1 **Thermodynamic and Conductivity Properties of Acetic Acid - EMIMOAc**

2 **Ionic Liquid Solutions**

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ABSTRACT

Acetic acid (HOAc) is a typical weak Brønsted acid that has been broadly used as a reactant in esterification reactions and can be used as such in ionic liquid (IL) solutions. The nature of the HOAc molecule as a solute in the IL 1-ethyl-3-methylimidazolium acetate (EMIMOAc) solutions was investigated with thermodynamic, vibrational spectroscopic, conductivity, and viscosity measurements. Calorimetry and vapor pressure-based thermodynamic measurements of the binary HOAc-EMIMOAc mixture were used to quantify the exothermic enthalpy of solution, ΔH_{sol} , as $\sim 3.2\text{--}4.9$ kJ/mol. FTIR and Raman spectroscopy showed that the structures of the HOAc molecule and IL molecular ions are unchanged in the solutions relative to the pure liquids, indicating that the HOAc is a negligibly-dissociated weak acid in the IL solutions. Temperature-dependent conductivity measurements quantify the effects of the HOAc on the IL solution conductivity and confirm that the HOAc remains a mostly neutral molecular solute that interacts with the EMIMOAc IL via ion-dipole and hydrogen bond interactions.

Keywords: Acidic Ionic Liquids; Conductivity Measurements; Solution enthalpy; Vapor Pressure Measurements; Vibrational Spectroscopy

Introduction

Acidic ionic liquids (AILs) contain active protons from Brønsted acids present as cations, anions, or solutes in ionic liquid (ILs) solutions. AILs have applications in diverse academic and industrial fields. They retain the unique properties of typical ILs such as negligible vapor pressure, excellent thermostability, and solvent compatibility with many organic and inorganic chemicals. Additionally, their acidity provides active hydrogen ions (H^+) for numerous chemical and electrochemical applications. AILs have been used as solvents and catalysts for the Fischer esterification reactions and for alcohol, amine, and starch acetylation reactions.¹⁻¹²

Fischer esterification is routinely used throughout the chemical, food, agriculture, and petroleum industries. This reaction requires homogeneous acidic catalysts that can be neutralized after use. Acid catalyst neutralization and removal is often costly and environmentally toxic. AILs can be used as dual solvent-catalysts with improved yields and catalytic activity.^{2, 13} Further, AILs are recoverable and reusable and can be separated easily from the esterification products. In this context acetic acid, HOAc, is an important reactant for the esterification and acetylation reactions because it is low-cost and can be easily added to ILs to create AILs.

In the Fischer esterification reactions, the H^+ catalyst adds to a carboxylic acid to make a reactive electrophilic intermediate which eventually results in an H^+ addition-elimination. Thus, the H^+ activity, solvation, and transportation in the reaction media are all important parameters for the catalyzed reaction. In previous reports we have studied the ionization of several strong Brønsted acids and their H^+ solvation and transportation mechanisms in AIL solutions using conductivity and viscosity measurements, spectroscopy, and computational simulation.¹⁴⁻¹⁷ For example, when a strong acid such bis-trifluoromethanesulfonylimide acid (HTFSI) dissolves in ILs, HTFSI can partially or completely ionize to produce a proton-bridged TFSI⁻ dimer.¹⁸

However, the fundamental solvation and transportation properties of weak Brønsted acids such as HOAc in AILs have not been carefully investigated. To this point, existing work has focused on HOAc proton transfer to amine bases to form protic ionic liquids, in which the proton associates with ammonium ions (which are even weaker acids than HOAc).¹⁹⁻²¹ In this work, we focus on the solution properties of HOAc in a common IL 1-ethyl-3-methyl-imidazolium acetate (EMIMOAc) and explore the solvation of this typical weak acid in IL solutions.

In addition to the Fischer esterification reactions, OAc^- / HOAc-based AILs have several other potential applications. Imidazolium acetates are very good solvents for CO_2 absorption and electrochemical reduction.²²⁻²⁶ The OAc^- anion in the ILs plays an important role in CO_2 capturing and solvation.²⁷⁻²⁸ When CO_2 dissolves in ILs EMIMOAc, a strong interaction exists between the CO_2 molecules and the OAc^- anions. This interaction results in higher CO_2 solubility in acetate-based ILs and a lower Henry's Law constant.²⁸⁻³⁰ Acetate-based ILs have also been used for chemical separations, e.g., extraction of HF from petroleum products³¹ or recovery of HOAc over water.³² Optimizing these applications will require a quantitative understanding of the HOAc solvation and ionization mechanisms in ILs, including thermodynamic solvation information and structural information about the HOAc ionization.

In this paper, we have characterized a series of EMIMOAc solutions with increasing HOAc concentration using conductivity measurements to investigate the ion transport mechanism, vapor pressure and calorimetry measurements to study the HOAc-EMIMOAc solvation interaction, and vibrational spectroscopy to investigate the structure of the solvent and solute. Considering that HOAc is an important reactant of the acid-catalyzed esterification reactions, a better understanding of the HOAc solvation and ionization in AILs will be helpful for the control of acetylation reactions.

Experimental

Sample preparation. EMIMOAc (>90%) and glacial acetic acid were purchased from Sigma-Aldrich. EMIMOAc was de-colored by active carbon powder and dried in a vacuum oven prior to use. Glacial acetic acid was used as received. HOAc/EMIMOAc solutions were prepared by carefully pipetting the two liquids with desired volume ratios. Molarities and molar fractions of HOAc were calculated based on the measured volume ratio and density values of pure HOAc and EMIMOAc. The solutions were stored in capped containers for all experimental measurements.

Conductivity, viscosity, and thermodynamic measurements. Conductivities of pure ILs and AIL solutions were measured by an AC Mode TraceableTM conductivity meter at a constant frequency of 3 KHz with a pair of parallel Pt plate electrodes and a temperature probe. The cell constant is designed to be unity. The cell was calibrated by standard solutions with conductivity of 1 and 10 mS/cm, respectively, prior to measurement. The conductivity was measured at room temperature, approximately 23 °C in our laboratory. For temperature-dependent measurements, a water bath was used to control the temperature. The built-in temperature probe in the conductivity meter allows the simultaneous reading of conductivity and temperature values.

The viscosities of pure ILs and AIL solutions were measured by a Brookfield rotational viscometer with a built-in temperature probe. All measurements were carried at ~23 °C. The instrument was calibrated by a mineral oil viscosity standard of 20 cP and 200 cP prior to use.

We measured the enthalpy of solution (ΔH_{sol}) by two different experiments. First, a standard “coffee-cup” calorimeter is used. EMIMOAc and HOAc were mixed in a plastic container with volume capacity of about 10 mL. The system was isolated with a rubber stopper and wrapped with aluminum foil and polystyrene foam. The temperature was monitored with time after

HOAc/EMIMOAc mixing by a thermocouple connected to a computer. We measured the solution's specific heat capacity by calibrating the system with a pre-heated copper slug. We also calibrated the systematic error (loss of heat) using the dissolution of CaCl_2 in H_2O . With ~5-10 mL of total liquid, it was estimated that there was a ~28% total heat loss when the maximum temperature was reached within several minutes.³³ The measured ΔH_{sol} values were compensated for this 28% heat loss. We also used this system to measure the heat capacity of the IL BMITFSI; the measured results were consistent with the reported values in literature.³⁴

Second, ΔH_{sol} can also be estimated by the HOAc vapor pressure values above the AIL solutions. Vapor pressure measurements enable the quantification of the AIL deviation from Raoult's Law using the following equations:

$$P_{\text{HOAc}} = \gamma_{\text{HOAc}} \chi_{\text{HOAc}} P_{\text{HOAc}}^{\circ} \quad (1)$$

In Equation (1), P_{HOAc} is the HOAc vapor pressure above the solution, χ_{HOAc} is the molar fraction of HOAc in solution, and P_{HOAc}° is the vapor pressure over pure HOAc. γ_{HOAc} is the activity coefficient of HOAc in the AIL solution, which would be unity for an ideal solution ($\Delta H_{\text{sol}} = 0$). Under the regular solution model³⁵ the value of ΔH_{sol} is related to the value of γ_{HOAc} through the β -parameter, which quantifies the net HOAc-solvent interactions:

$$\beta \chi_{\text{solvent}}^2 = RT \ln \gamma_{\text{HOAc}} \quad (2)$$

$$\Delta H_{\text{sol}} = \beta \chi_{\text{HOAc}} \chi_{\text{solvent}} \quad (3)$$

In Equations (2) and (3), χ_{solvent} is the molar fraction of the solvent, which would be the EMIMOAc IL in this work. Hence, by measuring the vapor pressure of HOAc over the AIL solutions, the ΔH_{sol} can be calculated.

The HOAc vapor pressure was quantified using the “headspace” injection technique with a GC-MS system (Agilent 6890N GC, 5973 MS, and 7683 Injector). 0.5 mL of solutions (prepared with different HOAc:IL molar ratios) were sealed in 2 mL vials and shaken thoroughly for 10 min to reach liquid-vapor equilibrium prior to the injection. 1 μ L of the vapor in the head-space was injected (split, 10:1 ratio) into the column. The oven temperature was ramped from 35 $^{\circ}$ C to 130 $^{\circ}$ C during the chromatography. Ions with m/z of 60 (HOAc molecular ion) were extracted and chromatographic peak areas were used to calculate the HOAc vapor pressure.

Vibrational Spectroscopy. Fourier Transform Infrared (FTIR) spectra of all samples were measured with a Varian FTS 7000 FTIR Spectrometer at 1 cm^{-1} resolution. A thin layer of liquid samples were sandwiched between two KRS-5 salt plates. Samples were thoroughly purged by dry air before data acquisition to remove the absorbed moisture. Spectra demonstrated were the average of 16 co-additions. Raman spectra were measured using a Horiba Jobin-Yvon LabRam Evolution Raman Microscope (Horiba, Edison, NJ) fitted with a liquid sample acquisition accessory. Samples were measured using either 532 nm or 633 nm excitation wavelengths. Fluorescence backgrounds were subtracted using the Labspec 6 software.

Results and Discussion

HOAc and EMIMOAc are completely miscible from 0 to 100% HOAc. The temperature vs. time curve of a calorimetry measurement is shown in Figure 1 for a 1:1 molar ratio. The temperature of the solution increases after mixing, indicating that is an exothermic process. Temperature reaches its maximum value, about 34 $^{\circ}$ C, after 5 minutes. Based on the temperature change, the solution heat capacity ($\sim 3.8 \text{ J}\cdot\text{g}^{-1}\cdot\text{K}^{-1}$), and the heat loss (28%), we calculate the value of ΔH_{sol} as -4.9 kJ/mol (total moles of HOAc and EMIMOAc at a 1:1 molar ratio).

Figure 1. Temperature vs. time curve when HOAc and EMIMOAc are mixed at a 1:1 molar ratio.

The GC-MS-based vapor pressure measurements are shown in Figure 2. We assume that the ratio of HOAc chromatographic peak areas is proportional to the HOAc vapor pressures (P_{HOAc} or P_{HOAc}°). Measurements of HOAc in water solutions are shown for reference. From Figure 2, the HOAc-EMIMOAc binary mixture clearly shows a negative deviation from the Raoult's Law, indicating a negative ΔH_{sol} value and hence strong HOAc-IL attractive interactions. By applying the Regular Solution model and using Equation (2) for the dilute solutions ($\chi_{HOAc} \leq 0.5$), we can calculate an average β -parameter as -13 ± 4 kJ/mol. From Equation (3) we can then predict the ΔH_{sol} value for a 1:1 HOAc-EMIMOAc solution as -3.2 kJ/mol. This value is relatively close to the ΔH_{sol} value measured from the calorimetry experiment (-4.9 kJ/mol, Figure 1).

Figure 2. Headspace vapor pressures of HOAc over HOAc/H₂O solutions and HOAc/EMIMOAc solutions shown as $P_{\text{HOAc}}/P_{\text{HOAc}}^{\circ}$ ratio vs. HOAc molar fraction.

It is well known that H-bonds and dipole-dipole interactions dominate the intermolecular forces between HOAc molecules in pure HOAc liquid and HOAc-water solutions, and that ionic interactions are important in pure EMIMOAc and other ILs. According to solution thermodynamics, in an HOAc-EMIMOAc solution the ionic interactions should be broken and replaced by strong HOAc-EMIMOAc interactions. From our analyses of Figures 1 and 2, we can quantify the net attractive interaction between the HOAc and the IL molecules as ~3.2-4.9 kJ/mol for a 1:1 HOAc:EMIMOAc molar ratio. The experimentally-measured solution thermodynamic parameter is a collective and statistical result of all solvation models and structures. It has been reported that molecular solutes such as water can form clusters in IL solutions.³⁶⁻³⁷ The enthalpy of solution may contain contributions from individual IL-solvated HOAc molecules, solvated HOAc dimers, and HOAc clusters imbedded in the bulk IL.

HOAc is a weak electrolyte in aqueous solutions and ionizes partially to produce H_3O^+ . However, the ionization/solvation of HOAc has not been reported in IL solutions. In one of our previous reports,¹⁸ vibrational spectroscopy results indicate the existence of a H^+ -bridged TFSI⁻

172 dimer after HTFSI ionization. In this paper, we measured the vibrational spectroscopy and
173 conductivity properties of the AIL solutions in order to elucidate the nature of the HOAc
174 molecule in solution and probe the solvation mechanism.

Figure 3. FTIR (A) and Raman (B) spectra of EMIMOAc, HOAc, and their mixtures. Spectra are normalized to the most intense peak. The complete sets of spectra are available as Figure S1 (FTIR) and Figure S2 (Raman) in the SI materials.

FTIR and Raman spectra of pure EMIMOAc, glacial HOAc, and AIL solutions with different HOAc concentrations are summarized in Figure 3. Only selected FTIR spectra are shown here (Figure 3A); and the FTIR spectra for all solutions are shown in Figure S1 in the Supporting Information. The IR spectrum of pure HOAc (top trace in Figure 3A) shows a broad band between 2500 and 3300 cm^{-1} , which corresponds to the -OH stretch vibrations and confirms the existence of hydrogen-bonded HOAc dimers.³⁸ This broad absorbance band is not detected significantly in the mixtures with HOAc molar fractions of 0.5 and below, although it is observed with HOAc molar fractions from 0.6 to 1.0 (Figure S1). Hence, the results show no evidence of hydrogen-bonded (or proton-bound dimers) in the dilute AIL solutions, although their complete absence cannot be confirmed. It appears that the majority of the HOAc molecules are solvated by clusters of the IL molecular cations and anions rather than interacting with each other.

The bands above 3500 cm^{-1} in the spectra with ILs may correspond to H_2O present as impurities in the EMIMOAc IL. Aside from these bands and the broad -OH stretch band, the FTIR spectra of the HOAc/EMIMOAc AIL solutions can be explained as superimpositions of the pure HOAc (top trace) and pure EMIMOAc (bottom trace) spectra; all bands are observed in the pure liquids spectra. This suggests that the structures of the HOAc and EMIMOAc molecules are not different in the AIL solutions relative to the pure liquid molecules.

For the Raman spectra (Figure 3B) we only show the results for the pure HOAc and EMIMOAc along with the 5.0 M (~0.54 molar fraction) HOAc AIL spectra. The Raman spectra

for all solutions are shown in Figure S2 in the Supporting Information. Careful inspection reveals that the spectrum of the 5.0 M AIL solution can be interpreted mostly as a superimposition of the pure HOAc and EMIMOAc spectra, as all bands observed in the AIL solution are also observed in either the pure HOAc or pure EMIMOAc spectra at the same positions. The only notable exception is in the HOAc C=O stretch band at 1675 cm^{-1} . This band, which is not observed in the EMIMOAc spectrum, must correspond to the carboxylic acid C=O vibration. It is clearly broader in the AIL spectrum, which likely indicates hydrogen bond interactions between the –OH group of the HOAc molecule and the IL molecular anion, OAc^- . However, the appearance of this band certainly indicates that the HOAc remains mostly undissociated in the AIL solution. In other words, the dissociation of HOAc, if any, is not detectable by the Raman spectra. Hence, the Raman spectra show that the HOAc molecule and EMIMOAc ions are structurally unchanged in the AIL solution and HOAc remains a weak acid, if it is acidic, since the HOAc ionization is not detected.

Figure 4. A) AIL solution conductivity (■) and viscosity (□) as a function of HOAc molarity at room temperature, 23 °C; (B) Arrhenius curves (conductivity vs. temperature). The errors in conductivity and viscosity values are estimated at $\sim\pm 5\%$.

Conductivity and viscosity measurements of ILs and AIL solutions can provide insight into their collective transport properties.³⁹ Solution conductivities are affected by the concentration of each component and their intermolecular interactions. Previous reports have indicated that IL solution conductivities decrease with increasing concentrations of ionic solutes such as Li^+ and Na^+ salts.^{33, 40} With strong acids (strong electrolytes), increasing the acid concentration to create an AIL solution results in increased conductivity at lower concentrations but decreased conductivity at higher concentrations due to reduced acid dissociation (i.e., protonation).^{15, 18} However, when a non-ionic molecular compound (nonelectrolyte or very weak acid) such as acetonitrile, methanol, or water is mixed with ILs, the solution conductivity increases until the molecular solute becomes the majority component.^{16, 33, 41-42} A universal theory about the effects on conductivity of ionic and molecular solutes has not been established due to the large diversity of the solute structures. This trend is valid empirically. Conductivity is tightly related to viscosity. In the cases mentioned above, the viscosity changed to the opposite direction of conductivity, as described by Walden's rule. In general, the conductivity and viscosity of IL solutions are both determined by the hindered drifting of ions driven by an electric field or mechanical shear. In this regards, the Stoke-Einstein Equation is approximately valid. When ions associate together forming larger ion clusters (larger hydrodynamic radius) the viscosity increases and the conductivity decreases.

We present the conductivity and viscosity measurements for the HOAc/EMIMOAc AIL solutions in Figure 4. For all conductivity and viscosity measurements, we estimate the errors as

~±5% based on repeated measurements of selected solutions. When HOAc is dissolved in EMIMOAc, the conductivity increases significantly from ~2.5 mS/cm in pure EMIMOAc to ~11 mS/cm in the 6.0 M HOAc ($\chi_{\text{HOAc}} = 0.60$) AIL solution (Figure 4A). Based on the empirical conclusion mentioned above that electrically neutral molecular solutes increase the IL conductivity, this conductivity result may support the conclusion from spectroscopic measurements that HOAc does not ionize in the AIL solution. HOAc may behave as a non-ionic molecular solute or at most as a very weak acid. In classic electrolyte theory, the conductivity of a liquid solution depends on the number density (concentration) of the charge carriers (ions) and the mobility of these particles. The addition of HOAc molecules to the IL may affect the solution conductivity in several different ways. Once the solute–solvent cluster is formed, the HOAc solvated by IL molecular ions may behave as a single charge carrier in the electric field. Because the size of the solute–solvent cluster would be larger than either the cation or the anion alone, it would have a lower electrical mobility and hence diminished solution conductivity. On the other hand, the HOAc may also perturb the ion nanoclusters in ILs⁴³⁻⁴⁴ and help release more “free” solvent ions as charge carriers, which would enhance the solution conductivity.⁴⁵ Likely, the latter effect is dominant in this system. Also, the increased solution conductivity with molecular solutes in IL solutions has been correlated to the decrease of viscosity because of the “diluting” effect of the molecular solutes.⁴⁶ The measured viscosity values of pure EMIOAc and solutions are shown in Figure 4A; the results are consistent with the current discussion.

To further characterize the HOAc effect on the EMIOAc solution conductivity at a molecular level, we measured the temperature-dependence of the solution conductivities between 30 to 70 °C. Arrhenius plots of the data are shown in Figure 4B. At all temperatures, the conductivity

increases with increasing HOAc molar fraction from 0 to 0.5. The Arrhenius plots are not linear, and are therefore fitted with the Vogel–Fulcher–Tamman (VFT) equation:

$$\sigma = \sigma_0 e^{\left(\frac{-B}{T-T_0}\right)} \quad (4)$$

where σ_0 , B , and T_0 are constants which have been described in the free-volume theory.⁴⁷⁻⁴⁸ In this theory, σ_0 is the infinite concentration conductivity (proportional of the number of charge carriers), B has a temperature unit and is related to the activation energy of charge carrier's motion, and T_0 is the “ideal” glass transition temperature of the liquid, which is usually 30-50 degrees below the measured glass transition temperature (T_g). Their values vary in different liquids and solutions.

Table 1. VFT equation parameters obtained from the experimental data in Figure 4B

χ_{HOAc}	σ_0 (mS)	B (K)	T_0 (K)
0	34±2	158±10	235±3
0.1	376±45	461±30	201±4
0.2	604±62	529±28	189±4
0.3	1111±183	703±54	163±6
0.5	1541±434	793±100	149±11

The values of σ_0 , B , and T_0 were obtained by fitting the experimental data with Equation (4) and are summarized in Table 1. The number of charge carriers in the AIL solutions (σ_0) increases with increasing HOAc concentration. As previously mentioned this may be the result of HOAc molecules disturbing the ion pairs or ion clusters in the pure IL and “freeing” the ions by dilution. Consequently, the apparent number of charge carriers increased. From Table 1, adding the HOAc to create the AIL solutions also reduces the glass transition temperature and increases the apparent charge transport activation energy.

Overall, the changes in the VFT parameters help verify the conclusions regarding the nature of HOAc in the EMIMOAc solution and provide insight into the microscopic solvation. The HOAc molecule remains mostly non-ionized but may disrupt the clusters of IL molecular cations and anions in EMIMOAc. This would likely result in an HOAc molecule solvated by the IL molecular ions. Acetate dimers bridged by one hydrogen ion are not observed by the spectroscopy and conductivity measurements. Such a molecular-level change may result in an effectively larger number of charge carriers, and hence a lower T_g value and larger free volume in the AIL solution. Regarding the activation energy (B), it is possible that the particles, including the HOAc molecule and both molecular ions, associate more tightly in the AIL solution based on the ion-dipole and hydrogen bond interactions. The thermodynamics results (Figs. 1 and 2) support this conclusion based on the negative solution enthalpy. These stronger interactions likely explain the higher apparent activation energy values for charge transport through the solution. While AIL solutions possess very high ion concentration and larger viscosity comparing with aqueous solutions, the molecular-level and time-resolved mechanism of ion transportation and solvation could be very complicated. Further details will need to be elucidated with additional experiments and simulations.

Conclusion

Acetic acid, a typical weak electrolyte in aqueous solutions, has been used for many purposes in IL solutions. Our spectroscopy investigation demonstrates that the HOAc molecules do not ionize to an observable extent in the IL solutions. Instead of ionization, the neutral HOAc molecules are likely solvated by the IL molecular ions via the strong ion-dipole and hydrogen bonding intermolecular forces. These strong interactions result in a negative solution enthalpy

and a negative deviation from Raoult's Law for the HOAc vapor pressure. The addition of the neutral HOAc molecules "dilutes" the IL and results in a higher ionic conductivity and a lower viscosity compared to the pure IL. Temperature-dependent solution conductivity measurements show that the number of charge-carriers and the apparent transport activation energy increase with increasing HOAc concentration. Overall, the HOAc dissolved in IL solutions may be a source of active protons, but it does not appear to ionize significantly in AIL solutions such as EMIMOAc.

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