics of lithium salts like lithium perchlorate (LiClO$_4$) and lithium bromide (LiBr) in mixed aprotic solvents were studied from precise density measurements [18,19]. Lithium salts are used as electrolytes in conducting polymers for secondary lithium batteries [20]. Solvation studies of lithium ion in aprotic solvents mixtures being an active field of research so there is a need to comprehend the solvation behaviour of akali metal electrolytes in non-aqueous mixed solvents. Precise compressibility data of alkali metal electrolytes in nitromethane (NM), dimethylsulfoxide (DMSO) and in NM + DMSO mixed binary solvents is completely lacking. The ultrasonic velocity and density measurements of Li, Na and some other salts in NM, DMSO and their binary mixtures are reported here. We expect interesting results as solvation aspects when we change the compositions of the individual

solvents *i.e.* NM and DMSO in the binary mixtures. Investigation of the solvation behaviour of Li$^+$ and Na$^+$ ions in these solvent systems can be helpful in selection of solvents for lithium battery as well as in the development of secondary batteries.

EXPERIMENTAL

Dimethyl sulfoxide (DMSO) (99%, Spectrochem) was purified as reported in literature [21]. Nitromethane (NM) (99%, Hi-Media) was stored over 4 Å molecular sieves for 48 h and then purified by vacuum distillation [22,23]. The purified DMSO and NM had ultrasonic velocities as 1494.97 m s^{-1} and 1317.10 m s^{-1} and densities as 1.09538 kg m^{-3} and 1.1329 kg m^{-3}, respectively which agree well with the literature values [10,24,25]. The experimental salts LiClO$_4$, NaClO$_4$ and NaBPh$_4$ were purified by recrystallization with acetone. The reference salts *i.e.* Bu$_4$NBPh$_4$ and Bu$_4$NClO$_4$ of the present work were also prepared by reported method [26] and purified by recrystallization with acetone.

Densities and ultrasonic velocities of solvent 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 ± 0.001 K. The physical parameters of the solvent binary mixtures are given in Table-1. The range of concentration of salts *i.e.* 0.001 to 0.60 mol Kg^{-1} in NM, DMSO and their binary mixtures were prepared by diluting stock solutions of appropriate concentrations. The mixtures were prepared by mass and kept in airtight stoppered glass bottles to avoid the absorption of atmospheric moisture. The probable error in the molality was estimated to be less than ± 1 × 10^{-4}. In all cases, the measurements were repeated two times to obtain reproducible results. Before each series of measurements, the instrument was calibrated with triple distilled freshly degassed water and dry air at atmospheric pressure. The densities and speeds of sound had precision better than ± 1 × 10^{-6} g cm^{-3} and ± 1 × 10^{-2} m s^{-1}, respectively. The uncertainties in the solution density and speed of sound were found to be better than ± 5 × 10^{-6} g cm^{-3} and ± 5 × 10^{-2} m s^{-1}, respectively.

TABLE-1
DENSITY (ρ_o), VISCOSITY (η_o), DIELECTRIC CONSTANT (ϵ_o), ULTRASONIC VELOCITY (u_o) AND ISENTROPIC COMPRESSIBILITY ($K_s°$) FOR SOME NM + DMSO MIXTURES AT 298.15 K

Mol% DMSO	ρ_o (g cm^{-3})	η_o (cP)	ϵ_o	u_o (m s^{-1})	$10^6 \times K_s°$ (bar^{-1})
0	1.12910	0.6120	47.52	1317.10	50.88
20	1.11782	0.9127	45.18	1347.32	49.28
40	1.10993	1.2698	41.87	1377.33	47.49
60	1.10355	1.5166	39.35	1411.05	45.51
80	1.09826	1.7643	37.84	1452.24	43.17
100	1.09742	1.9924	36.00	1486.97	41.21

RESULTS AND DISCUSSION

Ultrasonic velocities (u) and densities (ρ) of Bu$_4$NBPh$_4$, Bu$_4$NClO$_4$, NaBPh$_4$, LiClO$_4$ and NaClO$_4$ were measured at different salt concentrations in the range 0.001-0.60 mol Kg^{-1}

in the binary mixtures of nitromethane (NM) + dimethylsulfoxide (DMSO) with 0, 20, 40, 60, 80 and 100 mol% DMSO in NM at 298.15 K. The isentropic compressibilities (K_s) of solutions have been calculated from eqn. 1:

$$K_s = \frac{1}{u^2\rho} \tag{1}$$

The plots of K_s *versus m* are linear, in all cases K_s values fall with increase in molal concentration indicating non-association of the electrolytes in NM+DMSO mixtures (Fig. 1-6). The partial molal volumes (V_ϕ) and apparent molal isentropic compressibilities ($K_{s,\phi}$) of the salts were evaluated by using the following eqns.:

$$V_\phi = \frac{M}{\rho} - \frac{10^3[\rho - \rho_o]}{m\rho\rho_o} \tag{2}$$

$$K_{s,\phi} = V_\phi K_s - \frac{10^3[K_s - K_o]}{m\rho_o} \tag{3}$$

where m is molality, M is molecular weight of the solute, K_s and K_o are the isentropic compressibilities of the solutions and solvent binary mixtures and ρ and ρ_o are the densities of solution and solvent binary mixtures, respectively. The plots of $K_{s,\phi}$ *versus* $m^{1/2}$ were linear in the experimental concentration range. The apparent molal isentropic compressibilities at infinite dilution
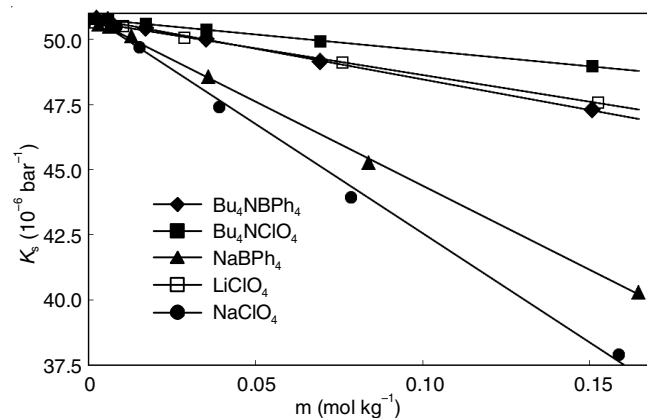

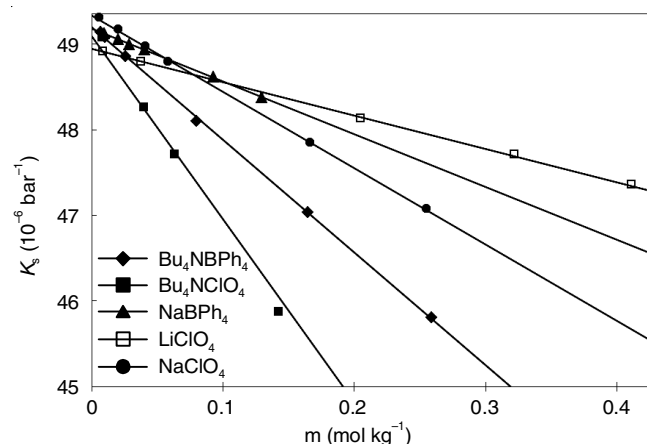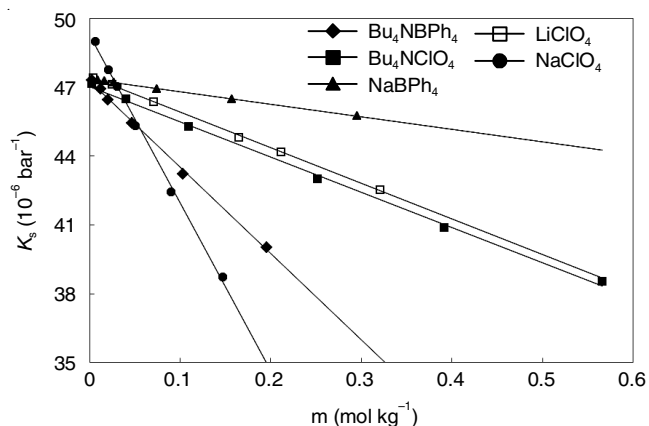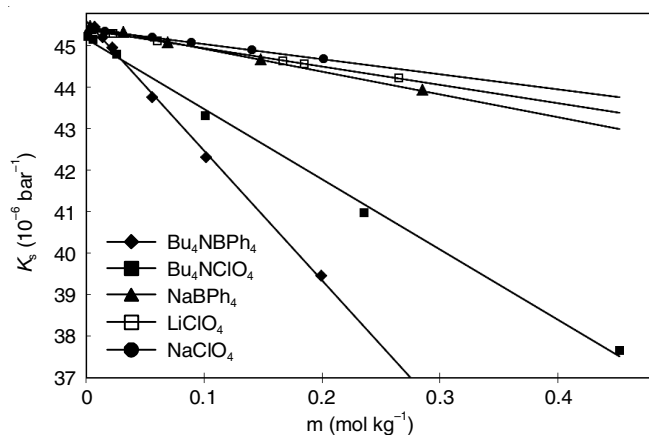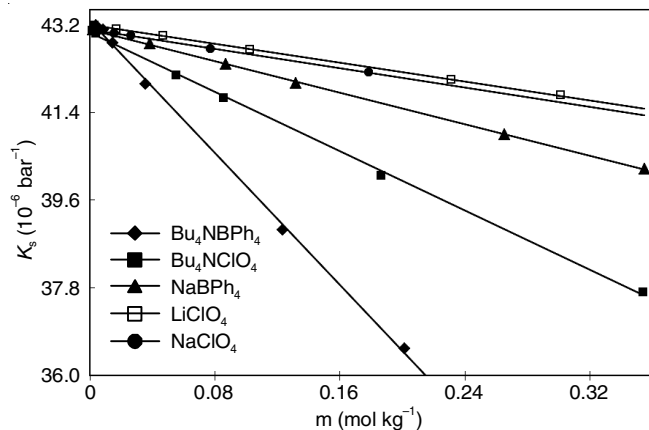Fig. 1. Plots of K_s *versus* m in nitromethane at 298.15 K

Fig. 2. Plots of K_s *versus* m in 20 mol% dimethyl sulfoxide in nitromethane at 298.15 K

Fig 3.   Plots of K_s *versus* m in 40 mol% dimethyl sulfoxide in nitromethane at 298.15 K

Fig. 4.   Plots of K_s *versus* m in 60 mol% dimethyl sulfoxide in nitromethane at 298.15 K

Fig. 5.   Plots of K_s *versus* m in 80 mol% dimethyl sulfoxide in nitromethane at 298.15 K

i.e. the limiting values ($K_{s,\phi}^{\circ}$) were obtained by extrapolating the linear plots of $K_{s,\phi}$ *versus* $m^{1/2}$ by the least squares method using eqn. 4:

$$K_{s,\phi} = K_{s,\phi}^{\circ} + A_{s,\phi}m^{1/2} \qquad (4)$$

The ($K_{s,\phi}^{\circ}$) values of various salts therefore obtained are reported in Table-2. The ($K_{s,\phi}^{\circ}$) values for these electrolytes are unavailable in the literature for NM + DMSO mixtures; therefore, a comparison of the present values could not be carried
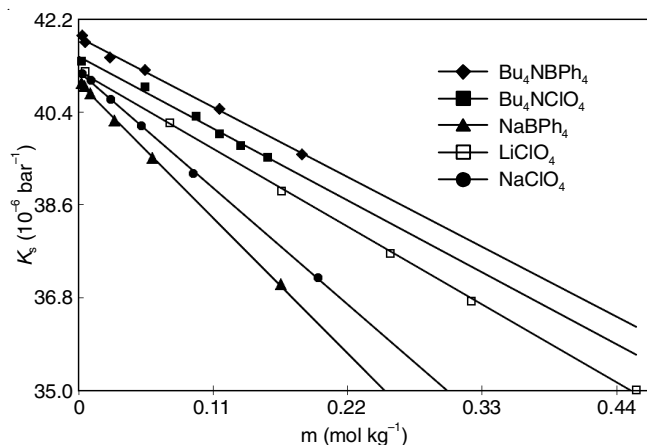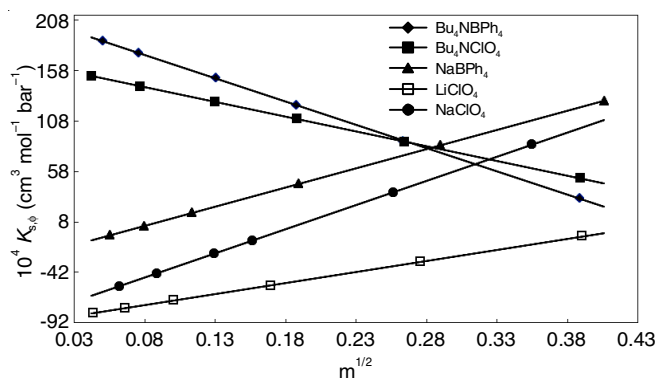

Fig. 6. Plots of K_s *versus* m in dimethyl sulfoxide at 298.15 K

TABLE-2
LIMITING APPARENT MOLAL ISENTROPIC
COMPRESSIBILITIES ($K_{s,\phi}^{\circ}$) OF SOME SALTS IN
NM + DMSO MIXTURES AT 298.15 K

Salt	Mol% NM					
	0	20	40	60	80	100
LiClO₄	-91.7	-297.6	-425.3	-431.5	-464.3	-515.8
NaClO₄	-85.3	-286.5	-410.3	-418.9	-445.1	-502.8
NaBPh₄	-26.2	-149.9	-184.8	-238.5	-285.4	-346.4
Bu₄NClO₄	164.7	085.1	-022.1	-052.3	-084.9	-125.7
Bu₄NBPh₄	210.4	222.9	202.7	126.2	076.8	028.5

out. In pure NM, the ($K_{s,\phi}^{\circ}$) values for Bu₄NBPh₄ (278.6×10^{-3} m³ mol⁻¹ TPa⁻¹) and for Bu₄NClO₄ (195.3×10^{-3} m³ mol⁻¹ TPa⁻¹) agree well with the literature [5] values (278.0×10^{-3} m³ mol⁻¹ Pa⁻¹ and 195.2×10^{-3} m³ mol⁻¹ Pa⁻¹, respectively). Figs. 7-12 for NM + DMSO binary mixtures, indicate that the $K_{s,\phi}$ values for Bu₄NClO₄ and Bu₄NBPh₄ decrease with increase in the concentration of salts, while $K_{s,\phi}$ values for LiClO₄, NaClO₄ and NaBPh₄, though negative, show an increase on enhancing the concentration of salts. The limiting $K_{s,\phi}$, *i.e.* $K_{s,\phi}^{\circ}$ values (Table-2) obtained from eqn. 4 for LiClO₄, NaClO₄ and NaBPh₄ are negative in NM + DMSO mixtures at all compositions of the solvent mixtures. The accuracy of these values can be obtained by comparing the experimental $K_{s,\phi}^{\circ}$ values for NaBPh₄ (Table-2) with the corresponding $K_{s,\phi}^{\circ}$ values for NaBPh₄ those obtained by adding values for Na⁺ and Ph₄B⁻ (Table-3). The experimentally measured values for NaBPh₄ are in good agreement with

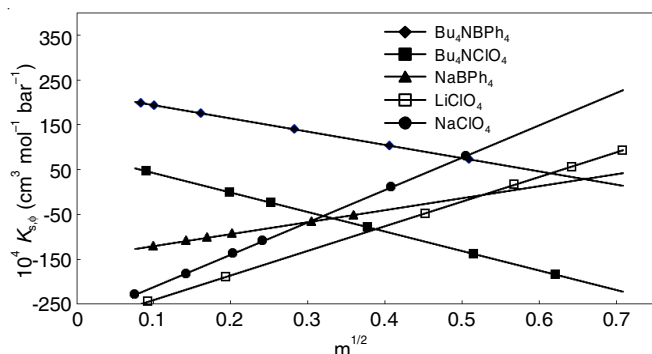Fig. 7. Plots of $K_{s,\phi}$ *versus* m in nitromethane at 298.15 K

Fig. 8. Plots of $K_{s,\phi}$ *versus* m in 20 mol % dimethyl sulfoxide in acetonitrile at 298.15 K
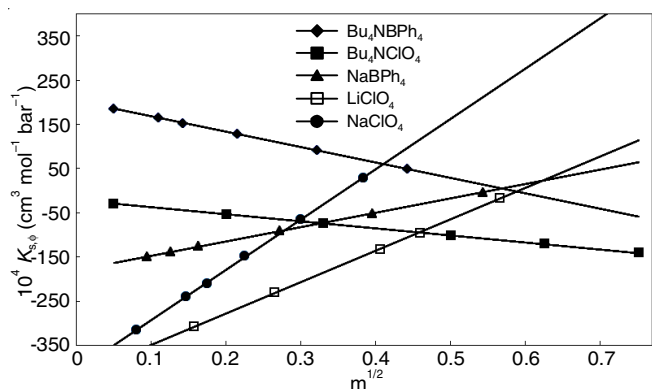

Fig. 9. Plots of $K_{s,\phi}$ *versus* m in 40 mol % dimethyl sulfoxide in acetonitrile at 298.15 K
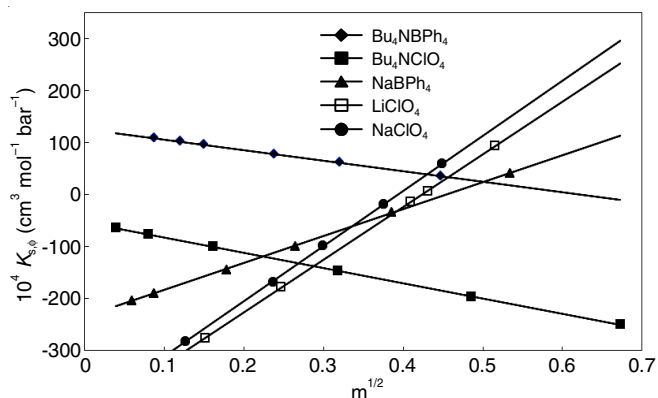

Fig. 10. Plots of $K_{s,\phi}$ *versus* m in 60 mol % dimethyl sulfoxide in acetonitrile at 298.15 K
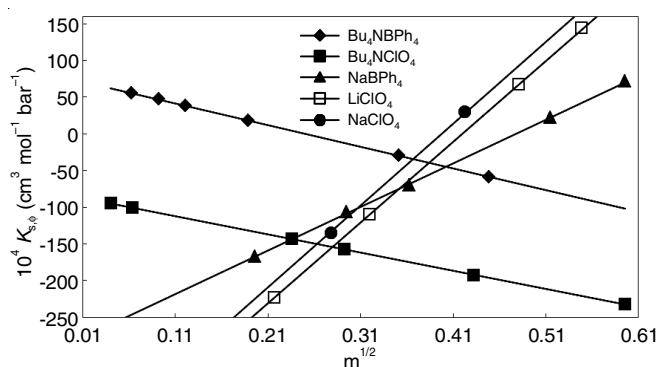

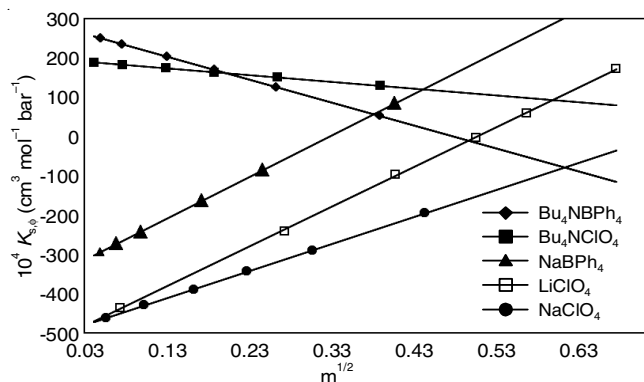Fig. 11. Plots of $K_{s,\phi}$ *versus* m in 80 mol % dimethyl sulfoxide in acetonitrile at 298.15 K

Fig. 12. Plots of $K_{s,\phi}$ *versus* m in dimethyl sulfoxide at 298.15 K

TABLE-3
LIMITING IONIC APPARENT MOLAL ISENTROPIC
COMPRESSIBILITIES ($K^{\circ}_{s,\phi})_{\pm}$ OF SOME IONS IN
NM + DMSO MIXTURES AT 298.15 K

Mol% DMSO	$10^4 \times (K^{\circ}_{s,\phi})_{\pm}$ (cm^3 mol^{-1} bar^{-1})					
	0%	20%	40%	60%	80%	100%
Li$^+$	-161.8	-282.5	-312.1	-322.5	-344.9	-377.3
Na$^+$	-139.8	-271.4	-297.1	-309.9	-325.7	-364.3
Bu$_4$N$^+$	94.6	100.2	91.1	56.7	34.5	12.8
Ph$_4$B$^-$	115.8	122.7	111.6	69.5	42.3	15.7
ClO$_4^-$	70.1	-15.1	-113.2	-109.4	-119.4	-138.5

the calculated values. The values of $K^{\circ}_{s,\phi}$ for the reference salts Bu$_4$NBPh$_4$ and Bu$_4$NClO$_4$ obtained are positive and large. For obtaining quantitative information regarding the tendency of each ion to produce structural or solvation effects, the values $K^{\circ}_{s,\phi}$ for the salt from were splited into the contributions of the individual ions (Table-2). As reported earlier [27-34] the limiting apparent molal isentropic compressibility ($K^{\circ}_{s,\phi}$) values are additive and can be directly split into the contributions of the individual ions. A similar model based on the Bu$_4$NBPh$_4$ assumption was suggested by Gill *et al.* [5,29]. In this model they recommended the use of the reference electrolyte Bu$_4$NBPh$_4$ to split the ($K^{\circ}_{s,\phi}$) values into its ionic contributions with the help of the following eqns.:

$$\frac{K^{\circ}_{s,\phi}(\text{Bu}_4\text{N}^+)}{K^{\circ}_{\phi}(\text{Ph}_4\text{B}^-)} = \frac{r_c^3(\text{Bu}_4\text{N}^+)}{r_c^3(\text{Ph}_4\text{B}^-)} = \frac{(5.00)^3}{(5.35)^3} \quad (5)$$

$$K^{\circ}_{s,\phi}(\text{Bu}_4\text{NBPh}_4) = K^{\circ}_{s,\phi}(\text{Bu}_4\text{N}^+) + K^{\circ}_{s,\phi}(\text{Ph}_4\text{B}^-) \quad (6)$$

where r_c is the crystallographic radius of the ions, which has also been used in the present work for splitting ($K^{\circ}_{s,\phi}$) values of Bu$_4$NBPh$_4$ into the ionic contribution for Bu$_4$N$^+$ and Ph$_4$B$^-$ ions by using eqns. 5 and 6. The ionic contribution of ClO$_4^-$ was obtained by subtracting the ionic ($K^{\circ}_{s,\phi}$) value of Bu$_4$N$^+$ from ($K^{\circ}_{s,\phi}$) value of Bu$_4$NClO$_4$ salt. By subtracting ($K^{\circ}_{s,\phi}$) of ClO$_4^-$ ion from those of the LiClO$_4$ and NaClO$_4$ salts, the ($K^{\circ}_{s,\phi}$) values of Li$^+$ and Na$^+$ ions have been calculated on the basis of additive principle and are given in Table-3.

Interesting results were found while perusing the data of Table-3, regarding solvation of Li$^+$ and Na$^+$ ions. The $K^{\circ}_{s,\phi}$ values of Li$^+$ and Na$^+$ are negative and these values for Li$^+$ have larger magnitudes than Na$^+$ in all composition of the solvent binary mixtures. The values becomes more negative for Li$^+$ and Na$^+$

with increase in DMSO mol%. The negative values indicate strong structural effects which arise due to solute-solute and solute-solvent interactions [9,28]. Negative ionic $(K°_{s,\phi})_\pm$ values for Li⁺ and Na⁺ (Table-3) are obtained due to the stronger solvation effects. The solvation exhibited by these ions is due to purely electrostatic ion-solvent interactions [30,31]. The plot of $(K°_{s,\phi})_\pm$ values *versus* mol% DMSO indicates the stronger solvation of these ions in DMSO than in NM and in all binary mixtures (Fig. 13). Thus, it evident that as the size of cation becomes small, the ion-dipole interaction increases, which is also supported by high negative $(K°_{s,\phi})_\pm$ values. As the size of cation increases and the distance of closest approach of cation and solvent molecules become greater, extent of ion-dipole interactions decreases. While positive values for Bu₄N⁺ and Ph₄B⁻ indicate some special type of interactions [32] (solvophobic or dispersive) with the molecules of the solvent, which decrease on increasing the DMSO composition of the mixtures. Exceptional interaction through dispersion forces of Ph₄B⁻ with acetonitrile has also been reported by Bose & Kundu [33]. The larger perchlorate ion does not suffer any affect by the acid properties of the solvent, but if at all, its solvation sheath is determined by the dipole moment of NM and DMSO. Low magnitude $(K°_{s,\phi})_\pm$ values of for ClO₄⁻ in NM, show its poor solvation by NM but negative values in DMSO show its substantial solvation than in NM as compared to the bulkier ions of the reference salts. The solvation, however, is weaker in comparison to the alkali metal ions. Previous analysis also explains that the anions have only weak interactions with the aprotic solvents [34]. The large and negative $(K°_{s,\phi})_\pm$ values for Li⁺ and Na⁺ indicate strong ion-solvent interactions in the binary mixtures, which are greater in magnitude in DMSO than in NM. Extent of such interactions for Li⁺ is greater than Na⁺ in both NM, DMSO and their mixtures**.**
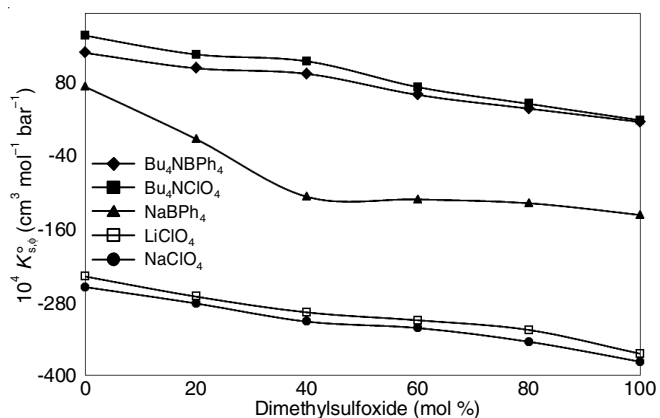

Fig. 13. Plots of $(K°_{s,\phi})_\pm$ *versus* mol % dimethyl sulfoxide in nitromethane 298.15 K

Conclusion

The large negative $(K°_{s,\phi})_\pm$ values for Li⁺ and Na⁺ ions indicate stronger solvation involving strong electrostatic ion-dipole interactions in all nitromethane (NM) + DMSO binary mixtures. In solvent binary mixtures, the solvation of ions increase with increase in mol% DMSO. In comparison to NM, DMSO interacts strongly with Li⁺ and Na⁺. Li⁺ ion shows better

solvation than Na⁺ ion in all NM + DMSO binary mixtures due to its high charge density. The ionic apparent molal isentropic compressibilities obtained for Bu₄N⁺ and Ph₄B⁻ ions are positive due to solvophobic or dispersive interactions exhibited by these ions with the solvent molecules. Bu₄N⁺ and Ph₄B⁻ ions were not solvated in NM + DMSO binary mixtures over the whole composition range whereas the solvation shown by ClO₄⁻ ions is weak.

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