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FT-IR SPECTRAL ANALYSIS OF IMIDAZOLIUM CHLORIDESeethalakshmi K.¹, Jasmine Vasantha Rani E.¹, Padmavathy R.¹, Radha N.²¹Department of Physics, Seethalakshmi Ramaswami College, Tiruchirapalli, Tamilnadu, India²Department of Chemistry, Seethalakshmi Ramaswami College, Tiruchirapalli, Tamilnadu, India

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ABSTRACT

IR spectra find wide spread applications for the qualitative and quantitative analysis of compounds and this technique is also well employed in the field of research to understand the nature of inter atomic bonding. In the present study, FT-IR spectra are recorded for 1-butyl-3-methyl imidazolium chloride (bmim)Cl⁻ and its solution in polar-protic solvent in the wave number region from 4000cm⁻¹ to 450cm⁻¹. The spectra are used to assign various stretching and bending modes of vibrations of the sample and also to identify the various phases present in the sample. A comparative study is made between the observed frequencies of the pure solvent and the solution. From this evaluation, the shifts in frequencies are corroborated. These shifts in the solution are ascribed to strong solute-solvent interaction by specific bonding between NH₂ and C=O of solvent and Cl⁻ and ⁺NCH₃ group of the imidazolium chloride.

Keywords: Ionic liquid, 1-Butyl-3-Methyl imidazolium Chloride, vibrational frequencies.

INTRODUCTION

Imidazolium chlorides are widely used as replacements for volatile organic solvents in industrial and laboratory processes as they are “environmentally benign”. They are non-volatile and non-flammable, with high thermal stability and show remarkable dissolution capabilities. Hence in the present investigation, solution of 1-butyl-3-methyl imidazolium chloride in formamide is analyzed for the specific bonding and interactions using IR spectral results.

RESEARCH METHODOLOGY**Experimental technique**

1-butyl-3-methyl imidazolium chloride (bmim)Cl⁻ and formamide (99% purity AR Merck) were used as such.^[1] The spectra are carried out in Sophisticated Analytical Instruments Facility (SAIF), IIT Madras. The IR spectroscopy is also carried out by using Fourier transform technique.

The FTIR spectra of the compounds are recorded using PERKIN ELMER SPECTRUM ONE FTIR Spectrometer with a scan range MIR 4000 cm⁻¹ - 450 cm⁻¹. This instrument has a typical resolution of 1.0 cm⁻¹.

RESULTS

The results of the current study are given under three headings.

Table.1 –Important stretching vibrations of Formamide

Formamide has two functional groups of importance that can be easily identified^[2] by the FTIR Spectrum (figure1). The ν_{NH} stretching vibration, the ν_{CH} vibration, the $\nu_{\text{C=N}}$ vibration, the $\nu_{\text{C=O}}$ vibration are observed at various frequencies and it reveals that the formamide exists both in amide and imide forms

Table.2 – Important stretching vibrations of 1-butyl – 3 methyl imidazolium chloride

1-butyl-3-methyl imidazolium chloride exists in the solid state (figure 2). A series of peaks are observed and from the observation made, it is concluded that the change in vibrations are due to the resonating forms of the sample.

Table.3 –Important stretching vibrations of Solution of 1-butyl- 3 methyl imidazolium chloride and formamide

In the solution spectrum of 1-butyl-3-methyl imidazolium chloride and formamide, the important peaks are observed for various frequencies. The corresponding shifts in all the peaks obtained in the solution spectrum reveals the nature of the solute and the solvent.

DISCUSSION

FTIR Spectrum of formamide

At 3409 cm^{-1} ν_{NH} stretching vibration is observed (Table.1). At 2886 cm^{-1} a sharp peak of CH stretching vibration is found. At 2771 cm^{-1} and 2689 cm^{-1} , the stretching vibrations are assigned to the CH of the enolic form. A small amount of enolic form is identified by the $\nu_{\text{C=N}}$ at 2395 cm^{-1} and 2198 cm^{-1} vibrations.^[3] The CO group appears as a sharp peak at 1688 cm^{-1} . The amide II bending modes are observed at 1390 cm^{-1} and 1308 cm^{-1} , $\nu_{\text{C=O}}$ vibration is observed at 1054 cm^{-1} . Thus, the amide exists as the dimer (figure 1.1) and the formamide exists both as the amide and imide forms (figure 1.2)^[4].

FTIR Spectrum of 1-butyl - 3 methyl imidazolium chloride

1-butyl-3-methyl imidazolium chloride in the solid state (figure 2) exhibits the characterization of a $>\text{N}^+\text{CH}_3$ group, the ammonium salt vibration at 2886 cm^{-1} . A series of peaks are observed in this region. (Table.2) At 2469 cm^{-1} , a broad absorption due to C=N is found. At 1624 cm^{-1} , C=C stretching vibration and CN bending vibration appeared as broad band. Further, at 1298 cm^{-1} , a

sharp peak is observed due to CH bending vibration. At 1094 cm^{-1} and 898 cm^{-1} two bands of equal intensities are found^[5,6]. This may be due to the resonating forms of the salt (figure 2.1 & 2.2). At 549 cm^{-1} , the CCl vibrations are observed.

FTIR Spectrum of Solution of 1-butyl 1- 3-methyl imidazolium chloride and formamide

The ν_{NH} vibration is observed at 3409 cm^{-1} in pure formamide and in the case of solution, the ν_{NH} vibration is changing from 3409 cm^{-1} to 3414 cm^{-1} (figure 3). A red shift of 5 cm^{-1} is observed in this solvent peak. (Table.3). The ν_{CH} vibration at 2887 cm^{-1} has not undergone much shift. Hence solvation has occurred at the N-H bond in formamide. The important peak corresponding to amide- I vibration is noticed at 1689 cm^{-1} ($\nu_{\text{C=O}}$) has shifted only by 2 cm^{-1} .^[7,8] The characteristic change in absorption frequency ($\nu_{\text{C=O}}$) is found at 1059 cm^{-1} in the solution and in the pure solvent, it is found at 1054 cm^{-1} . The solution spectrum is thus indication of solvation at NH_2 group (figure 3.1) and the enolate position of formamide (figure 3.2). This is further supported by the C=N vibration of formamide at 2395 cm^{-1} which is blue shifted (11 cm^{-1}) to 2384 cm^{-1} in the solution.

CONCLUSION

- From the present study, FTIR spectral analysis leads to new insights about solvation.
- Strong solute-solvent interaction occurs in the non-aqueous solution of formamide and 1-butyl -3 methyl imidazolium chloride.
- Binding occurs between: NH_2 and C=O of the solvent and Cl^- and $^+\text{NCH}_3$ group of the imidazolium chloride through strong, coulombic and ion-dipole interactions.
- A chloride ion bridge exists between solute and the solvent molecule.

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FTIR SPECTRAL ASSIGNMENTS

Table.1 –Important stretching vibrations of Formamide

ν_{NH}	ν_{CH}	$\nu_{\text{C=N}}$	$\nu_{\text{C=O}}$	$\nu_{\text{C-O}}$
3409 cm^{-1}	2886 cm^{-1}	2771 cm^{-1} 2689 cm^{-1} 2395 cm^{-1} 2198 cm^{-1}	1688 cm^{-1}	1054 cm^{-1}

Table.2 – Important stretching vibrations of 1-butyl – 3 methyl imidazolium chloride

ν_{NH}	$\nu_{\text{C=N}}$	$\nu_{\text{C=C}}$	ν_{CH}	$\delta_{\text{C-N}}^*$	ν_{Cl^-} (chloride bridge)
2886 cm^{-1}	2469 cm^{-1}	1624 cm^{-1}	1298 cm^{-1}	1094 cm^{-1}	898 cm^{-1}
				898 cm^{-1}	549 cm^{-1}

*Resonating forms (3,4)

Table.3 – Solution of 1-butyl- 3 methyl imidazolium chloride and formamide

ν_{NH}	ν_{CH}	$\nu_{\text{C=N}}$	$\nu_{\text{C=O}}$	$\nu_{\text{C-O}}$
3414 cm^{-1}	2887 cm^{-1}	2395 cm^{-1}	1689 cm^{-1}	1059 cm^{-1}

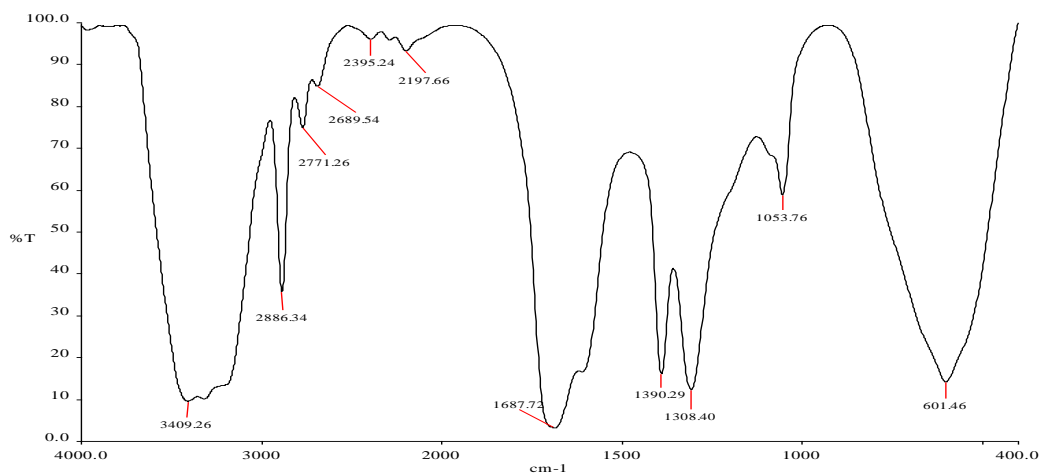
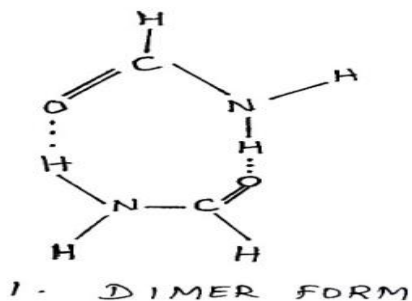
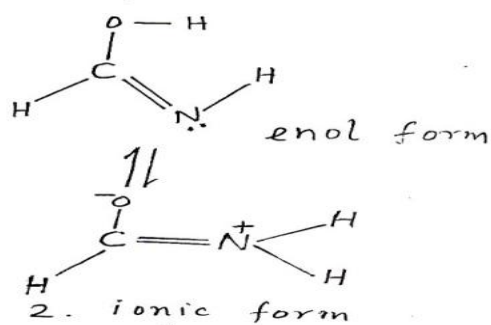
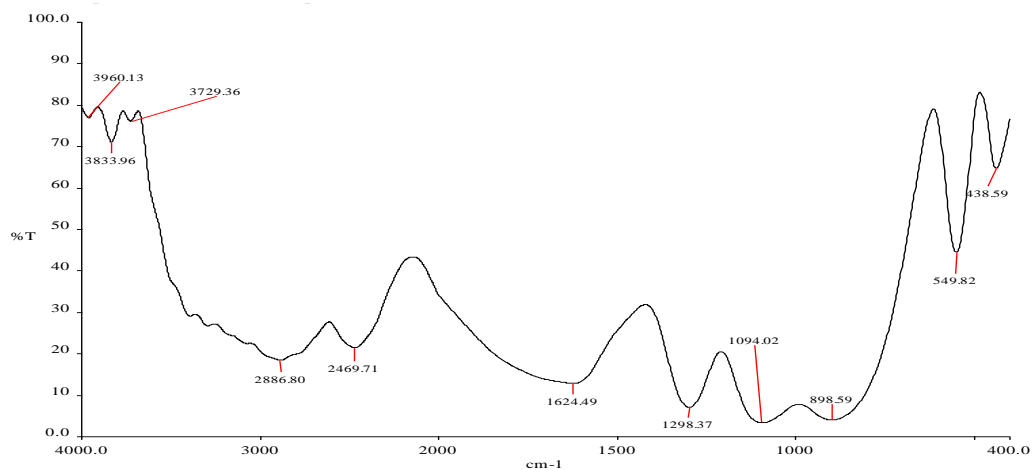
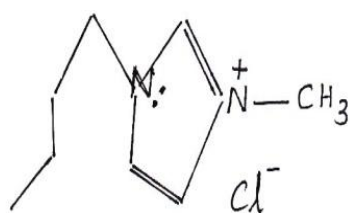
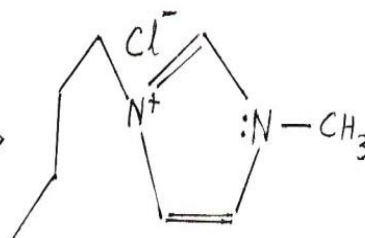
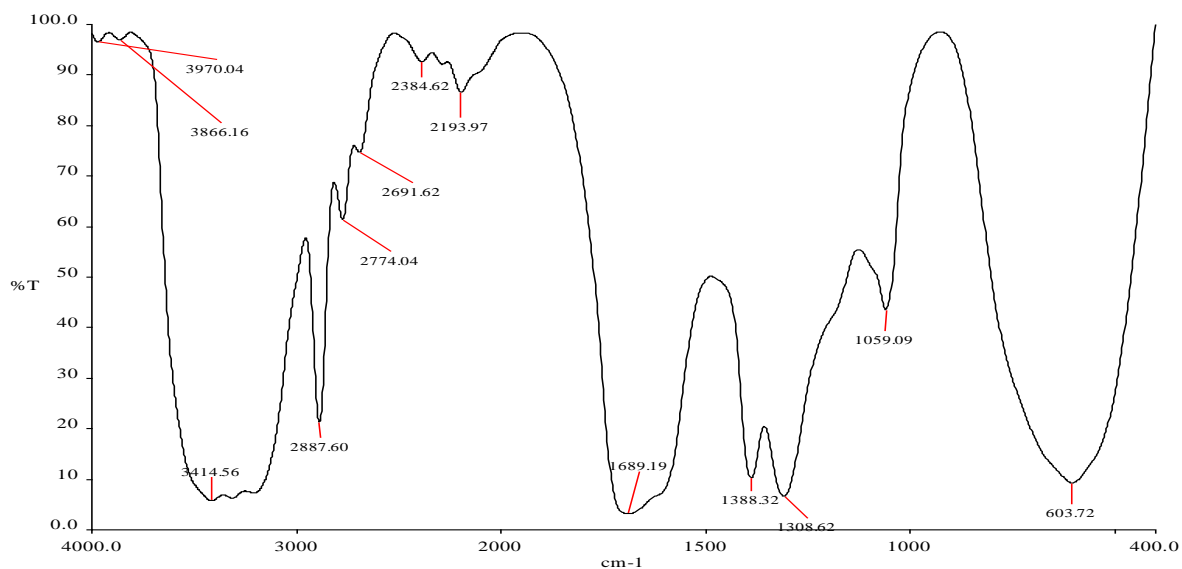
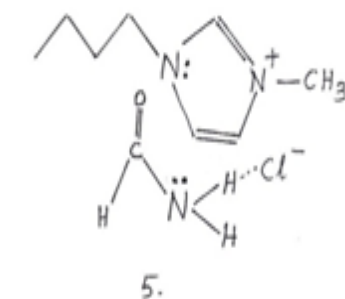
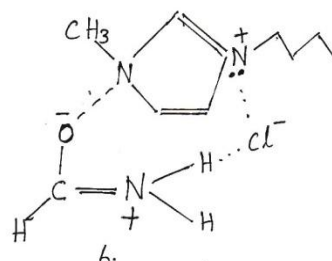
Figure 1: FTIR Spectrum of formamide**Figure 1.1****Figure 1.2**

Figure 2 FTIR Spectrum of 1-butyl- 3 methyl imidazolium chloride**Figure 2.1****Figure 2.2**

3. Resonating forms of 1-butyl-3-methyl imidazolium chloride

Figure 3 FTIR Spectrum of solution of 1-butyl – 3 methyl imidazolium chloride and formamide**Figure 3.1**

5.
ion-dipole interaction in
the amide form of formamide

Figure 3.2

6.
Strong ion-solvent interaction
in the enolate form of formamide