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质子型离子液体*N,N*-二甲基乙醇胺丙酸盐的密度、粘度及电导率

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摘要: 在283.15−333.15 K温度范围内, 测量了质子型离子液体*N*,*N*-二甲基乙醇胺丙酸盐(DMEOAP)的密度、粘度及电导率. 讨论了温度对密度、粘度和电导率等物理化学参数的影响. 通过经验和半经验方程得到了该离子液体的热膨胀系数、分子体积、标准摩尔熵及晶格能等热力学性质参数. 由电导率和密度计算出了该离子液体的摩尔电导率. 利用Vogel-Fulcher-Tamman (VFT)方程, 将测量的动力粘度和电导率对温度拟合, 得到了动力粘度和电导率随温度变化方程式. 并通过Walden规则, 建立了粘度与摩尔电导率之间的联系.

关键词: 质子型离子液体; 密度; 粘度; 电导率
中图分类号: O642

Density, Viscosity and Conductivity of Protic Ionic Liquid *N,N*-Dimethylethanolammonium Propionate

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Abstract: The density, viscosity, and conductivity of protic ionic liquid (PIL) *N*,*N*-dimethylethanolammonium propionate (DMEOAP) were determined in the temperature range of 283.15−333.15 K. The influence of temperature on density, viscosity, and conductivity is discussed. The thermal expansion coefficient, molecular volume, standard molar entropy, and lattice energy of DMEOAP were calculated using empirical and semiempirical equations. The molar conductivity of DMEOAP was determined from density and conductivity data. The temperature dependence of viscosity and conductivity data was fitted using the Vogel-Fulcher-Tammann (VFT) equation. The relationship between molar conductivity and viscosity was determined by the Walden rule.

Key Words: Protic ionic liquid; Density; Viscosity; Conductivity

1 Introduction

Nowadays, more and more attention has been paid to the pollution from fuel combustion exthaust.[1−3] So much emphasis has been put on the clean diesel fuels by most countries, especially the sulfur content.[4−6] As a conventional method, the hydrodesulfurization (HDS) is widely used for the removal of sulfur compounds in the petroleum refining industry.[7] However, the traditional extractants used for the desulfurization process are organic solvents, which are volatile and toxic. So, the finding of greener, more safe, and efficient novel extractants is necessary

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to replace the traditional ones.

Ionic liquids (ILs) have many advantages, such as low vapor pressure, thermal and chemical stability, designability, etc.[8−11] They are considered to be the green solvents that replace the volatile organic solvents.[12,13] In recent years, ILs applied for extraction desulfurization of diesel fuels have been widely studied. As the green solvents, the ILs can be designed, which provides us with more choice for the option of ILs. Nowadays the ILs used for desulfurization is mainly imidazole-based or pyridine-based ILs. The expensive materials become the main problems for the industrialization. At the same time, the viscosity of existing ILs is still very high, which is harmful for the dispersion and mass transfer. It is another problem for industrial application. So the development of novel ILs with cheap materials, low viscosity, and easily synthesis route is very urgent.

Recently, the authors found that protic ionic liquids (PILs) not only have the excellent physico-chemical properties of traditional ILs, but also have the unique advantages, such as high extraction efficiency, low cost, low viscosity, and easily recycling compared to traditional ILs.[14] The materials of the PILs are also cheap and the process of the synthesis is simple. At the same time, PILs are environmentally favorable because their anions are mostly composed of non-toxic anion such as organic acids.[15−18] PILs have become a potential greener desulfurization solvents. However, the lack of physico-chemical properties data of PILs has become a hinder for their future industrial application.

Herein, a PIL *N*,*N*-dimethylethanolammonium propionate (DMEOAP) was synthesized. And some important physico-chemical properties such as density, viscosity, and conductivity were determined and discussed. The relationship of the density, viscosity, and conductivity was built in terms of the Walden rule.

2 Experimental

2.1 Materials

N,*N*-dimethylethanolamine (99%, Aladdin, China), Propionic acid (AR grade, Aladdin, China) was provided by Sigma-Aldrich.

2.2 Synthesis and characterization of the PIL DMEOAP

The PIL DMEOAP was synthesized and characterized according to our previous method.[17] ^{1}H nuclear magnetic resonance (^{1}H NMR) was used for determination of the PIL structure with dimethyl sulfoxide as the solvent, the other basic parameters are shown in Fig.S1 (Supporting Information). No impurity was found in PIL from the ^{1}H NMR. The water content (mass fraction) is 486×10^{-6} by a Cou-Lo Aquamax Karl Fischer moisture meter (v.10.06). The structure of the DMEOAP is listed as below:

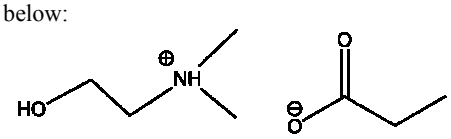

Table 1 Experimental values of density (ρ), viscosity (η), conductivity (σ), and molar electrical conductivity (Λ) at pressure p=0.1 MPa and different temperatures

T/K	ρ/(g·cm^{-3})	η/(mPa·s)	σ/(mS·cm^{-1})	Λ/(S·cm^2·mol^{-1})
283.15	1.0290	102.6*	0.580	0.092
288.15	1.0239	75.65	0.750	0.120
293.15	1.0196	55.94	0.949	0.152
298.15	1.0153	43.67	1.18	0.190
303.15	1.0110	33.80	1.44	0.232
308.15	1.0071	26.45	1.73	0.281
313.15	1.0029	21.01	2.04	0.332
318.15	0.9979	17.01	2.41	0.394
323.15	0.9933	14.00	2.77	0.455
328.15	0.9888	11.62	3.17	0.523
333.15	0.9848	9.743	3.60	0.597

* the calculated value

2.3 Density, viscosity, and conductivity measurements

The density, viscosity, and conductivity were determined according to a previous method at atmosphere.[19,20] The density was determined by a Westphal balance in the temperature range of 283.15−333.15 K within experimental error ±0.0002 g·cm^{-3}. The viscosity was determined using an Ostwald viscometer in the temperature range of 288.15−333.15 K and the uncertainties were estimated to be ±1%. The conductivity was carried out on a MP522 conductivity instrument with the cell constants of 1 cm^{-1} (the cell was calibrated with the aqueous KCl solution) in the temperature range of 283.15−333.15 K and the uncertainties were estimated to be ±1%. The experimental values are listed in Table 1.

3 Results and discussion

From Table 1, the density and viscosity decrease with increasing the temperature. However, different from the density and viscosity, the conductivity shows the inverse trend shown in Fig.1.

3.1 Density

The density data *versus* temperature was fitted by following equation:

$$\rho=A+BT \quad (1)$$

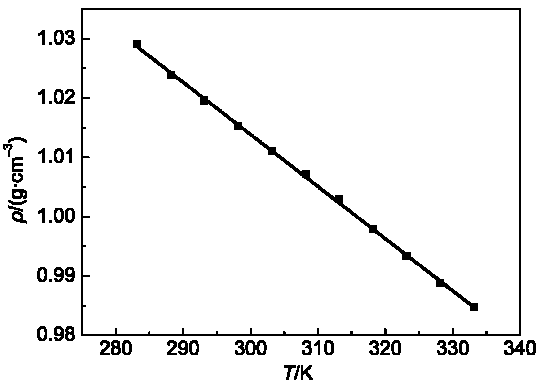

Fig.1 Density of PIL DMEOAP as a function of temperature

where ρ is the density; A, B are fitting parameters. The fitted equation is $\rho=1.2774-8.79\times10^{-4}T$. The correlation coefficient is 0.999.

The thermal expansion coefficient, α, can be obtained by the $\ln\rho$ *versus* T fitted according to a straight line. The fitting equation is below:

$$\ln\rho=b-\alpha T \quad (2)$$

where b is an empirical constant, α is thermal expansion coefficient. The thermal expansion coefficient is 8.73×10^{-4} K^{-1} for the sample.

The molecular volume, V_m, can be calculated by the following equation:

$$V_m=M/(N\rho) \quad (3)$$

where M is molar mass, N is Avogadro′s constant. The value of molecular volume, V_m, is 0.2670 nm^3 at 298.15 K.

The standard molar entropy can be estimated according to the following equation:[21]

$$S^0=1246.5\cdot V_m+29.5 \quad (4)$$

The value is 362.4 $J\cdot K^{-1}\cdot mol^{-1}$ for sample at 298.15 K.

The lattice energy, U_{POT}, was calculated according to the following equation:[21]

$$U_{POT}=1981.2(\rho/M)^{1/3}+103.8 \quad (5)$$

The lattice energy value is 468.2 $kJ\cdot mol^{-1}$ at 298.15 K. The value is lower than that of melt salts. For example, the fused CsI[22] has the lowest lattice energy among the alkali halides and the value is 613 $kJ\cdot mol^{-1}$. This is the reason that the PIL can exist as liquid state at room temperature.

3.2 Molar conductivity

The molar conductivity data can be determined according to the following equation:

$$\Lambda=\sigma\cdot M\cdot\rho^{-1} \quad (6)$$

where Λ is the molar conductivity, σ is the conductivity. The molar conductivity values are listed in Table 1.

The molar conductivity, Λ, *versus* temperature, T, of the ILs can be fitted according to the following Vogel-Fulcher-Tamman (VFT) equation:

$$\Lambda=\Lambda_0\exp(-B/(T-T_0)) \quad (7)$$

where Λ_0, B are adjustable parameters. The fitting equation is $\Lambda=29.23\cdot\exp(-598.7/(T-179.3))$. The correlation coefficient is 0.99996.

3.3 Viscosity

Usually, the VFT equation was used for the fitting of the viscosity *versus* temperature according to the following equation:

$$\eta=\eta_0\exp(B/(T-T_0)) \quad (8)$$

where η is the viscosity; η_0, B are fitting parameters. The fitting equation is $\eta=0.0116\cdot\exp(1296.6/(T-140.5))$. The correlation coefficient is 0.9998, which indicates that the VFT equation can be used for the viscosity fitting of PILs. Fig.2 shows the variation of the viscosity *versus* temperature.

According to the Arrhenius equation, the viscosity *versus* temperature can be described as follows:

$$\eta=\eta_\infty\exp(E_\eta/(k_BT)) \quad (9)$$

where E_η is the activation energy for dynamic viscosity, η_∞ is the maximum electrical conductivity, and k_B is the Boltzmann constant.

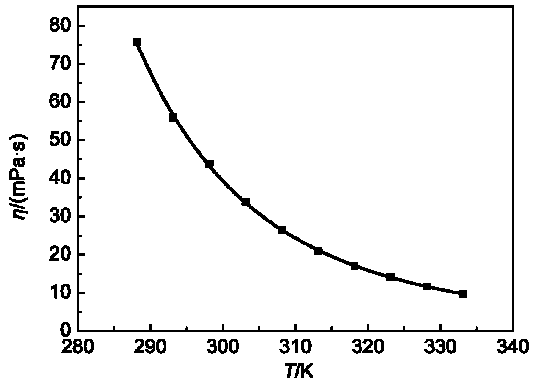

Fig.2 Viscosity of PIL DMEOAP as a function of temperature

Recently, Vila *et al.*[23] have built the relationship of the VFT equation and Arrhenium equation for conductivity. Here, for dynamic viscosity, the VFT equation and Arrhenius equation can also be combined according to the discussion by Vila *et al.*[23] and the final version of VFT equation is:

$$\eta=\eta_\infty\exp(E_a/(k_B(T-T_0))) \quad (10)$$

here, $\eta_0=\sigma_\infty$. The viscosity activation energy value is 111.9×10^{-3} eV.

3.4 Conductivity

Usually, the VFT equation was also used for the fitting of the conductivity data *versus* temperature:

$$\sigma=\sigma_0\exp(-B/(T-T_0)) \quad (11)$$

here σ_0, B are adjustable parameters, $B=E_\eta/k_B$. The fitting equation is $\sigma=141.8\cdot\exp(-552.2/(T-182.8))$. The correlation coefficient is more than 0.99996, which indicates that the VFT equation can be used for the viscosity fitting of PILs. Fig.3 shows the variation of the conductivity *versus* temperature.

According to the Arrhenius equation, the conductivity *versus* temperature can be described:

$$\sigma=\sigma_\infty\exp(-E_a/(k_BT)) \quad (12)$$

where E_a is the activation energy, which indicates the energy needed for an ion to hop to a free hole, σ_∞ is the maximum electrical conductivity.

For conductivity, the VFT equation and Arrhenius equation can be combined according to the discussion by Vila *et al.*[23]

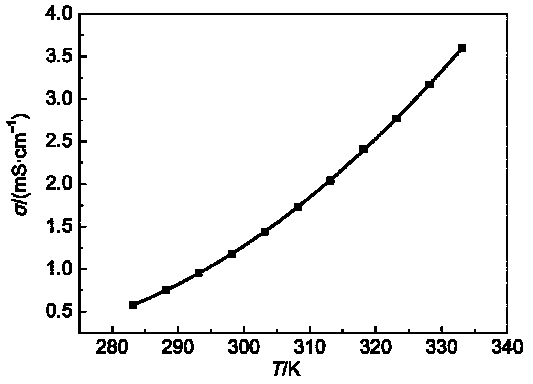

Fig.3 Conductivity of PIL DMEOAP as a function of temperature

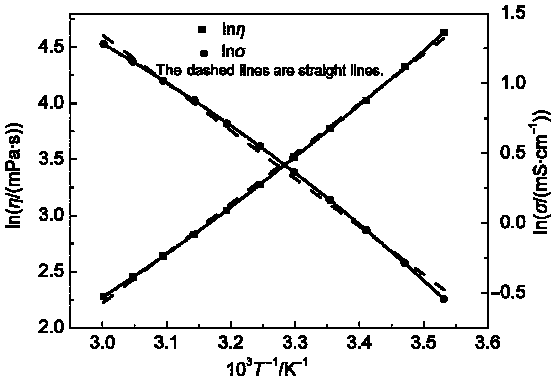

Fig.4 Plots of lnη and lnσ *versus* 1/*T* for PIL DMEOAP

and the final version of VFT equation is:

$$\sigma = \sigma_\infty \exp(-E_\sigma/(k_B(T-T_0)) \quad (13)$$

here, $\sigma_0=\sigma_\infty$ and $B=E_\sigma/k_B$. The electrical conductivity activation energy value is 47.65×10^{-3} eV.

The lnη and lnσ *vs* T^{-1} were plotted for PIL DMEOAP (see Fig.4). According to the Arrhenius equations (9) and (12), the lines should be the straight lines for viscosity and conductivity, however, the curves are not ideal straight lines in Fig.4 (the broken straight lines are plotted on the curves). So, the viscosity and conductivity do not well follow the Arrhenius behavior according to the Arrhenius equation.

3.5 Walden product

According to the Walden rule, the molar conductivity and viscosity can be described according to the following equation:

$$\Lambda\eta^{\alpha}=k \quad (14)$$

$$\lg\Lambda=\lg k+\alpha\lg\eta^{-1} \quad (15)$$

where k is a temperature dependent constant. The variation of lgΛ *versus* lgη^{-1} is shown in Fig.5 for DMEOAP and [$C_n$py][NTf_2] (n=2, 4, 5).[20] Recently, the authors have studied molar conductivity and viscosity of the normal ILs [$C_n$py][NTf_2] (n=2, 4, 5) using the same measurement. So, the ILs [$C_n$py][NTf_2] (n=2, 4, 5) were chosen as the references with the desired PIL. The slope, α, was obtained and the value is 0.925 for DMEOAP. From Fig.5, the curve of PIL DMEOAP is under the ideal line,[20]

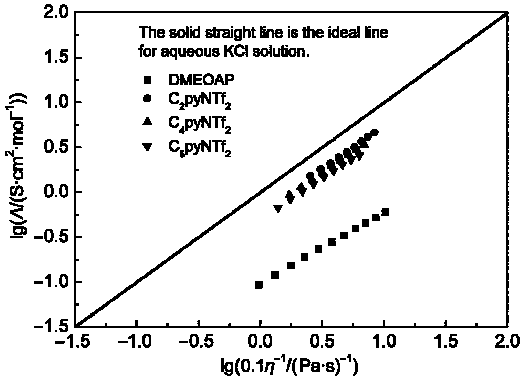

Fig.5 Plot of lgΛ *versus* lgη^{-1} for PIL DMEOAP and pyridinium-type ILs[20]

C_2pyNTf$_2$: *N*-ethylpyridinium bis(trifluoromethylsulfonyl)imide; C_4pyNTf$_2$: *N*-butylpyridinium bis(trifluoromethylsulfonyl)imide; C_5pyNTf$_2$: *N*-pentylpyridinium bis(trifluoromethylsulfonyl)imide

the position of the ideal line is obtained using aqueous KCl solutions at high dilution.[24] It means that the PIL is also "subionic".[25] The curve of PIL DMEOAP is also much lower than ILs [$C_n$py][NTf_2] (n=2, 4, 5).[20] The probable reason for this is that PIL has more tendency of the lower ionic capability than the traditional pyridine based ILs. At the same time, its special accumulation structure would also account for this phenomenon.

4 Conclusions

The density, viscosity, and conductivity of PIL were determined in the temperature range 283.15−333.15 K. The thermal expansion coefficient, molecular volume, standard molar entropy, and lattice energy of DMEOAP were estimated by the density values. The VFT equation can be used for the viscosity or conductivity fitting. The Arrhenius equation cannot be well used for the fitting of the viscosity or conductivity. The density, viscosity, and conductivity relationship can be set up according to the Walden rule.

Supporting Information: The ^{1}H NMR spectrum of *N*,*N*-dimethylethanolammonium propionate has been included. This information is available free of charge *via* the internet at http://www.whxb.pku.edu.cn.

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质子型离子液体 *N,N*-二甲基乙醇胺丙酸盐的密度、粘度及电导率

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Density, Viscosity and Conductivity of Protic Ionic Liquid *N,N*-DimethylethanolammoniumPropionate

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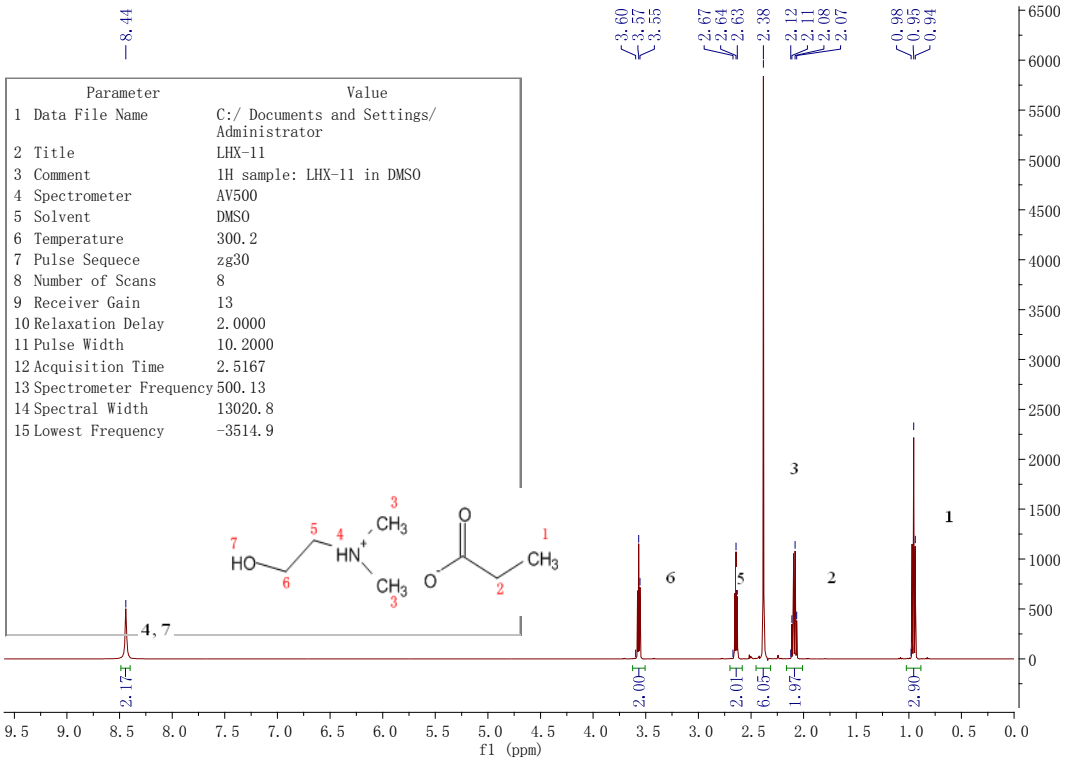

Fig.S1 ^{1}H NMR of *N*, *N*-dimethylethanolammonium propionate