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Intermolecular Interaction Studies of Ethyl Bromide in Non-Aqueous Solution

Seethalakshmi .K[1], Jasmine Vasantha Rani .E[2],

PG & Research Department of Physics, Seethalakshmi Ramaswami College, Tiruchirapalli-2, Tamilnadu, India

Abstract: ***Ultrasonic technique is the vital probe in evaluating the thermo-dynamical parameters such as internal pressure and free volume. Compressibility measurements are highly accurate and yield interesting informations. The sign and magnitude of compressibility indicates the solvation effects. The structural changes in the primary and secondary regions are generally referred to as solvation. The solvation of emimBr in non-aqueous medium is taken for interpreting the various interactions occurring between the solute and solvent and the effect of temperature and concentration on solvation is also analyzed. The thermochemical parameters have been proven to be a very useful tool in elucidating the structural interactions taking place in the solutions. In the present investigation, non-aqueous solutions of emimBr have been prepared with various concentrations and the experiments were carried out to measure ultrasonic velocity(v), density (ρ),viscosity(η) from a low temperature of 5°C To a high temperature of 55°C. Using these experimental data, the acoustical parameters such as adiabatic compressibility (β), apparent molal volume (φ_v), apparent molal compressibility(φ_k) were calculated. These experimental values have been analyzed and eventually emphasizing the possible molecular interactions in terms of structure promoting nature of the sample in the solvent.***

Keywords: ultrasonic velocity, density, viscosity, solvation number, compressibility

1. Introduction

Intermolecular interactions and thermodynamic properties of ionic liquids can be estimated more precisely using ultrasonic technique [1,2]. In recent years, significant progress has been made in the application of room temperature ionic liquids [3,4,5]. The liquid structure of ILs seems to be heterogeneous, unlike that of molecular solvents [6–9]. An ionic liquid typically consists of organic nitrogen-containing heterocylic cations and inorganic anions. In the present investigation, solvation effects of emimBr are studied in non-aqueous medium. By measuring the fundamental quantities such as density and ultrasonic velocity of emimBr in formamide from 5°C to 55°C at different concentration, the solvation number were computed. From the analysis of solvation, the imidazole salts in formamide reveals the structural interaction taking place in the solution. Krishnamurthy Subba Rao [10], Sastry and Krishnamurthy [11], Sathya Narayanamurthy [12], Sinhal [13], Seshagiri Rao and Ramachandran Rao [14], Prakash et al [15] and many others have carried out ultrasonic study of aqueous and non-aqueous solutions.

2. Experimental

Here, emimBr and formamide are purchased from Sigma Aldrich chemicals, USA with high purity (99%) and hence used without any further purification. The solutions of emimBr in formamide are prepared with five different molalities. Density of the solution is measured using 25 ml specific gravity bottle, using thermostatic bath with a compressor unit with an accuracy of 0.001gm/cc. Canon Fenske viscometer was used for the viscosity measurements. Variable path interferometer having a frequency of 2 MHz with an overall accuracy of 0.1% was used for velocity measurements. A constant temperature path (digitalized) was used to circulate water through the double-walled measuring cell of steel containing the experimental solution at the desired temperature (5°C to 55°C).

3. Computation

Using the experimentally measured values, the following thermo dynamical parameters are computed using the standard formulae [16]

(i) Adiabatic compressibility:

$$\beta = \frac{1}{U^2 \rho} \frac{cm^2}{dyne}.$$

(ii) Apparent molal volume:

$\varphi_v = 1000/ m_1\rho_0 (\rho_0 - \rho) + M / \rho_0$ ml/mol

(iii) Apparent molal compressibility:

$\varphi_k = 1000/ m\rho_0 (\rho_0\beta - \rho \beta_0) + [\beta_0 M / \rho_0]$ ml/mol/cm^2/dyne

(iv) Inter molecular free length:

$L_f = K / \sqrt{\rho}\, U$

(v) Specific Acoustic Impedance:

$Z = \rho U$ Rayl (Kgm^{-2}s^{-1})

(vi) Internal Pressure and Free Volume:

$\Pi_i = bRT(k\eta/U)^{1/2} * (\rho^{2/3} / M_{eff}^{7/6})$ atms;

$V_f = (M_{eff} * U/k\eta)^{3/2}$cc

(vii) Solvation Number:

$$n_h = \left(\frac{n_s}{n_i}\right)\left[1 - \frac{\beta}{\beta_0}\right]$$

Where

R – gas constant(8.314 x10^7)

T – temperature

b – cubic constant(2)

k – constant equal to 4.28 x 10^9

η – viscosity of the solution in poise

U – ultrasonic velocity in cm/sec

ρ - density of the solution in gm/cc.

ρ_0 - density of the solvent

m_1 – molal concentration of the solute

M – molecular mass of the solute

M_{eff} - Effective molecular weight of the solution in gm

β_0 & β - the compressibility of the solvent & solution in cm^2/dynes.

n_h, n_s & n_i are the primary solvation number, moles of solvent and moles of ions respectively.

4. Results and Discussion

(i) Adiabatic compressibility:

Adiabatic compressibility of EMIMBr values are reported in Table 3 and the graphical representations are shown in Figure 3.In lower temperatures, adiabatic compressibility is found to increases and then decreases. But above room temperature (25^0C-45^0C), the adiabatic compressibility decreases and then increases with concentration and also increases with rise in temperature. These rise and fall variations suggest that there is a strong solute-solvent interaction[17].

Table 1: Adiabatic Compressibility x 10^{-11} (cm^2/dyne)

Molality(m)	5°C	15°C	25°C	35°C	45°C	55°C
0.001	3.21	3.33	3.46	3.55	3.70	3.79
0.005	3.26	3.37	3.44	3.57	3.64	3.76
0.01	3.26	3.34	3.44	3.51	3.62	3.79
0.015	3.23	3.35	3.41	3.48	3.65	3.81
0.02	3.22	3.32	3.45	3.50	3.66	3.79

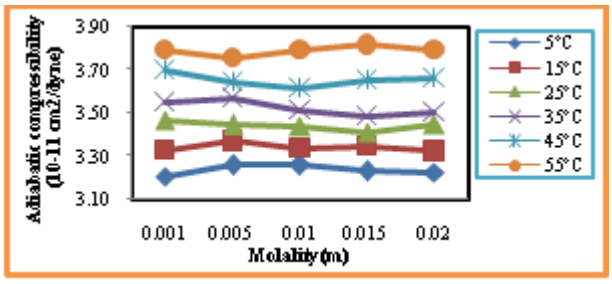

Figure 1: Molality v_s Adiabatic compressibility

(ii) Apparent molal volume

The apparent molal volume of the solution is important in the study of the structural occuring in solutions. The concentration dependence of the apparent molal volumes of the solution can be used to study ion-ion interactions. Not much variation is observed for apparent molal volume φ_v with change in concentration. However at low concentration φ_v variation is predominant at all temperatures. Negative values of φ_v are observed at 25^0c for all concentrations. Positive values of φ_v are observed at 55^0c for all concentrations. This behavior suggest that there is a strong ion-ion interaction occuring in the solution. It is represented in Table.2 and Figure 2.

Table 2: Apparent molal volume

Molality(m)	5°C	15°C	25°C	35°C	45°C	55°C
0.001	-143	-4584	-4167	-1549	-2175	2058
0.005	-161	-243	-102	305	-132	206
0.01	-55	21	-153	-66	-42	25
0.015	18	-158	-97	160	41	125
0.02	182	51	-2	81	89	71

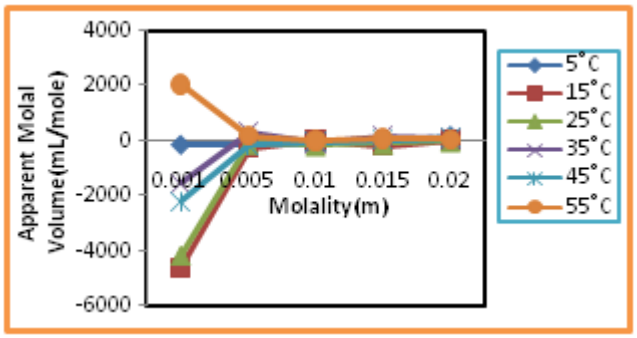

Figure 2: Molality v_s Apparent Molal Volume

(iii) Apparent molal compressibility:

Apparent molal compressibility [18] φ_k of the solute is the compressibility of an amount of solution containing one mole of the solute minus the compressibility of the solvent. Apparent molal compressibility increases with increase in concentration at 45^0C.At low molality (0.001) apparent molal compressibility shows a negative value in all temperatures. This result supports that there is a strong ion-ion interaction occuring in the solution[19].It is represented in Table.3 and Figure 3.

Table 3: Apparent molal compressibility

Molality(m)	5°C	15°C	25°C	35°C	45°C	55°C
0.001	-6942	-6940	-7030	-2190	-1680	-3322
0.005	168	565	644	279	-1540	-1520
0.01	92	0	223	-588	-1030	-419
0.015	-127	68	-35	-545	-397	30
0.02	-81	-89	183	-303	-219	-425

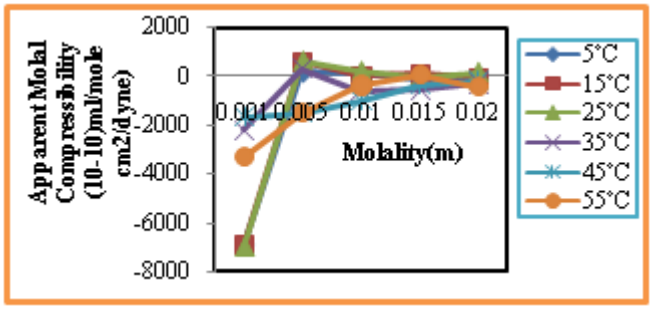

Figure 3: Molality v_s Apparent Molal compressibility

(iv) Inter molecular free length

An examination of Table 4 shows that the inter molecular free length (L_f) increases with rise in temperature. The increase in inter molecular free length leads to an increase in compressibility with rise in temperature. The intermolecular free length depends on adiabatic compressibility and shows similar behavior to that of adiabatic compressibility and inverse to that of ultrasonic velocity[20]. The intermolecular free length decreases with increases of concentration and temperature. This indicates possibility of breaking dipole in emimBr.

This prevails that specific strong intermolecular interaction between the solute and solvent molecules takes place. At above room temperatures, decreased value of free length indicates structure promoting behavior of solute molecule. From Table 4 and Figure. 4, it is observed that intermolecular free length (L_f) shows similar behavior as reflected by β[21]. The decreased compressibility brings the molecules to a closer packing resulting into a decrease of intermolecular free length (L_f). L_f is a predominant factor in determining the variation of U in solutions.

Table 4: Intermolecular free length

Molality(m)	5°C	15°C	25°C	35°C	45°C	55°C
0.001	0.10643	0.11080	0.11500	0.12000	0.12440	0.12779
0.005	0.10759	0.11200	0.11600	0.12040	0.12340	0.12719
0.01	0.10759	0.11150	0.11600	0.11940	0.12300	0.12776
0.015	0.10714	0.11180	0.11600	0.11890	0.12360	0.12837
0.02	0.10703	0.11120	0.11600	0.11930	0.12380	0.12703

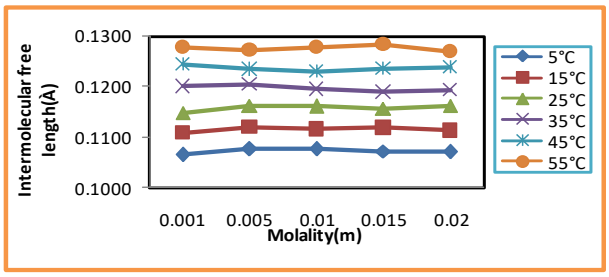

Figure 4: Molality v_s Intermolecular Free Length

(v) Specific Acoustic Impedance

Specific Acoustic Impedance is a measure of the strength of intermolecular attraction. The acoustic impedance decreases with increase in temperature. The variations in acoustic impedance with various concentrations and temperatures are shown in Table.5 and figure.5

Table 5: Specific Acoustic Impedance

Molality(m)	5°C	15°C	25°C	35°C	45°C	55°C
0.001	18.72	18.52	18.15	17.89	17.61	17.20
0.005	18.75	18.42	18.05	17.87	17.49	17.01
0.01	18.89	18.38	18.09	17.80	17.46	17.21
0.05	18.68	18.48	18.18	17.76	17.56	17.25
0.1	18.71	18.51	18.23	17.73	17.53	17.19

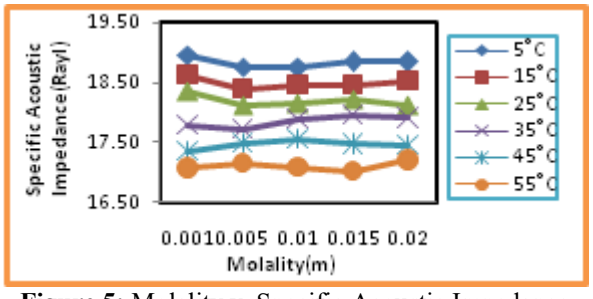

Figure 5: Molality v_s Specific Acoustic Impedance

(vi) Internal Pressure and Free Volume:

The variations in the Π_i and V_f with different concentrations have been used to explain the ion-solvent interactions and hence to study the structural changes in the solution. The dependence of these parameters on temperature has also been used to explain the strength of interactions with change in temperatures. Internal pressure is a single factor which varies due to all the internal interactions. The variations of internal pressure and free volume with temperatures and molalities are shown in Figures 6 & 7 and the values are tabulated in Tables 6 & 7. From the figure, it is observed that the internal pressure shows an increasing trend with respect to molalities in the solution. This increasing trend suggests the presence of strong solute-solvent interactions or increase in the cohesive energy of the system. Hence, this may be attributed to the structure enhancing nature of the solutes in the solvent. [22]

Table 6: Internal Pressure

Molality(m)	5°C	15°C	25°C	35°C	45°C	55°C
0.001	20259	16887	14385	13199	12150	11053
0.005	19593	17035	14450	13591	12042	11176
0.01	20547	16920	14635	13597	12087	11295
0.015	20647	17178	14658	13188	12341	11357
0.02	20425	17098	14313	13476	12153	11349

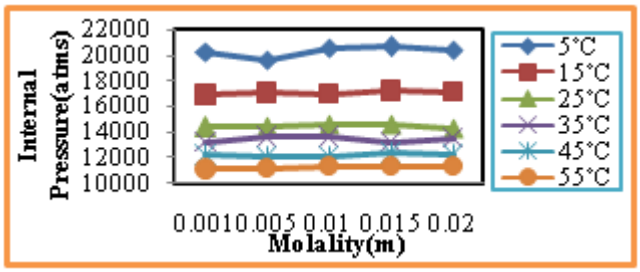

Figure 6: Molality v_s Internal pressure

Table 7: Free Volume

Molality (m)	5°C	15°C	25°C	35°C	45°C	55°C
0.001	0.007385	0.014109	0.024936	0.034967	0.048675	0.069548
0.005	0.008179	0.013674	0.024461	0.031879	0.049892	0.067456
0.01	0.007083	0.013911	0.023571	0.031942	0.049288	0.065405
0.015	0.006971	0.013354	0.023461	0.034816	0.046228	0.064154
0.02	0.007159	0.013462	0.025134	0.032675	0.048301	0.06435

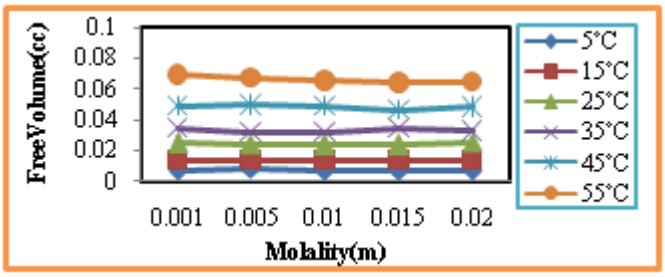

Figure 7: Molality v_s Free Volume

(vii) Solvation Number

Solvation Number of emimBr are reported in Table 8 and the variations are shown in figure 8. In the present study, the solvation number is computed from compressibility measurements. At lower concentrations, a positive solvation number is observed at all temperatures and at higher concentrations, no abrupt change in solvation is found at higher molalities. Solvation Number is positive at high temperatures. It is negative at low temperatures and at low concentration (0.005).These temperature effects observed in this solution support the strong solute-solvent interaction. It indicates the presence of H-bonding interactions.

Table 8: Solvation Number

Molality(m)	5°C	15°C	25°C	35°C	45°C	55°C
0.001	401	308	315	89	46	209
0.005	-13	-37	-38	-9	78	81
0.01	-6	0	-15	30	53	22
0.015	8	-7	0	32	22	1
0.02	8	6	-10	18	13	23

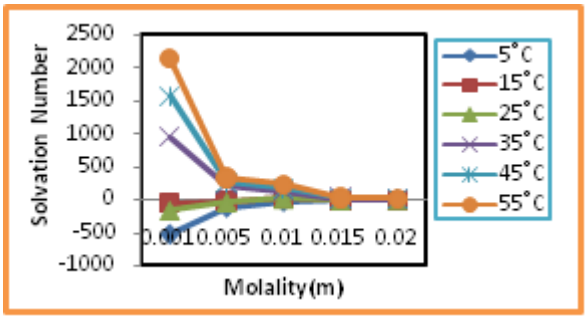

Figure 8: Molality v_s Solvation Number

5. Conclusion

In the present work, the acoustic studies are carried out to analyze the various molecular interactions occurring in the solution of emimBr. Experimentally measured and other calculated acoustical and thermochemical parameters contain valuable information about ion-solvent interactions. The non-uniform variation in the acoustical parameters proves that there is considerable amount of interactions between emimBr and solvent molecules and it shows moderate change with very small change in concentration and temperature.

References

[1] S.Jayakumar, N.Karunanithi and V.Kamappan, Indian J Pure Appl PHY.34 (1996)761.
[2] S.K.Dash,V.Chakravorthy and B.B.Swain,Acoust Leto 19(1996) 142.
[3] D. B. Zhao, M. Wu, Y. Kou, E. Z. Min, Catal. Today, 2002, 2654, 1.
[4] H. Olivier-Bourbigou, L. Magna, J. Mol. Catal. A: Chem., 2002, 182-183, 419.
[5] T. Welton, Chem. Rev., 1999, 99, 2071.
[6] J. N. Canongia Lopes, A. A. H. Padua. J. Phys. Chem. B 110, 3330 (2006).
[7] J. N. Canongia Lopes, M. F. C. Gomes, A. A. H. Padua. J. Phys. Chem. B 110, 16816 (2006).
[8] A.Triolo, O. Russina, H.-J. Bluif, E. D. Cola. J. Phys. Chem. B 111, 4641 (2007).
[9] R.Atkin, G. G. Warr. J. Phys. Chem. B 112, 4164 (2008).
[10] Suryanarayanan.C.V and Kuppusamy J.- journal of acoustical society of india(1976)
[11] Sastry G.L.N and Krishnamurthy B.A, Ind.j.pune appl.phy.vol 6(1968)
[12] M.Sathyanarayanmurthy-Ind.J.pune appl.phy; vol 3(1965).
[13] S.P.Singhal-Ind.J.pune appl.phy; vol 3(1965).
[14] M.G.Seshagiri Rao and B.Ramachandra Rao-Ind.J.pune appl.phy; vol 1(1963).
[15] Prakash S. and Singh R.,-J Acoustical society of India 4,(1976).
[16] Suryanarayana C.V. J. Acou .Soc. India 7(1979) 131-136
[17] JasmineVasanthaRaniE, Geetha.K, Solachi.V, Padmavathy.R and Kavitha.J. J.Acous.Soc.India, Vol.31,1-4(2003),323-326
[18] Dhanalakshmi.A, Jasmine Vasantha Rani and Padmavathy.R, J.Acoust.soc.India, vol xxiii,2; vol xxvii.
[19] Indian journal of Pure and applied physics-vol31 Dec(1993) p(869-876)
[20] Eyring H, Kincaid J F. J Chem. Phys.(USA), 1938,6,620-629
[21] Sunanda S. Aswale, Shashikant R. Aswale, Rajesh S. Hajare Journal of Chemical and Pharmaceutical Research, 2012, 4(5):2671-2677
[22] Sayal V K, Kumari U, Chauhan S and Chauhan M.S., Ind. J. Pure App Phys, 1992,30,719-723.