Asian Journal of Chemistry; Vol. 33, No. 6 (2021), 1447-1451

ASIAN JOURNAL OF CHEMISTRY

https://doi.org/10.14233/ajchem.2021.23279

Ion-Solvent Interactions Investigated by Isentropic Compressibility Measurements of Lithium and Sodium Salts in Binary Mixtures of Acetonitrile and Nitromethane at 298.15 K

HARDEEP ANAND[1], NARENDER SINGH[1] and SURESH KUMAR[1,2,*]

[1]Department of Chemistry, Kurukshetra University, Kurukshetra-136119, India
[2]Department of Chemistry, Markanda National College, Shahabad Markanda-136135, India

*Corresponding author: E-mail: suresh980980@gmail.com

Received: 2 April 2021; *Accepted*: 5 May 2021; *Published online*: 5 June 2021; AJC-20382

Ultrasonic velocities (*u*) and densities (ρ) of lithium perchlorate ($LiClO_4$), sodium perchlorate ($NaClO_4$), sodium tetraphenylborate ($NaBPh_4$), tetrabutylammonium tetraphenylborate (Bu_4NBPh_4) and tetrabutylammonium perchlorate (Bu_4NClO_4) were measured in the concentration range 0.001-0.25 mol kg^{-1} in acetonitrile (AN) and nitromethane (NM) binary mixtures consisting of 0, 20, 40, 60, 80 and 100 mol%NM in AN at 298.15 K. The isentropic compressibility (K_s) and apparent molal isentropic compressibility ($K_{s,f}$) values of the above salts in all solvent mixtures have been evaluated from experimental data. Limiting apparent molal isentropic compressibilities ($K^o_{s,\phi}$) for various salts were evaluated and split into the ionic contributions $(K^o_{s,\phi})_\pm$. The variation of $(K^o_{s,\phi})_\pm$ with solvent compositions shows that Li^+ and Na^+ ions have very large negative $(K^o_{s,\phi})_\pm$ values indicating strong solvation of both Li^+ and Na^+ ions in AN + NM mixtures over whole binary solvent composition range. Stronger solvation was further observed in the intermediate compositions of AN + NM mixtures. Li^+ ions, however, showed much higher solvation as compared to Na^+ ions at all compositions. The ClO_4^- ions showed feeble solvation in AN + NM mixtures through some interaction with AN binary mixtures with higher mol% of AN. The positive values of $(K^o_{s,\phi})_\pm$ with large magnitude for Bu_4N^+ and Ph_4B^- ions indicate solvophobic type of interaction with the solvent molecules, which is stronger in the intermediate compositions of AN + NM mixtures.

Keywords: Acetonitrile, Nitromethane, Isentropic compressibility, Ion-solvent interactions, Lithium ions, Sodium ions.

INTRODUCTION

Solvation studies interactions have been extensively performed in a variety of mixed solvents using various techniques [1-4]. A large number of studies have shown that acoustical parameters such as compressibility combined with density have gained importance in providing extremely useful information regarding interactions of ion with another ion and a solvent molecule(s) in pure solvents and solvent mixtures [5-10]. Data of compressibility are usually required to make prediction about pressure dependent properties of the salt solutions. Limiting ionic apparent molal isentropic compressibility $(K^o_{s,\phi})_\pm$ is an important parameter, which not only provides the magnitude as well as predicts the nature of the interactions taking place in the solution [11-13].

Precise compressibility data of alkali metal salts in acetonitrile (AN) and nitromethane (NM) solvent system is completely lacking in literature. The ultrasonic velocity and density measurements of $LiClO_4$, $NaClO_4$, $NaBPh_4$, Bu_4NBPh_4 and Bu_4NClO_4 in AN + NM binary mixtures are reported in the present investigation. Both acetonitrile and nitromethane have almost same dielectric constant (AN = 36.0 and NM = 35.9) but different viscosities (AN = 0.341 mPa and NM = 0.614 mPa). Purpose of the present study was to investigate the ion-solvent interaction behaviour of Li^+ and Na^+ ions in acetonitrile (AN) and nitromethane (NM) in pure state as well as in mixed solvents. These studies have an application in searching an appropriate solvent or a solvent mixture for lithium batteries [14], which are widely used in products like portable consumer electronic devices and also in hydrometallurgical purification of metals like Cu, Ag and Pd [15].

EXPERIMENTAL

Acetonitrile (AN) (99.7%, Rankem) [16-18] and nitromethane (NM) (99%, Hi-Media) [15] were purified as reported earlier. The purified solvents AN and NM had ultrasonic velocity

1280.3 &1317.1 m s^{-1} and density 0.77686 & 1.1329 kg m^{-3}, respectively which are in adequate agreement with the available literature values [6]. Bu_4NBPh_4 and Bu_4NClO_4, used as reference electrolytes in the present work, were prepared by the reported methods [15]. The salts *i.e.* $LiClO_4$, $NaClO_4$ and $NaBPh_4$ were purified by recrystallization with acetone.

Densities and speeds of sound measurements of solvent binary mixtures and also of the salt solutions were performed using Anton Paar digital densimeter (Model DSA 5000), which was operated in the static mode and thermostated automatically within ± 0.001 K. A range of concentration of the salts in AN, NM and AN + NM mixtures were prepared by diluting the stock solutions of suitable concentrations. The mixtures of the solvents were prepared by mass and kept in air tight stoppered glass bottles to prevent the absorption of moisture from the atmosphere. Solutions were prepared by mass using a A&D company limited electronic balance (Japan, Model GR-202) having a precision of ±0.01 mg. The probable error in the molality calculations was estimated to be less than $\pm 1 \times 10^{-4}$. In all cases, the measurements were repeated two times to obtain reproducible results. Before measuring each series, the instrument was calibrated with triple distilled freshly degassed water and dry air at atmospheric pressure. The densities and speeds of sound have precision better than $\pm 1 \times 10^{-6}$ and $\pm 1 \times 10^{-2}$ m s^{-1}, respectively. The uncertainties in the densities of solutions as well as speeds of sound were found to be better than $\pm 5 \times 10^{-6}$ g cm^{-3} and $\pm 5 \times 10^{-2}$ m s^{-1}, respectively.

RESULTS AND DISCUSSION

Compressibility studies: Measurements of speed of sound (u) and densities (ρ) of $LiClO_4$, $NaClO_4$, $NaBPh_4$, Bu_4NBPh_4 and Bu_4NClO_4, were performed at different salt concentrations in the range of 0.001-0.25 mol kg^{-1} in acetonitrile (AN), nitromethane (NM) and their binary mixtures consisting of 0, 20, 40, 60, 80 and 100 mol% NM in AN at 298.15 K (Table-1). The isentropic compressibilities (K_s) of solutions have been determined from the eqn. 1:

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

TABLE-1
DENSITIES (ρ_o), VISCOSITIES (η_o), DIELECTRIC CONSTANTS (ε_o), ULTRASONIC VELOCITIES (u_o) AND ISENTROPIC COMPRESSIBILITIES (K_s°) FOR SOME AN + NM MIXTURES AT 298.15 K

Mol% NM	$10^3 \times \rho_o$ (Kg m^{-3})	$10^{-3} \times \eta_o$ (Pa-s)	ε_o	u_o (m s^{-1})	$10 \times K_s^{\circ}$ (Pa^{-1})
0	0.77686	0.342	36.00	1280.30	78.47
20	0.83101	0.415	36.00	1271.60	74.43
40	0.92352	0.456	36.10	1270.50	67.09
60	0.98911	0.493	36.20	1277.40	61.97
80	1.06020	0.507	36.30	1292.70	56.47
100	1.32900	0.612	36.00	1317.10	50.90

The graphs obtained of K_s *versus* concentration are linear (Fig. 1). It was observed that the K_s values linearly decrease when the salt concentration was increased in all the cases, which indicates non-association of the electrolytes in AN + NM binary mixtures over the salt concentration studied.

The partial molal volumes (V_ϕ) and apparent molal isentropic compressibilities ($K_{s,\phi}$) of salts have also been computed (eqns. 2 & 3):

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

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

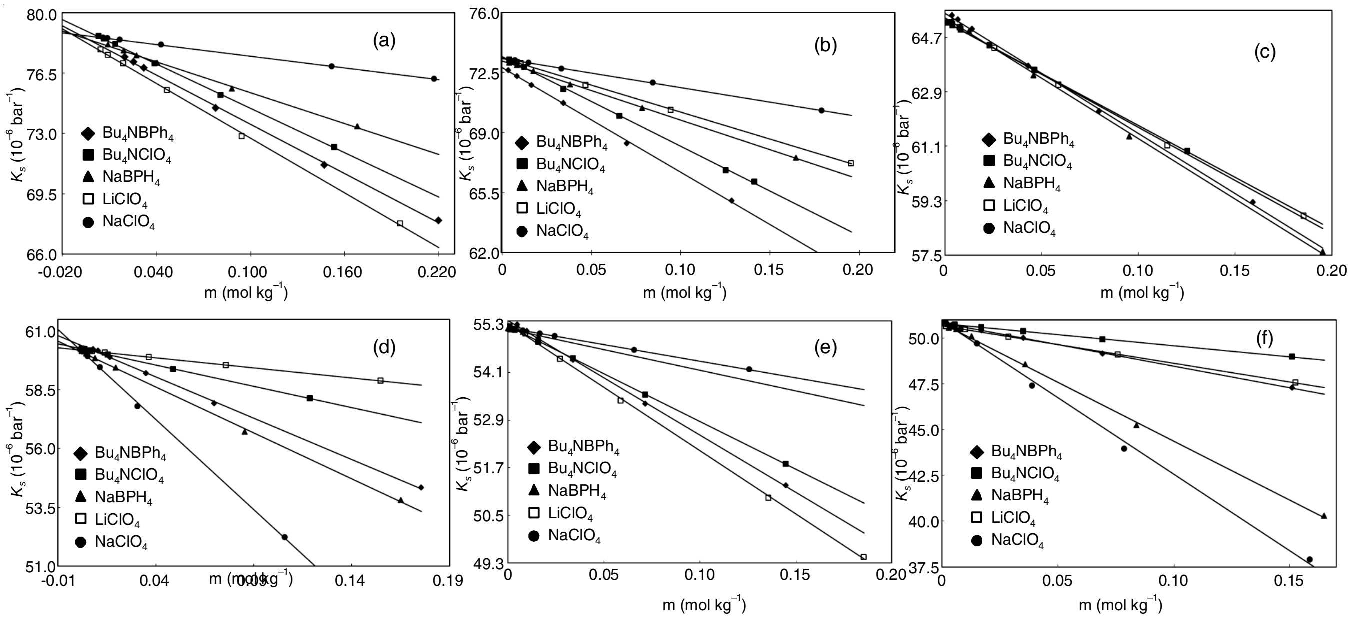

Fig. 1. Plots of K_s *versus* m in 0.0 mol% (a), 20 mol% (b), 40 mol% (c), 60 mol% (d), 80 mol% (e), 100 mol% (f) nitromethane acetonitrile at 298.15 K

where m is molality, M is molecular weight of the electrolyte, K_o and K_s are the isentropic compressibilities and ρ_o and ρ are the densities, respectively of the solvent mixtures and the solutions. The plots of $K_{s,\phi}$ *versus* $m^{1/2}$ obtained were found to be linear in the investigated range of concentration. The limiting apparent molal isentropic compressibilities $(K^o_{s,\phi})_\pm$ were achieved by extrapolating the linear graphs of $K_{s,\phi}$ *versus* $m^{1/2}$ using eqn. 4:

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

The $(K^o_{s,\phi})_\pm$ for the studied salts thus obtained from eqn 4 are given in Table-2. The $(K^o_{s,\phi})_\pm$ for these salts are not already given in literature for AN + NM mixtures, hence, no comparison of the obtained values could be carried out. In pure AN, the $(K^o_{s,\phi})$ for Bu_4NBPh_4 (106.8×10^{-11} m^3 mol^{-1} Pa^{-1}) and Bu_4NClO_4 (22.6×10^{-11} m^3 mol^{-1} Pa^{-1}) are in satisfactory agreement with the values (106.5×10^{-11} and 22.1×10^{-11} m^3 mol^{-1} Pa^{-1}, respectively) as reported in the literature [19,20]. Although negative $(K^o_{s,\phi})$ values for $LiClO_4$, $NaClO_4$ and $NaBPh_4$, show a rise with increase in concentration of the salts (Fig. 2). Whereas for Bu_4NBPh_4 and Bu_4NClO_4, the $(K^o_{s,\phi})$ values fall with increase in the concentration of salts. The $(K^o_{s,\phi})$ of lithium and sodium salts become minimum at 40 mol% NM and then increase. The accuracy of these values can be compared with the experimental $(K^o_{s,\phi})$ values for $NaBPh_4$ from Table-2 with the corresponding experimental $(K^o_{s,\phi})$ values for $NaBPh_4$ obtained by for Na^+ and Ph_4B^- $(K^o_{s,\phi})_\pm$ values from Table-3. The experimentally measured values for $NaBPh_4$ agree well with the calculated values. The $K^o_{s,\phi}$ for Bu_4NBPh_4 and Bu_4NClO_4 obtained are positive and large. For procuring quantitative information regarding the inclination of each ion to cause structural or solvation effects, the $(K^o_{s,\phi})$ values for the salts from Table-2 were split into the contributions of their separated ions.

Study of apparent molal isentropic compressibilities $(K^o_{s,\phi})_\pm$: As reported earlier [21,22], the values of electrolytes being additive, can be directly split to obtain the contribution of individual cations and anions. No standard method of splitting the salt $(K^o_{s,\phi})$ into ionic components is available and as a result some approaches were proposed by some researchers [23,24]. The method [25] already utilized in AN is established upon equating $(K^o_{s,\phi})_\pm$ value equal to zero for Ph_4B^- ion. This method is less befitting since the size of Ph_4B^- ion is large (0.535 nm) and even larger than Bu_4N^+ on (0.500 nm). Therefore, the compressibility contribution cannot be taken equal to zero. Millero [26] had splitted the partial molar volume of electrolyte

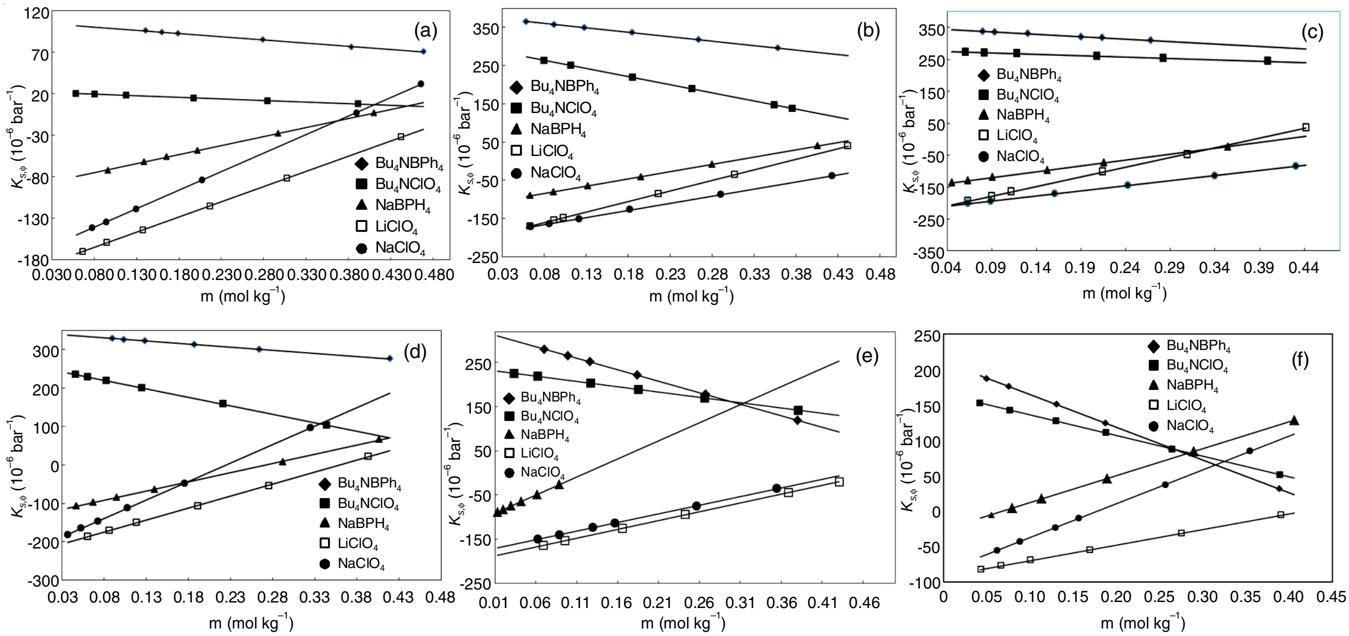

Fig. 2. Plots of $K_{s,\phi}$ *versus* m in 0.0 mol% (a), 20 mol% (b), 40 mol% (c), 60 mol% (d), 80 mol% (e), 100 mol% (f) nitromethane acetonitrile at 298.15 K

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

Salt	$10^{-7} \times (K^o_{s,\phi})$ (m^3 mol^{-1} Pa^{-1})					
	Mol% NM					
	0	20	40	60	80	100
$LiClO_4$	-194.3	-204.9	-232.9	-224.5	-191.6	-91.7
$NaClO_4$	-176.6 (-176.9)^d	-195.9	-221.7	-216.1	-174.5	-85.3
$NaBPh_4$^{a}	-92.5	-114.9	-152.7	-130.6	-99.8	-26.2
$NaBPh_4$^{b}	-92.8	-114.9	-149.7	-128.6	-91.0	-24.0
Bu_4NBPh_4	106.8 (108.1)^d; (106.5)^c	378.6	350.4	342.6	316.9	210.4
Bu_4NClO_4	22.6 (22.1)^d	297.6	278.4	255.1	233.4	164.7

^{a}Experimentally measured values; ^{b}Obtained by adding values for Na^+ and Ph_4B^-; ^{c}Ref. [18]; ^{d}Ref. [19]

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

Ion	$10^{-7} \times (K^{o}_{s,\phi})_{\pm}$ (m^3 mol^{-1} Pa^{-1})					
	Mol% NM					
	0%	20%	40%	60%	80%	100%
Li^+	-168.5	-332.3	-353.8	-325.6	-282.6	-161.8
Na^+	-150.8	-323.3	-342.6	-317.2	-265.5	-139.8
Bu_4N^+	48.0	170.2	157.5	154.0	142.4	94.6
Ph_4B^-	58.8	208.4	192.9	188.6	174.5	115.8
ClO_4^-	-25.4	127.4	120.9	101.1	91.0	70.1

in ionic component by making use of Bu_4AsBPh_4 as a reference electrolyte. An equivalent model based on Bu_4NBPh_4 assumption was suggested by Gill *et al*. [9,13], in which they recommended making use of the reference electrolyte Bu_4NBPh_4 to split the $(K^{o}_{s,\phi})$ into its cationic and anionic contributions utilizing the eqns. 5 and 6:

$$\frac{K^{o}_{s,\phi}(Bu_4N^+)}{K^{o}_{\phi}(Ph_4B^-)} = \frac{r_c^3(Bu_4N^+)}{r_c^3(Ph_4B^-)} = \frac{(5.00)^3}{(5.35)^3} \qquad (5)$$

$$K^{o}_{s,\phi}(Bu_4NBPh_4) = \mathrm{K}^{o}_{s,\theta}(Bu_4N^+) + K^{o}_{s,\phi}(Ph_4B^-) \qquad (6)$$

where r_c refers to the crystallographic radius of the ion. Eqns. 5 and 6 were used to split $(K^{o}_{s,\phi})$ value for Bu_4NBPh_4 into the contributionsof Bu_4N^+ and Ph_4B^-. By utilizing these ionic contributions, $(K^{o}_{s,\phi})_{\pm}$ for the ions of the remaining electrolytes have been estimated by applying the additive principle and are given in Table-3. From Table-3, interesting results were found for Li^+ and Na^+ ions. The $(K^{o}_{s,\phi})_{\pm}$ values of Li^+ are negative and larger in magnitude than Na^+ in all compositions of the AN + NM solvent mixtures. The values become more negative for Li^+ and Na^+ with increase of NM composition, reach to a minimum at 40 mol% NM and then become less negative in pure NM. The magnitude of $(K^{o}_{s,\phi})$ values for Li^+ and Na^+ is greater at the intermediate compositions from 20 to 80 mol% NM than in pure AN and NM. The negative $(K^{o}_{s,\phi})_{\pm}$ values for Li^+ and Na^+ obtained (Table-3) suggest strong structural effects, which arise due to solute-solvent interactions [10,13]. The solvation exhibited by the said ions is due to pure electrostatic ion-solvent interactions [27,28]. As the size of cation increases, the distance of closest approach of cation and solvent molecules increases resulting in decrease in extent of ion-dipole interactions. It is evident that for the cation of smaller size the ion-dipole interactions are stronger. Negative $(K^{o}_{s,\phi})_{\pm}$ values are a parameter for these interactions. This is clearly observed for Li^+ ions, the $(K^{o}_{s,\phi})_{\pm}$ values are more negative as compared to Na^+ ions. While positive $(K^{o}_{s,\phi})_{\pm}$ values for Bu_4N^+ and Ph_4B^- suggest some special type of interactions [19,29] with the solvent in the mixed binary solvents, which are solvophobic or dispersive. The magnitude of such interactions increases with increase in NM mol% in the mixtures. Special interaction through dispersion forces of Ph_4B^- with acetonitrile has also been reported by Bose & Kundu [30]. The ClO_4^- ion does not seem to be affected by the acid properties of solvent molecules, but the dipole moment of AN and NM determines its solvation sheath. Positive as well as less negative values for ClO_4^- show its poor solvation by both AN and NM. Previous analysis also explains that the anions have only weak inter-actions with the aprotic solvents [31]. The large and negative values for Li^+ and Na^+ indicate their stronger solvation. Extent of such interactions for Li^+, however, is greater than Na^+ in both AN and NM and their binary mixtures.

Conclusion

The large magnitude and negative $(K^{o}_{s,\phi})_{\pm}$ values for Li^+ and Na^+ ions indicated strong ion-solvent interactions, which are essentially of the ion-dipole type. The Li^+ and Na^+ ions both are preferentially solvated by in AN + NM binary mixtures. The Li^+ and Na^+ ions both showed a stronger solvation in the intermediate compositions of AN + NM mixtures. Due to smaller size and higher charge density of Li^+ ion, it shows stronger solvation than Na^+ ion in the binary mixtures of AN and NM at all compositions. The ClO_4^- exhibits much weaker solvation as compared to Li^+ and Na^+ ions in AN + NM mixtures by making some interaction with AN in the binary mixtures with higher AN mol%. The Bu_4N^+ and Ph_4B^- ions show solvent repelling or dispersive interactions.

ACKNOWLEDGEMENTS

One of the authors, (NS) is grateful to the University Grants Commission (UGC), New Delhi, India, for the award of Junior Research Fellowship (JRF).

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

1. J. Barthel, R. Buchner and E. Wismeth, *J. Solution Chem.*, **29**, 937 (2000); https://doi.org/10.1023/A:1005186701329
2. M.F.J. Mabesoone, A.R.A. Palmans and E.W. Meijer, *J. Am. Chem. Soc.*, **142**, 19781 (2020); https://doi.org/10.1021/jacs.0c09293
3. D.S. Gill, L. Byrne and T.I. Quickenden, *Z. Naturforsch. A*, **53**, 1004 (1998). https://doi.org/10.1515/zna-1998-1213
4. R. Cabota and C.A. Hunter, *Chem. Soc. Rev.*, **41**, 3485 (2012); https://doi.org/10.1039/C2CS15287H
5. M.N. Roy, D. Ekka and R. Dewan, Fluid Phase *Equilib.*., **314**, 113 (2012); https://doi.org/10.1016/j.fluid.2011.11.002
6. D.S. Gill, V. Pathania, A. Kumari, H. Anand and S.P. Jauhar, *Z. Phys. Chem.*, **218**, 857 (2004); https://doi.org/10.1524/zpch.218.7.857.35729
7. V.K. Syal, A. Chauhan, P. Sharma and S. Chauhan, *J. Polym. Mater.*, **22**, 363 (2005).
8. B.K. Sarkar, B. Sinha and M.N. Roy, *Russ. J. Phy. Chem. A*, **82**, 960 (2008); https://doi.org/10.1134/S0036024408060174
9. J.S. Singh, T. Kaur, V. Ali and D.S. Gill, *J. Chem. Soc., Faraday Trans.*, **90**, 579 (1994); https://doi.org/10.1039/ft9949000579
10. D.S. Gill, P. Singh, J. Singh, P. Singh, G. Senanayake and G.T. Hefter, *J. Chem. Soc., Faraday Trans.*, **91**, 2789 (1995); https://doi.org/10.1039/ft9959102789
11. H. Anand and R. Verma, *Z. Phys. Chem.*, **230**, 185 (2016); https://doi.org/10.1515/zpch-2015-0636

12. M.S. Chauhan, K. Sharma and G. Kumar, *Indian J. Chem.*, **41A**, 483 (2002).
13. D.S. Gill, H. Anand and J.K. Puri, *J. Mol. Liq.*, **108**, 265 (2003); https://doi.org/10.1016/S0167-7322(03)00186-7
14. M.N. Roy, D. Ekka, I. Banik and A. Majumdar, *Thermochim. Acta*, **547**, 89 (2012); https://doi.org/10.1016/j.tca.2012.08.009
15. D.S. Gill and A.N. Sharma, *J. Chem. Soc*., *Faraday Trans. I*, **78**, 475 (1982); https://doi.org/10.1039/f19827800475
16. D.S. Gill, D.S. Rana and S.P. Jauhar, *J. Chem. Eng. Data*, **55**, 2066 (2010); https://doi.org/10.1021/je900915p
17. J.A. Riddick, W.B. Bunger and T.K. Sakano, Organic Solvents, Physical Properties and Methods of Purification, Wiley Interscience: New York, Eds. 4 (1986).
18. M.N. Roy, A. Banerjee and R.K. Das, *J. Chem. Thermodyn.*, **41**, 1187 (2009); https://doi.org/10.1016/j.jct.2009.03.005
19. D.S. Gill, R. Singh, H. Anand and J.K. Puri, *J. Mol. Liq.*, **98-99**, 15 (2002); https://doi.org/10.1016/S0167-7322(01)00303-8
20. J. Krakowiak and W. Grzybkowski, *J. Chem. Thermody*., **33**, 121 (2001); https://doi.org/10.1006/jcht.2000.0725
21. J. Krakowiak, D. Bobicz and W. Grzybkowski, *J. Chem. Thermodyn.*, **33**, 121 (2001); https://doi.org/10.1006/jcht.2000.0725
22. G. Hefter and Y. Marcus, *J. Solution Chem.*, **26**, 249 (1997); https://doi.org/10.1007/BF02767997
23. D.S. Gill, B.K. Vermani and R.P. Sharma, *J. Mol. Liq.*, **124**, 58 (2006); https://doi.org/10.1016/j.molliq.2005.07.006
24. I. Davidson, G. Perron and J.E. Desnoyers, *Can. J. Chem.*, **59**, 2212 (1981); https://doi.org/10.1139/v81-319
25. J. Barthel, L. Iberl, J. Rossmaier, H.J. Gores and B. Kaukal, *J. Solution Chem.*, **19**, 321 (1990); https://doi.org/10.1007/BF00648139
26. F. Millero, *J. Phys. Chem.*, **75**, 280 (1971); https://doi.org/10.1021/j100672a016
27. D.S. Gill and M.S. Chauhan, *Z. Phys. Chem.*, **140**, 139 (1984); https://doi.org/10.1524/zpch.1984.140.2.139
28. D.S. Gill, S. Chauhan and M.S. Chauhan, *Z. Phys. Chem.*, **150**, 113 (1986); https://doi.org/10.1524/zpch.1986.150.1.113
29. I. Bahadur and N. Deenadayalu, *J. Solution Chem.*, **40**, 1528 (2011); https://doi.org/10.1007/s10953-011-9740-0
30. K. Bose and K.K. Kundu, *Indian J. Chem.*, **17A**, 122 (1979).
31. D.M. Seo, O. Borodin, S.D. Han, Q. Ly, P.D. Boyle and W.A. Henderson, *J. Electrochem. Soc.*, **159**, A553 (2012); https://doi.org/10.1149/2.jes112264