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RESEARCH ARTICLE

STUDY OF VIBRATIONAL SPECTRA AND SOLVATION NUMBER OF NON-AQUEOUS SOLUTIONS OF 1-BENZYL-3-METHYLIMIDAZOLIUM CHLORIDE THROUGH ULTRASONIC TECHNIQUE

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ABSTRACT

Ultrasonics is an interesting field of study which makes an effective contribution to many areas of human endeavor. One of two fundamental types of solutpe–solvent intermolecular interactions is the specific interactions, such as hydrogen bonding complexation between solute and solvent. In the present investigation, non-aqueous solution of the selected ionic liquid, 1-benzyl-3-methylimidazolium chloride (bzmimCl) have been prepared with various concentrations and the experiments were carried out to measure ultrasonic velocity, density, viscosity from 5˚C to 55˚C. Using these experimental data, the thermo dynamical parameters and solvation number are studied to reveal the nature and strength of the interactions taking place in the solution. These experimental values have been analyzed and eventually emphasizing the possible molecular interactions. Solute–solvent interactions are conveniently studied by several spectroscopic techniques. They provide information about the structure of the solvent around the solute molecules. Infrared spectroscopy is one of the most powerful analytical techniques which offer the possibility of chemical identification. The results are also compared with FT-IR spectrum.

INTRODUCTION

The study of molecular interaction plays a vital role in the development of molecular science. Molecular interactions and structural behavior of the solutions can be identified using these studies. 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, and 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 heterocyclic cations and inorganic anions. In the present investigation, acoustical parameters are studied in non-aqueous medium by measuring the fundamental quantities such as density and ultrasonic velocity of bzmimCl in formamide from 5˚C to 55˚C at different concentrations.

Experimental

Here, 1-benzyl-3-methylimidazolium chloride and formamide are purchased from Sigma Aldrich chemicals, USA with high purity (99%) and hence used without any further purification. A solution of bzmimCl in formamide is prepared with five different molarities. 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 (Mittal's Enterprises, New Delhi, Model: F-81) with an overall accuracy of 0.1% was used for velocity measurements. A constant temperature bath (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).

Computation

Using the experimentally measured values, the following thermo dynamical parameters are computed using the standard formulae [10]

1. $\pi_i = bRT\,(k\eta/u)^{1/2}\,[\rho^{2/3} / M_{eff}^{7/6}]$ atms ;
2. $V_f = [Mu / \eta k]^{3/2}$ CC and
3. $n_s = \left[\frac{n_f}{n_i}\right]\left[1 - \frac{\beta_{soln}}{\beta_{solv}}\right]$

RESULTS AND DISCUSSION

Internal pressure and free volume are the thermo dynamical properties which explain the interaction in the solution. Internal pressure is a single factor that appears to vary due to all the intermolecular interactions. Internal pressure plays an important role in explaining molecular interaction, as this represents the resultant of the forces of attraction and repulsion between the molecules. Free volume is the average volume in which the center of the molecule can move inside the hypothetical cell due to the repulsion of surrounding molecules.

In the case of bzmimCl, the internal pressure increases for lower concentration at all temperatures. But it is found to be decreased for higher molarities. A dip is observed at 0.05m (Table 1). This behavior suggests that there is a weak solute–solvent interaction (Fig 1). In bzmimCl, free volume increase with increasing concentration at all temperatures. The changes

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in free volume are in the figure 2 and the values are tabulated in table 2.

Table1 Internal Pressure **(**atms**)**

Morality(m)	5˚C	15˚C	25˚C	35˚C	45˚C	55˚C
0.001	17937	15324	13325	12275	10881	10541
0.005	18451	15690	13543	12386	11391	10553
0.01	18631	15775	13712	12566	11465	10481
0.05	18227	15818	13573	12420	11506	10587
0.1	16924	15018	13220	12083	10937	10046

Broad absorption band due to N–H stretching vibration is shifted on dilution from 3418 to 3412 (blue shift of 6 cm^{-1}) and for CH stretching vibration, shift from 2890 cm^{-1} to 2888 cm^{-1} (blue shift of 2 cm^{-1}) are observed.

Compared to solid state spectra, these shifts are 3410–3418 cm^{-1} (ν_{NH} red shift 8 cm^{-1}) and 2857–2890 cm^{-1} ($\nu_{C\text{-}H}$ red shift 33 cm^{-1}) respectively. At saturation morality, a new peak at 1694 cm^{-1} is attributed to the keto group of the solvent.

Table2 free volume (cc)

Morality(m)	5˚C	15˚C	25˚C	35˚C	45˚C	55˚C
0.001	0.010585	0.018635	0.031118	0.04335	0.067818	0.08069
0.005	0.009766	0.017439	0.029661	0.042175	0.058965	0.080369
0.01	0.00946	0.017149	0.028413	0.04034	0.057661	0.08196
0.05	0.009992	0.016741	0.029044	0.041235	0.056357	0.078421
0.1	0.012259	0.01928	0.03098	0.044091	0.064859	0.090331

Table3 salvation number

Morality(m)	5˚C	15˚C	25˚C	35˚C	45˚C	55˚C
0.001	-650	-675	-397	183	1305	1571
0.005	-120	-83	-50	61	258	336
0.01	-76	-51	-31	29	124	164
0.05	-14	-10	-4	7	26	32
0.1	-6	-2	1	7	17	20

The interactions occurring in different solutions can also be confirmed by the salvation number, which is measure of structure making or structure breaking tendency of solute in a solution. Salvation number values are found decrease with concentration of solute [11]. Salvation number clearly represents the salvation of solute in solvent causes interactions giving rise to increase the solubility of solute [12]. The salvation number reflects the dynamic situation of the ion as it moves around in the solution [13]. The sign and magnitude of compressibility indicates the salvation effects. The Salvation approach is used to interpret ion-solvent interaction energy may be equal to intermolecular interaction energy [15]. Which results in zero values of solvation number. Negative Salvation number emphasizes that solution are more compresible than solvent.

Negative Salvation number for various molarities is reported in literature [16]. In the present study, the salvation number is computed using compressibility measurements. In bzmimCl, salvation number is positive at high temperatures and it is negative at low temperatures for all concentrations.(Table 3).This behavior suggests that solution is more compressible than solvent above room temperature. It supports that there is a weak solute–solvent interaction between solute and solvent. The variation with respect to temperature and concentration are shown in the figure 3.

FT–IR spectral analysis of 1–benzyl–3–methylimidazolium chloride in formamide

In the solid state FT–IR spectrum, the broad absorption band at 3410 cm^{-1} indicate strong N…H–CH linkages between two imidazole rings. The $>C=N^{+}$ stretching vibration occur as a sharp band at 2114 cm^{-1}, C–N stretching vibration is found at 1634 cm^{-1} while C–C stretching ring vibration occur at 1574 cm^{-1}.The series of peaks at 1456 cm^{-1} to 1002 cm^{-1} indicates several stretching modes that may result from resonance stabilization. The bending modes due to C–H, C–N and ring occur in the region 931 to 623 cm^{-1}. On dissolution in formamide, (Fig 4) the solvent stretching vibration encompasses several stretching vibrations occurring in the solid state.

In the region 1000–1500 cm^{-1}, the series of stretching and bending vibrations in the solid state spectra are replaced by fewer peaks in the solution spectra.

The ring bending vibration at 623 cm^{-1} are shifted to 610 cm^{-1} (blue shift of 13 cm^{-1}) on dissolution in formamide (Table 4).

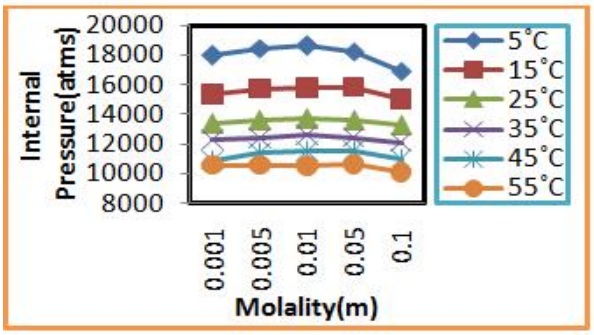

Figure 1 Internal Pressure Vs Morality

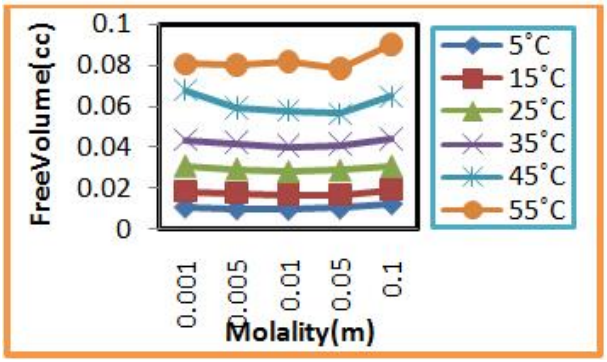

Figure 2 Free Volume Vs Morality

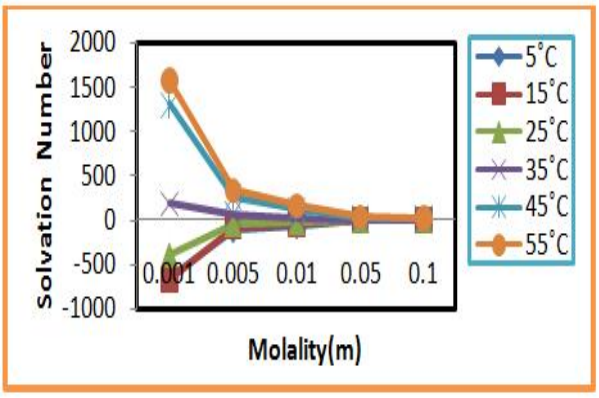

Figure 3 Salvation Number Vs Morality

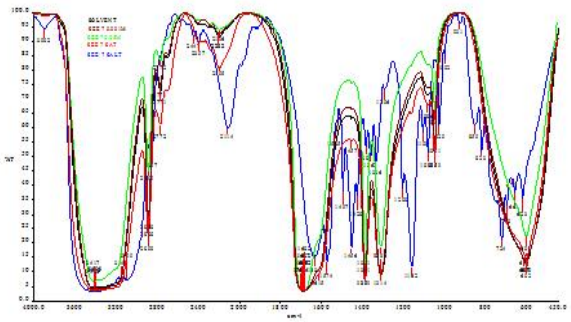

Figure 4 FT–IR spectra

Table 4 FT–IR spectral frequencies - 1-benzyl-3-methylimidazolium chloride solution

Band Assignment	Solvent cm^{-1}	Solid cm^{-1}	Solution cm^{-1}
ν_{NH}	3422	3902,3410	3902,3418
ν_{CH}	2889,2771,2690	2857	2890,2772,2704
$\nu_{C=N}^{+}$	2402,2198	2447,2114	2400,2287,2195
$\nu_{C=C}$	1685	1634,1574	1694
$\nu_{C=N}$	1390,1313,1051	1497, 1456, 1386, 1336,1162, 1083	1457, 1391,1314, 1165,1086, 1051
$\delta_{CH,}$	—	931	—
$\delta_{N^{+}Cl^{-}}$	605	623	610

CONCLUSION

The observed trends and variations of thermo dynamical parameters with concentrations of solutions provide useful information about the nature of intermolecular forces existing in the solution. The existence of solute –solvent interaction resulting the structure – breaking/loosening nature of solute behavior is seen in bzmimCl. The results of spectral analysis of bzmimCl solution indicate weak binding between the imidazolium ring and keto form of formamide. This result is in good agreement with thermodynamic study.

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