Conductivity and Viscosity of 1-Allyl-3-methyl-imidazolium Chloride + Water and + Ethanol from 293.15 K to 333.15 K

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The room-temperature ionic liquid 1-allyl-3-methyl-imidazolium chloride [amim][CI] was synthesized. The conductivities and viscosities of [amim][CI] + water and + ethanol binary mixtures were determined in the temperature range from 293.15 K to 333.15 K, and the mole fraction of the solvents in the mixtures was in the range of 0 to 0.80 for water and 0 to 0.55 for ethanol. The conductivities of the mixtures increased with increasing concentration of the solvents and temperature in the solvent concentration range studied. The viscosities of the mixtures decreased with increasing temperature.

Introduction

It is a great challenge to reduce the amount of volatile organic compounds in chemical and industrial processes. Room-temperature ionic liquids (RILs) are a class of organic salts that are liquids at or near room temperature in their pure state. They exhibit many interesting properties such as negligible vapor pressure, low melting point, favorable solvation behavior, chemical and thermal stability, nonflammability, high ionic conductivity, and a wide electrochemical potential window. Because of their nonvolatile nature and favorable solvation properties, RILs have been suggested as green and benign replacements for traditional volatile organic solvents.

Room-temperature ionic liquids (RTILs) have been used as a new generation of green solvents for a number of organic reactions,[1−3] such as alkylation, hydrogenation, Diels−Alder addition, and the Suzuki cross-coupling reaction. In recent years, room-temperature ionic liquids such as *N,N'*-dialkyimidazolium salts have attracted significant and growing interest.[4−7] When the counteranion of such an imidazolium salt is exchanged from halogens to another species such as tetrafluoroborate, hexafluoroarsenate, hexafluorophosphate, and bis(trifluoromethylsulfonimide), they are known to be water stable and less viscous liquids at ambient temperature.[8]

Water, ethanol, and their mixtures, independently of their well-known fundamental importance, constitute by far the most commonly used media for many technological processes.[9] RTILs show high potential as possible extractants of a wide variety of components in aqueous solution media. In particular, they may come to play an important role in the recovery of acetone, butanol, and ethanol produced in fermentation processes.[10]

Physical properties of different RTILs have been reported in the literature.[11,12] Zhang et al.[13] determined the physical properties of the binary system of 1-ethyl-3-methylimidazolium tetrafluoroborate + H_2O. Their results show that the densities and viscosities are strongly dependent on the water content and weakly dependent on the temperature. Heintz[14] reported the excess molar volumes and viscosities of binary mixtures of methanol and 4-methyl-*N*-butylpyridinium tetrafluoroborate. The results reveal that the excess molar volume is negative and that the excess logarithm of viscosity is positive over the entire mixture composition. Han et al.[15] presented some work on conductivity and viscosity for [bmim][PF_6] + water + ethanol and [bmim][PF_6] + water + acetone ternary mixtures.

The viscosity of RTILs depends on hydrogen bonding and the van der Waals force,[16] but mainly on hydrogen bonding. The conductivity of RTILs is in the range of (10^{-3} to 10^{-5})S·cm^{-1}. Conductivity is related to the molecular weight, density, size of the ions, and especially viscosity.[16] The viscosity of RTILs may be decreased while their conductivity is increased by adding some organic or inorganic solvents.

Before the full potential of RTILs as solvent systems can be explored, much more information about their physicochemical properties needs to be gathered. Presently, the amount of physicochemical data available for ionic liquids is insufficient to create a database of knowledge relating to their applicability in separation processes.[17]

In this work, we study the relations of conductivity to the temperature and the composition of a mixture. [amim][CI] is a new type of ionic liquid that may be polymerized with other monomers. Its conductivity and viscosity have not been reported. [amim][CI] was synthesized, and then the conductivity and viscosity of binary mixtures of [amim][CI] with water and ethanol were studied.

Experimental Section

Materials. Ethanol (>99.8%) was produced by Beijing Chemical Reagent Factory. *N*-methyl-imidazolium was purchased from Kaile Chemical Reagent Factory and was purified before used. Allyl chloride was from Shanghai Chemical Reagent Company. Deionized water with a conductivity of 2×10^{-7} S·cm^{-1} was used. [amim][CI] was prepared and purified using the procedures reported in the literature.[18] Because trace amounts of water would have a dramatic effect on the physical properties, samples were dried under vacuum at 353 K for 48 h. Karl-Fisher analysis of the samples subjected to this treatment indicated that the water content was reduced to 0.18 mass %. Another impurity that may affect the physical properties is the residual chloride ions. A chloride content of 0.0016 mol·kg^{-1} was determined in the ionic liquid by using a chloride-selective electrode. The density was measured using calibrated 10-cm^3 density bottles.

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10.1021/je049787p CCC: $30.25
Published on Web 12/14/2004

Table 1. Conductivities σ and Viscosities η of [amim][CI] (1) + Water (2) and + Ethanol (3) Mixtures[a]

T/K	x_2	$10^4\sigma$/ S·cm^{-1} (2)	η/ mPa·s (2)	x_3	$10^4\sigma$/ S·cm^{-1} (3)	η/ mPa·s (3)
293.15	0.0	38.2	66.0	0.00	38.2	66.0
303.15		44.0	44.7		44.0	44.7
313.15		50.1	25.3		50.1	25.3
323.15		56.2	20.6		56.2	20.6
333.15		62.4	16.2		62.4	16.2
293.15	0.30	81.7	51.3	0.10	48.5	54.6
303.15		87.4	40.7		54.3	44.1
313.15		93.0	24.1		60.4	24.6
323.15		98.5	19.6		66.0	20.0
333.15		104.1	15.0		72.2	16.0
293.15	0.45	111.4	42.7	0.20	62.7	45.7
303.15		117.1	31.4		68.2	42.2
313.15		122.5	22.9		74.0	24.1
323.15		128.0	18.2		80.1	19.5
333.15		133.4	15.1		85.9	15.4
293.15	0.59	136.2	34.4	0.30	70.3	39.1
303.15		141.9	27.5		75.9	30.9
313.15		147.3	22.7		81.8	22.6
323.15		152.7	18.3		87.6	18.7
333.15		158.0	14.9		93.5	15.1
293.15	0.65	155.5	29.1	0.35	80.0	30.5
303.15		160.9	24.2		85.5	25.1
313.15		166.2	20.9		91.0	19.4
323.15		171.6	17.6		96.9	16.0
333.15		177.0	14.3		102.4	14.4
293.15	0.70	173.0	26.1	0.45	88.4	26.4
303.15		178.4	22.0		94.3	22.1
313.15		183.7	19.5		99.9	20.1
323.15		189.0	16.4		105.6	16.7
333.15		194.2	13.0		111.0	13.1
293.15	0.75	184.2	22.6	0.50	95.2	23.2
303.15		189.4	18.7		100.6	18.1
313.15		194.8	15.4		106.0	15.3
323.15		199.9	12.2		111.3	13.6
333.15		205.1	10.1		116.6	11.2
293.15	0.80	193.5	19.3	0.55	103.3	20.4
303.15		198.6	15.6		108.9	16.3
313.15		203.5	12.7		114.3	14.0
323.15		208.6	11.1		119.7	12.5
333.15		213.5	9.2		125.0	10.1

[a] x, mol fraction of solvent.

Conductivity. The conductivity was determined with a conductivity meter produced by Shanghai Precision & Scientific Instrument Co., Ltd (DDS-304) that is equipped with a water bath maintained at the desired temperature and controlled to within ±0.05 K. All of the samples were dried under vacuum at 353 K for 48 h before measurement.

Viscosity. The viscosity was determined by using an Ubbelohde viscometer. The viscometer was calibrated using standard pure-water samples. The temperature of the water bath was controlled with a WMZK-01 controller, and the temperature fluctuation was less than ±0.05 K.

All measurements were performed in a glovebox filled with dry nitrogen gas in the temperature range from 293.15 K to 333.15 K. According to the precision of all experimental instruments, the experimental uncertainties in density, conductivity, and viscosity were calculated to be ±0.03%, ±0.2%, and ±0.15%, respectively.

Results and Discussion

Table 1 lists the conductivities and viscosities of [amim]-[CI] + water and + ethanol with different compositions in the temperature range from 293.15 K to 333.15 K. The dependence of the conductivity on temperature and composition is illustrated in Figures 1 and 2. The conductivities increase with temperature. The conductivity (σ) is related to the ion mobility and the number of charge carriers, which can be expressed by the following equation:[19]

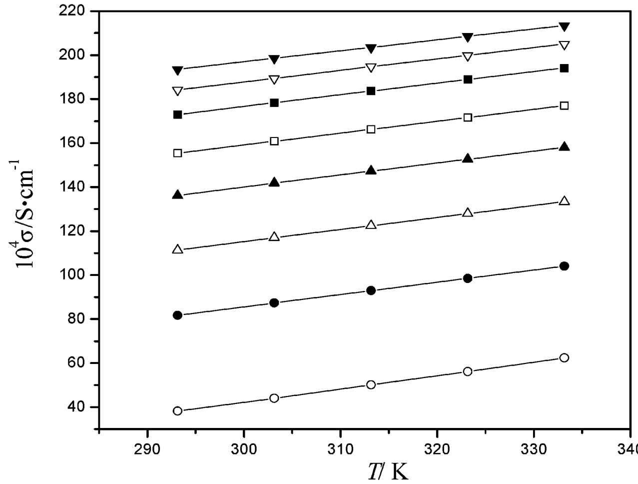

Figure 1. Relationship between the conductivity (σ) of [amim]-[CI] (1) + water (2) mixtures and temperature and composition. x, mol fraction; ○, $x_2 = 0.0$; ●, $x_2 = 0.30$; △, $x_2 = 0.45$; ▲, $x_2 = 0.59$; □, $x_2 = 0.65$; ■, $x_2 = 0.70$, ▽, $x_2 = 0.75$; ▼, $x_2 = 0.80$.

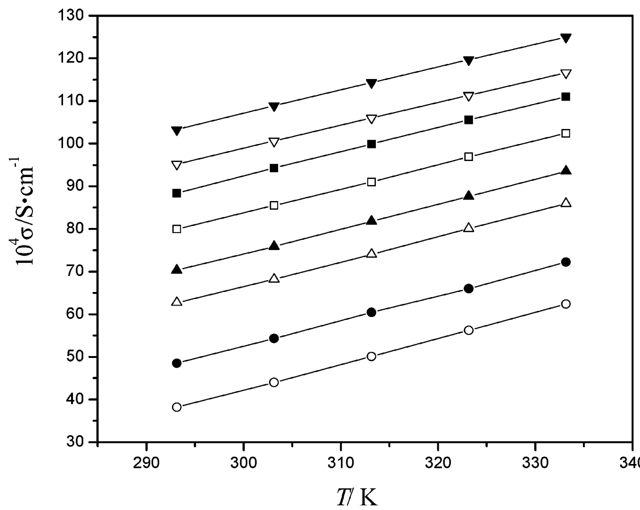

Figure 2. Relationship between the conductivity (σ) of [amim]-[CI] (1) + ethanol (3) mixtures to temperature and composition. x, mol fraction; ○, $x_3 = 0.0$; ●, $x_3 = 0.10$; △, $x_3 = 0.2$; ▲, $x_3 = 0.30$; □, $x_3 = 0.35$; ■, $x_3 = 0.45$; ▽, $x_3 = 0.50$; ▼, $x_3 = 0.55$.

$$\sigma = \Sigma n_i q_i \mu_i$$

where n_i is the number of charge carriers of species i, q_i is the charge, and μ_i is the mobility. An increase in temperature results in an increase in the mobility because the viscosity of the liquids is reduced. This is one of the main reasons for the enhancement of the conductivity with increasing temperature. Figures 3 and 4 show the effects of temperature on viscosity for the mixtures. Viscosity decreases with increasing temperature. The increase in temperature would enhance the mobility of the molecules and increase the amount and volume of free volume. With increasing solvent mole fraction, viscosity decreases at the same temperature. It can be explained that increasing amounts of water or ethanol weaken the interaction force among ions and enhance the movement of ions. In the temperature range of 290 K to 310 K, the decrease in viscosity at high [amim][CI] concentration is much faster than that at low concentration. Seddon et al.[20] state that

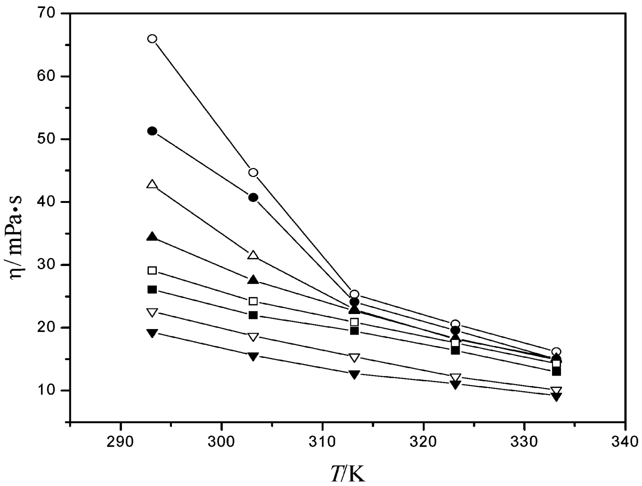

Figure 3. Relationship between the viscosity (η) of [amim][CI] (1) + water (2) mixtures to temperature and composition. x, mol fraction; ○, $x_2 = 0.0$; ●, $x_2 = 0.30$; △, $x_2 = 0.45$; ▲, $x_2 = 0.59$; □, $x_2 = 0.65$; ■, $x_2 = 0.70$; ▽, $x_2 = 0.75$; ▼, $x_2 = 0.80$.

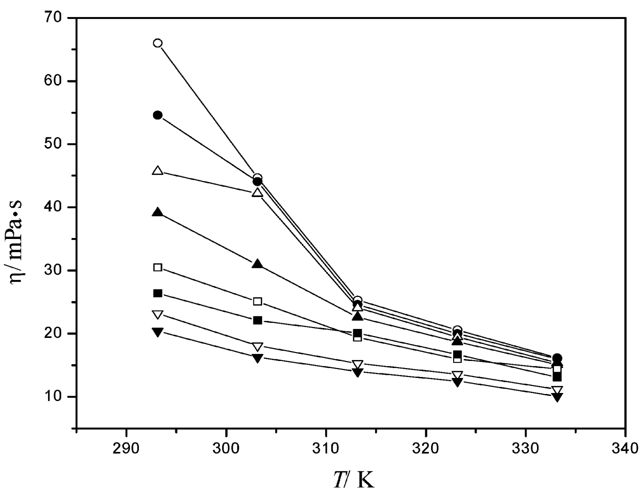

Figure 4. Relationship between the viscosity (η) of [amim][CI] (1) + ethanol (3) mixtures to temperature and composition. x, mol fraction; ○, $x_3 = 0.0$; ●, $x_3 = 0.10$; △, $x_3 = 0.2$; ▲, $x_3 = 0.30$; □, $x_3 = 0.35$; ■, $x_3 = 0.45$; ▽, $x_3 = 0.50$; ▼, $x_3 = 0.55$.

the viscosity can generally be described by the exponential expression

$$\eta = \eta_{IL} \exp\left[-\frac{x_s}{a}\right]$$

where x_s is the mole fraction of the solvent, a is a constant characteristic of the mixture, and η_{IL} is the viscosity of the pure ionic liquid. Over the entire composition range, it can be divided into two different regions: the water-rich ($x_s > 0.5$) and salt-rich regions ($x_s < 0.5$). The results of our study suggest that water is accommodated in the ionic liquid structure in the salt-rich region ($x_s = 1$ to $x_s < 0.5$), possibly by forming hydrogen bonds with both the anion and the cation.[20] With increasing temperature, forming hydrogen bonds are broken, so the viscosity decreases rapidly. At higher x_s, an appreciable fraction of the water may be regarded as free water in the sense that is not linked to the salt, so the structure of the mixtures tends progressively to that of pure water.[21]

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Received for review June 4, 2004. Accepted October 28, 2004.

JE049787P