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Investigation of 1-(2-carboxyethyl)-3-methylimidazolium chloride[HOOCEMIM][Cl] ionic liquid effect on water activity and solubility of L-serine at $T = 298.15$ K

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ABSTRACT

Water activity measurements by the isopiestic method have been carried out on the aqueous ternary system of {L-serine + 1-(2-carboxyethyl)-3-methylimidazolium chloride[HOOCEMIM][Cl]} ionic liquid and the aqueous binary system of IL at $T = 298.15$ K and atmospheric pressure. The data obtained were used to calculate the vapor pressure and osmotic coefficient of solution as a function of concentration. The experimental results for the activity of water were accurately correlated with segment-based local composition models of modified NRTL and UNIQUAC. The fitting quality of the above models has been favorably compared with the NRTL and Wilson models. From these data, the corresponding activity coefficients have been calculated. For the same system, the solubility of the L-serine at various [HOOCEMIM][Cl] ionic liquid concentrations was measured at $T = 298.15$ K using the gravimetric method. A chemical model was employed to describe the dissociation equilibria of all amino acid species with hydrogen ions in water. Moreover, for L-serine, the chemical model indicated that the formation of cations is insignificant in the [HOOCEMIM][Cl] solution. Also the above local composition models were used to predict the solubility of L-serine in aqueous IL solutions. To provide information regarding (solute + solute) interactions, transfer Gibbs free energies (ΔG_{tr}) of amino acid from water to aqueous IL solutions have been determined.

1. Introduction

Solubility and activity coefficients are physical properties essential to the design and scale-up of chemical processes for separation, concentration, and purification of biomolecules. In such cases, the information of the solubility of amino acids in the presence of acids, bases and electrolyte is required for design of above process [1,2]. All amino acids have in common an amino and a carboxyl group combined with one of the twenty different side chains called the hydrocarbon backbone. The dissolution of amino acids in aqueous solutions forms several ionic species due to the ionization of their carboxyl and amino groups. The neutral dipolar species or zwitterions are the predominant species in the isoelectric solution of amino acids ($NH_3^+RCOO^-$). At acidic solutions, cationic amino acid species (NH_3^+RCOOH) become predominant while anionic amino acid species ($NH_2\,RCOO^-$) become predominant at the basic solutions. The predominant form of the amino acid in solution is affected by the presence of electrolyte by changing the pH of the solution.

The TSIL (Task-Specific Ionic Liquid) which the cation has a functional group –COOH is a new kind of ionic liquid with a diversified range of applications has been developed recently [3–10]. Due to the ionic nature of the materials, TSILs have essentially negligible vapor pressure [3]. Studies of ionic liquid toxicity including ecotoxicity have advanced at a significant rate and a great deal of information has been accumulated. Over the previous decade the link between antimicrobial toxicity and side chain length of imidazolium ILs has been extensively reported [11–15]. However, as this is related to the lipophilicity of the IL, introduction of heteroatoms would be expected to reduce antimicrobial toxicity via this mode of action [16–18]. Furthermore, the authors [12,19,20] proposed that the introduction of oxygen-functionalized side chains can increase the biodegradability of ILs via hydrolysis. The above explanations well illuminate that studied TSIL in the present work is less toxic and more environmentally friendly ionic liquid. We

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guess that the TSIL, which is studied in the present work, by virtue of its functional carboxylic group, promotes remarkable changes in the solubility of the studied amino acid by reducing the pH of the solution. In this way, a few studies have been performed to investigate the effect of pH on amino acids activity coefficients and solubility [21–25]. In some of these studies, the conventional local composition models were used to correlate the activity coefficients and solubility of amino acids in aqueous solutions [26–33]. In this work, in continuation of our previous work [33], water activity of ternary system {L-serine + 1-(2-carboxyethyl)-3-methylimidazolium chloride[HOOCEMIM][Cl] + H_2O} and their corresponding binary aqueous IL system have been measured using the improved isopiestic method at $T = 298.15$ K. In this way, we measured the solubility of L-serine in aqueous [HOOCEMIM][Cl] solutions at $T = 298.15$ K using the gravimetric method. These data permit us to investigate the effect of the, [HOOCEMIM][Cl], on the solubility of L-serine at low pHs. The measured values of pH of aqueous [HOOCEMIM][Cl] solutions in L-serine solutions are 3.7 to 3.3 at (0.104 to 0.386) $\text{mol} \cdot \text{kg}^{-1}$, respectively, and therefore in the aqueous [HOOCEMIM][Cl] solutions, the cationic form of L-serine (NH_3^+RCOOH) become predominant. The segment-based local composition models such as modified NRTL (mNRTL) [34] and UNIQUAC [35] along with Wilson [36] and NRTL [26] models have been used to predict and correlate the solubility of amino acid.

2. Experimental

2.1. Materials

Sodium chloride (solute for the isopiestic reference standard solution) was dried in the electrical oven about 110 °C for 24 h prior to use. L-Serine was used without further purification. The reagents used for the synthesis of [HOOCEMIM][Cl] were *N*-methylimidazole, acetonitrile, methanol and 3-chloropropionic acid all with mass fraction purity of >0.99 purchased from Merck. The purity of the used materials is shown in table 1. All chemicals were used without further purification. The double distilled water was used.

2.2. Synthesis of ionic liquid

The 1-(2-carboxyethyl)-3-methylimidazolium chloride, [HOOCEMIM][Cl], was synthesized according to a modified procedure [37]. Under an inert nitrogen atmosphere, anhydrous acetonitrile and 3-chloropropionic acid were charged into a flask at room temperature. Thereafter, 1-methylimidazole was added to the flask with vigorous stirring. The reaction mixture was refluxed for 5 h under nitrogen atmosphere. After removing the solvent under reduced pressure, the remaining oil phase was further subjected to three-circle of rinse with ethyl acetate and a pale yellow viscous oil was formed. Finally, 1-(2-carboxyethyl)-3-methylimidazolium chloride, [HOOCEMIM][Cl], was obtained after drying in a vacuum oven at 50 °C for 12 h. The ionic liquid obtained has purity greater than mass fraction 0.98 and verified by 1H NMR spectroscopy. The ionic liquid was further dried under high vacuum at $T = 333.15$ K for 24 h to remove trace amount of moisture. The water content of the IL was determined using a microprocessor based automatic Karl–Fischer Titrator. The mass fraction of water for [HOOCEMIM][Cl] was less than 0.0005. This water content was taken into account in the calculation. Ionic liquid was analyzed by 1H NMR, 13C NMR (Brucker Av-400) and FTIR (Perkin Elmer, Spectrum RXI) to confirm the absence of any major impurities and they were found to be in good agreement with those reported in the literature [38]. The characterization of synthesized IL, which is studied in the present work, is summarized in table 2.

TABLE 1
Provenance and mass fraction purity of the materials studied.

Material[a]	Mass fraction purity
NaCl	(GR, min99.5%)
L-serine	>0.99
N-methylimidazole	>0.99
3-Chloropropionic	>0.99
Acetonitrile	>0.99
Methanol	>0.99

[a] All materials were supplied from Merck.

2.3. Apparatus and procedure

2.3.1. Water activity measurements

The isopiestic apparatus employed to obtain water activity and osmotic coefficient data of {L-serine + [HOOCEMIM][Cl] + H_2O} system at $T = 298.15$ K. This apparatus in the present work is essentially similar to the one used and described previously [33]. The apparatus used for determination of water activity of ternary aqueous {L-serine + [HOOCEMIM][Cl] + H_2O} consisted of a seven-leg manifold attached to round-bottom flasks. Two flasks contained the standard pure NaCl solutions; one flask contained the pure IL solution, one flask contained the pure amino acid solution, two flasks contained (amino acid + IL) solutions and the central flask was used as a water reservoir. This apparatus for binary {[HOOCEMIM][Cl] + H_2O} system consisted of a five-leg manifold attached to round-bottom flasks. Two flasks contained the standard pure NaCl solutions; two flasks contained the pure IL solution, and the central flask was used as a water reservoir. The isopiestic apparatus was immersed in a constant-temperature bath at least 120 h for equilibrium using a temperature controller (Julabo, MB, Germany) with an uncertainty of ±0.01 K. After equilibrium the apparatus was removed from the bath. Then the manifold was slowly evacuated to remove the air and to degas the solutions. It was necessary to evacuate the manifold several times because the dissolved air was slowly released from the solutions. The mass of each flask was calculated using an analytical balance (Shimadzu, 321-34553, Shimadzu Co., Japan) with an uncertainty of $\pm 1 \times 10^{-7}$ kg. When the difference between the mass fractions of two NaCl solutions was less than 0.1%, we assumed that equilibrium was reached. For the calculation of water activity of standard aqueous NaCl solutions at different concentrations and temperatures, the correlation given by Colin *et al.* [39] was used. The accuracy of the method depends upon the standard solutions, sample mixing during the equilibrium period, temperature stability, and the time allowed for the equilibrium process. The uncertainty in the measurement of solvent activity was estimated to be $\pm 5 \times 10^{-4}$.

2.3.2. Solubility measurement

In this study, the gravimetric method applied without any modification is that described in our previous work [33] to measure the solubility of L-serine in the presence of [HOOCEMIM][Cl]. The compositions of the initial solutions were accurate within ±0.1 mg. The bath was controlled to keep a constant temperature with an accuracy of ±0.01 K. The experiments were performed by preparing solutions at various molalities of IL with different pH and adding the amino acid in excess amount to that required for saturation. To reach equilibrium conditions, the solution is continuously stirred for 48 h. The temperature of the solution was first maintained for 3 h at $T = 303.15$ K and then it was lowered to $T = 298.15$ K. After 48 h stirring was discontinued and the solution is allowed to settle for at least 7 h before sampling. Before sampling, the final pH values of the equilibrium solutions were recorded by a pH meter (Metrohm, 692 pH/Ion meter, ±0.01). The calibration of the