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Ultrasonic and Spectroscopic Investigations on 1-Hexyl-3-Methylimidazolium Solution

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Abstract: ***The study of ions in liquids and solutions is a part of chemical Physics. The passage of ultrasonic waves through solutions and liquids disturb the equilibrium between the solvent molecules. The measurement of ultrasonic velocities in liquids and solutions is found to be one of the convenient tools for studying the physico-chemical behavior in solution. It provides very useful information related to intermolecular interaction. In the present investigation, an attempt has been made to evaluate various thermo dynamical parameters of imidazolium salt in non-aqueous medium at different concentrations. The ultrasonic technique provides a powerful, effective and reliable tool to investigate properties of the solution. The fundamental properties namely ultrasonic velocity, density and viscosity are determined experimentally. The measured data are used to calculate the internal pressure and free volume. The results obtained from ultrasonic technique elucidate the various intermolecular interactions in the solution and the results are also compared with FT-IR spectrum.***

Keywords: ionic liquid, imidazolium, internal pressure, free volume, FT-IR spectrum.

1. Introduction

Ionic liquids (ILs) are low-melting molten salts composed entirely of ions, and many of them are liquids at room temperature [1-6]. These novel solvents are attracting interest as greener alternatives to conventional organic solvents with the aim of facilitating sustainable chemistry. Imidazolium halides are compounds consisting of an organic cation with an organic or inorganic anion, with melting points below the boiling point of water [7]. They are gaining interest as alternatives to conventional molecular samples [8]. In the synthesis of nano materials, it has been found that the samples are used as templates. So, they are called “ALL–IN–ONE”. They can be easily manufactured to be hydrophobic or hydrophilic by designing their structures [9]. The study of internal pressure and free volume of solutions yield valuable information regarding various molecular interactions in them. Measurement of ultrasonic velocity helps to evaluate internal pressure and free volume of solutions. 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. This sample is used as solder containing colophony, zinc chloride, or ammonium chloride flux. It is used as pesticide handlers, sprayers and applicators [10].

2. Experimental

A solution of hmimCl in formamide is 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 (Mittal’s Enterprises, New Delhi, Model: F-81) 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. Results and Discussion

(i)Internal Pressure (π_i) and Free Volume (V_f)

Study of these parameters requires ultrasonic velocity, viscosity and density. The variations in these parameters play a significant role in understanding solute–solvent, intra and intermolecular interactions. Internal pressure arising out of the attractive forces of the molecules can be called as cohesive pressure and is dimensionally equivalent to the energy density.

In hmimCl, the internal pressure values are increasing with concentration for all temperatures and also decreasing with temperatures. (Table 1 and Fig 1). An increase in internal pressure indicates the orientation of the solvent molecules around the hmimCl ions, which may be due to the influence of electrostatic field of ions[11].This result suggests that when hmimCl dissolved in formamide a strong ion–solvent interaction occurs in solution. This result indicates that there is a structure strengthening property of solute in solvent [12].In hmimCl (Table 2 and Fig 2) free volume decreases with increasing concentration at all temperatures. This behavior supports that there is a strong solute–solvent interaction.

Table 1: Internal pressure

Molality (m)	*5˚C*	*15˚C*	*25˚C*	*35˚C*	*45˚C*	*55˚C*
0.001	16564	15378	13669	12323	11335	10050
0.005	17734	15624	13943	12585	11342	10692
0.01	18439	15711	13900	12685	11733	10707
0.05	18589	16052	14073	12834	11736	10814
0.1	19248	16131	14079	12952	11881	10807

Table 2: Free volume

Molality (m)	*5˚C*	*15˚C*	*25˚C*	*35˚C*	*45˚C*	*55˚C*
0.001	0.013456	0.018486	0.028853	0.042959	0.059998	0.093085
0.005	0.011001	0.017698	0.027191	0.040289	0.059793	0.077297
0.01	0.00977	0.017357	0.027285	0.039245	0.053868	0.076725
0.05	0.009382	0.01601	0.026045	0.037395	0.053061	0.073411
0.1	0.00829	0.015499	0.025543	0.035747	0.050255	0.072348

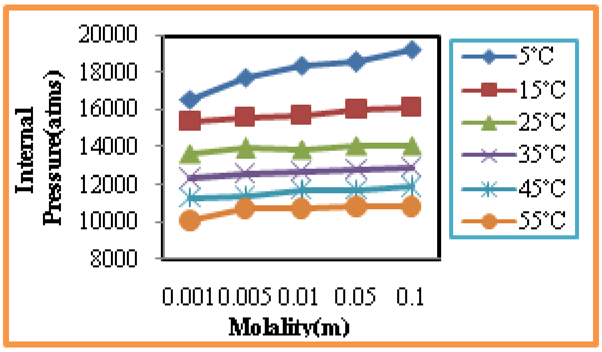

Figure 1: Internal pressure

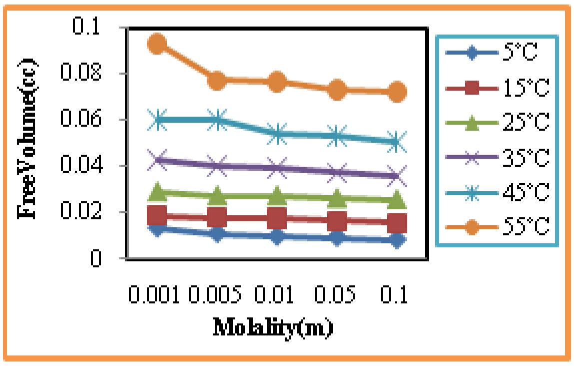

Figure 2: Free volume

(ii)FT-IR Spectral analysis of 1- hexyl-3-methylimidazolium chloride solution

The NH stretching vibration of the solvent has shifted from 3403 cm^{-1} to 3433 cm^{-1} (0.05m).This large significant red shift (30 cm^{-1}) indicates strong solute-solvent interaction. However the amide stretching vibration at 1694 cm^{-1} of the solvent is not at all affected; hence, there is no binding between CO group of solvent and solute molecule. The solvent may solvate the imidazolium salt through enol form. The imidazolium ring vibrations occurring at 623 cm^{-1} has shifted to 604 cm^{-1} (0.05m). A blue shift of 19 cm^{-1} of the solute band indicates intermolecular binding between solute and solvent through ring nitrogen atoms. Based on all spectral studies the solute-solvent interaction between the 1-hexyl-3-methylimidazolium chloride and enol form of formamide may be the principal cause of solvation.

The C-H stretching vibrations occurring as twin band in the FT-IR spectra at 2957 cm^{-1} and 2931 $cm^{-1}$and a separate sharp peak due to C-H stretching of the ring CH groups at 2860 cm^{-1} in the solid state spectra are significant for this imidazolium salt. The sharp peak at 2114 cm^{-1} is attributed $C=N^+$ vibration mode. This peak is replaced by three broad absorption bands at 2395, 2291, 2195 cm^{-1} (0.005m) on dilution. All these sharp peaks in the solid state spectra have disappeared in the solution spectra, but appear as broad absorption bands encompassed by the solvent stretching vibrations.

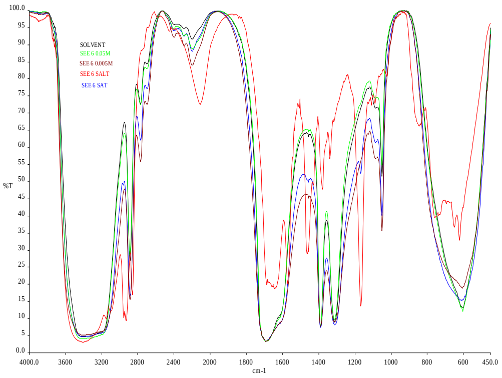

Figure 3: FT-IR spectra

4. Conclusion

The observed trends and variations of thermodynamical parameters with concentrations of solutions provide useful information about the nature of intermolecular forces existing in the solution. The existence of ion-solvent (or) solvent – solvent interaction resulting in attractive forces promote the structure – making tendency/enhancing nature of solute behavior is observed in the sample. Based on spectral studies, it is to be noted that the solute – solvent interaction between the hmimCl and enol form of formamide may be the principal cause of solvation. This result is in good agreement with thermodynamic study.

5. Acknowledgements

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