Nucleobases and C2 and C4 Imidazolium Acetate Interactions: FTIR-ATR, Raman and NMR Spectra and ab Initio Calculations Insights

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Nucleobases and C_2 and C_4 Imidazolium Acetate Interactions: FTIR-ATR, Raman and NMR Spectra and ab Initio Calculations Insights

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1. Introduction

Room Temperature Ionic Liquids (RTILs) are revolutionizing the world of solvents due to the unique combination of their many interesting properties. The number of synthesized RTILs continues to rise, and by judicious choice of the constituent cations and anions, RTILs tailor-made for specific applications can be designed. The tunable nature of the solubility of various compounds, including molecules of pharmaceutical and biological interest, in RTILs makes extraction them attractive for many separation and purification processes [1;2]. Exploring new applications requires fundamental understanding of the phase behavior.

In the present work, we explore the use of RTILs to dissolve Nucleobases, Nucleosides and Nucleotides. Nucleobases are the parts of Nucleic Acids (DNA and RNA) that are involved in pairing. The system of a base covalently bound to the 1' carbon of a ribose or deoxyribose is called a Nucleoside, and a nucleoside with one or more phosphate groups attached at the 5' carbon is called a Nucleotide. Nucleotides comprise the structural units of RNA and DNA. The structural elements of the most common Nucleotides are depicted in the Figure 1. Uracil, a common and naturally occurring pyrimidine derivative [3], was selected as illustrative model for deeper solubility study of nucleobases. Found in RNA, it base pairs with adenine and is replaced by thymine in DNA translation. In this work, we focus on uracil, adenine and thymine solubility.

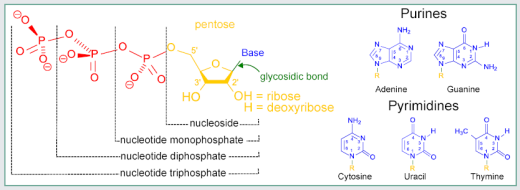

Figure 1. Structural elements of the most common nucleotides.

2. Experimental

Scanning of the solubility of uracil, adenine and thymine bases in wide variety of RTIL was performed in order to establish the most promising solvents. The solubilities studies were accomplish using visual detection method. Approximately 1mg of solute was added to 1g of RTIL, at room temperature and atmospheric pressure. Continuous stirring was applied until the total solubility was achieved and 1-2 mg were added until a saturated solution was obtained. The obtained solubilities are depicted in Figure 2. The spectroscopic methods used for the study of the uracil, adenine and thymine bases in $[C_4mim][CH_3COO]$ and interpretation of the solubility mechanism comprises UV-spectroscopy, FTIR-spectroscopy. Ab-initio calculations were also used for further support of the experimental evidences.

3. Results

Purine and Pyrimidine Bases Solubility in Imidazolium-based ILs, Phosphonium-based Ils and Ammonium-based Ils

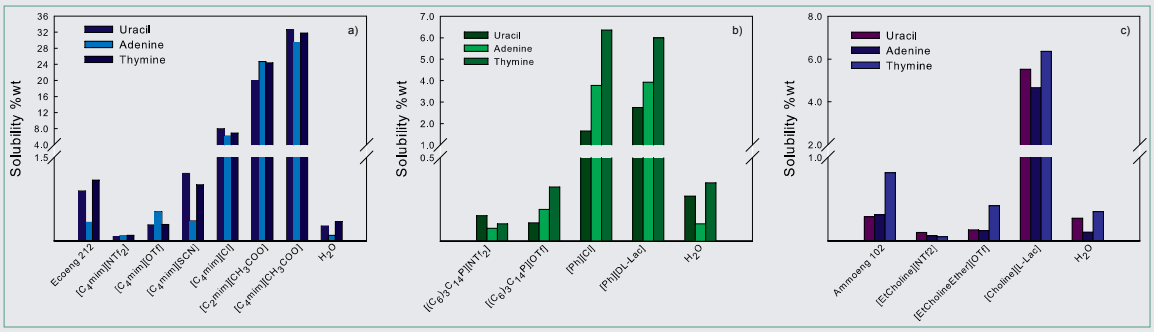

Figure 2. Weight fraction solubility of Uracil, Adenine and Thymine in RTILs: a) Imidazolium-based ILs; b) Phosphonium-based Ils; c) Ammonium-based Ils. The solubility in water is also presented, for factor scale [4;5].

Most stable conformation Uracil + $[C_4mim][CH_3COO]$

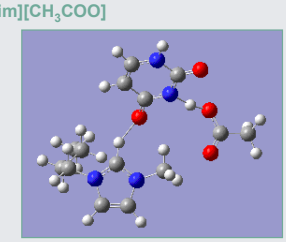

Figure 5. *Ab initio* results using GaussView4.1 assert the most stable conformation between uracil and $[C_4mim][CH_3COO]$.

UV Spectra Uracil + $[C_4mim][CH_3COO]$ + H_20

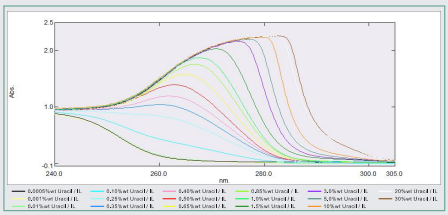

Figure 3. UV spectra of assorted solutions of uracil in $[C_4mim][CH_3COO]$, at different weight fraction concentrations. All spectra were acquired after the dilution 0.5%wt IL / H_2O . This procedure was attained due to detection limits issues depicted in Figure 4.

Effect of $[C_4mim][CH_3COO]$ in UV Spectrum

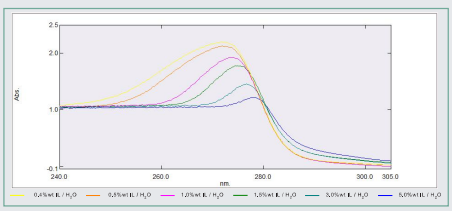

Figure 4. Effect of $[C_4mim][CH_3COO]$ IL in the UV spectra of a aqueous solution of uracil with a concentration of 0.0079%wt. The weight fractions of $[C_4mim][CH_3COO]$ in H20 range between 0.4%wt and 5.0%wt.

FTIR Spectra Uracil and $[C_4mim][CH_3COO]$

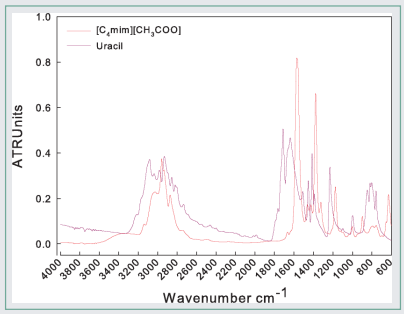

Figure 6. FTIR spectra of pure uracil and pure $[C_4mim][CH_3COO]$.

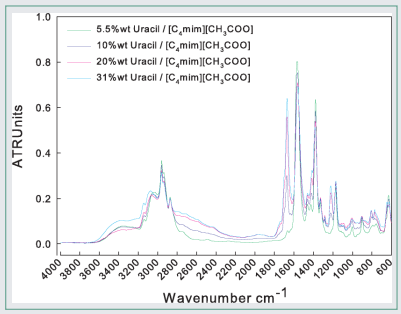

Figure 7. FTIR spectra of assorted solutions of uracil in $[C_4mim][CH_3COO]$, at different weight fraction concentrations. The quantification of uracil could be attained by using the carbonyl group band (1700 cm^{-1}). From the "fingerprint region" (1600 cm^{-1} - 400 cm^{-1}) interactions between uracil – IL can be inferred.

4. Conclusions

- The capability of RTILs as tunable solvents to dissolve nucleobases is perceived. The results obtained for the three ILs families outlined, Imidazolium-, Phosphonium- and Ammonium-based ILs, show that the ILs containing a carbonyl group in the anion present higher dissolution capabilities. This is due to the establishment of hydrogen bonds between uracil and IL.
- The combined use of FTIR, FTRAMAN and NMR-spectroscopy, as well as computer simulation, will be attain to better understand the solubility mechanism of nucleobases, nucleosides and nucleotides.
- The results here obtained show the enormous potential of the use of RTILs to dissolve nucleobases, nucleosides and nucleotides and disclose a favorable trends in the application of RTILS in DNA extraction and purification.

References

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Acknowledgments

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