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Physical Properties of [BPy] [L-Pro] Chiral Ionic Liquids with Asymmetric Catalytic Performance

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Abstract. A pyridine-containing chiral ionic liquid [BPy][L-Pro] with an amino acid as the anion was synthesized, and its synthesis process is very simple with 86.6% yield and 97% purity. Some important physical properties including specific rotation, refractive index, conductivity and density of [BPy][L-Pro] have been comprehensively determined. The dependence of main properties of the [BPy][L-Pro] aqueous solution at different concentrations and temperatures was also explored and fitted, which can provide useful information for its asymmetric catalytic application.

1. Introduction

Owing to the great potential as environmentally benign reaction media, ionic liquids (ILs) could be designed to get special physicochemical properties, by which various chemical reactions could be performed smoothly. Studies have shown that the scope of application of ILs has been no longer limited to solvents, as new catalysts and reagents, ILs have attracted significant attention in the context of green chemistry, with which the progress of reactions could be controlled. The past decades have witnessed the burgeoning progress of chiral ionic liquids (CILs) along this line[1]. Numerous ionic liquids based on chiral structure were employed as chiral-resolution reagents, chiral solvents, or chiral additives in the initial work, which have a wide range of applications in some fields[2]. However, the use of CILs as organocatalysts have facilitated catalysts recycling and increased reactivity and enantioselectivity, which thus making them ideal ILs for exploration.

Some CILs could promote the asymmetric organic reaction as catalysts recently[3]. But these ILs have exhibited poor catalytic activity, so some reaction requires a large quantity of catalysts to carry out. Their chiral control centers are basically cation-based, thus they can only be modified by modifying the cationic structure. Since the research of L-proline as asymmetric catalyst, it has become the research hot spot of organic chemists, plenty of proline derivatives have undoubtedly had a significant impact on the field of asymmetric catalysis[4]. To the best of our knowledge, few study has reported the use of anions as chiral control centers, which limits the application of CILs as catalysts.

In our continuing efforts to explore CILs catalysis, we found that a pyridine-containing chiral ionic liquid with an amino acid as the anion i.e. [BPy][L-Pro] could provide a possible way to solve problems above. Preliminary, its asymmetric catalytic performance has been investigated with Aldol reaction with acetone and p-Nitro-benzaldehyde as substrates, ionic liquid [BMIM]BF_4 as solvent can produce high to 95% yield and 94% e.e. at room temperature. Therefore, in this study, a series of physical properties of the [BPy][L-Pro] would be measured and correlated for providing useful base to its further application.

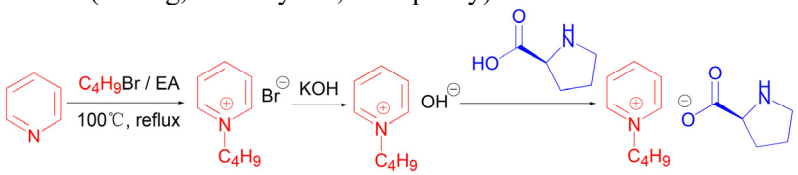
2. Experimental

2.1. Synthesis of the [BPy][L-Pro]

The synthetic procedure of [BPy][L-Pro] (scheme 1):

The synthesis of N-n-butylpyridinium bromide: pyridine (3.955g, 0.05mol) and an appropriate amount of ethyl acetate were placed in a 100mL round-bottom flask equipped with a magnetic stirrer. Then n-Butyl bromide (7.537g, 0.055mol) was dropped slowly into the flask under stirring at room temperature, and the reaction mixture was heated to reflux for 24h. After that, the solution was cooled for at least 0.5h to get white solid. The product was washed three times with ether and then the crude ILs were recrystallized with isopropanol, which were dried for 8h under high vacuum at T=323.15K to get the product as white powdery solid (9.953g , 92.1% yield).

The synthesis of [BPy][L-Pro]: potassium hydroxide(1.680g, 30mmol) was dissolved in ethanol (50mL) and placed in a three-necked flask equipped with a magnetic stirrer, then the solution was cooled to room temperature and ethanol solution (4mL) of N-n-butylpyridinium bromide (6.484g, 30mmol) was dropped slowly into the stirred mixture under nitrogen protection. After 15min, aqueous solution (10mL) of L-proline (3.454g, 33mmoL) was added dropwise, and the reaction mixture was continuously stirred for 24h at room temperature. Then the solvent was removed under vacuum and ethanol (20mL) was added to the mixture, the KBr solid was removed by filtration. After drying ethanol, acetonitrile-methanol mixed solvent was added to separate out excess L-proline. The [BPy][L-Pro] was successfully synthesized after the solvent was removed and dried for 8h under high vacuum at T= 323.15 K (6.396g, 86.6% yield, 97% purity).



Scheme 1. Synthesis procedure of the [BPy][L-Pro].

2.2. Determination of physical properties

2.2.1. Specific Rotation of [BPy][L-Pro]. The specific rotation is a very important parameter for CILs, which may make asymmetric synthesis be directly or indirectly influenced. However, there is very little information involving specific rotation of CILs in present literatures. In this study, the optical rotation data were measured by Auto Polarimeter at different temperature, concentration, and wavelengths. For each measurement, a certain amount of [BPy][L-Pro] was added to ultra-pure water to formulate into aqueous solution to be tested, and the measurement was conducted three times to calculate the specific rotation.

2.2.2. Refractive Index of [BPy][L-Pro]. Refractive index can be used to estimate other several related properties of optical materials and is significantly important in the quality control, determination of the identity and concentration of ILs[5]. The water concentration dependence of the refractive index of IL aqueous solution was rarely measured, although the temperature dependence of the refractive index has been more reported[6]. In the present study, the refractive index dates of the [BPy][L-Pro] aqueous solution across the composition range ranging from 0.1mol/L to 1.0mol/L at different temperatures (from 278.15K to 323.15K) in air were measured using Abbe refractometer at 589nm. Before the measurement, refractive index was calibrated by pure water and same to that of literature's[7] with an error of ±0.0001. The temperature was controlled by a cryostat with an accuracy of ±0.01K. Each measurement was repeated three times to calculate average values.

2.2.3. Conductivity of [BPy][L-Pro]. The conductivity of ILs is important to the application of ILs in electrochemistry. In this study, the electrical conductivities of the [BPy][L-Pro] aqueous solution

(from 0.01mol/L to 0.10mol/L) were measured in 278.15K to 323.15K by a digital conductivity meter. Similarly, each set of experiments was repeated three times to calculate average values as the conductivity values of samples.

2.2.4. Density of [BPy][L-Pro]. The pycnometer method[7] was applied to measure the density of the ionic liquid at different temperature ranging from 278.15K to 313.15K with the uncertainty of 0.0002g/cm^{-3} for the density and 0.01K for the temperature.

3. Results and discussion

3.1. Specific rotation of [BPy][L-Pro]

The specific rotation data of [BPy][L-Pro] aqueous solution at different concentration gradients, temperature and wavelengths are presented in the figures below. As shown in figure 1, the specific rotation of [BPy][L-Pro] in solvents is almost constant as the concentration increases, no correlation between the different concentration and the specific rotation was observed. Considering the specific rotation variation of 1mol/L [BPy][L-Pro] aqueous solution within a certain temperature range (278.15K to 313.15K), it could be observed that the specific rotation increases with a rise in temperature (figure 2). That means temperature is an important factor affecting optical performance.

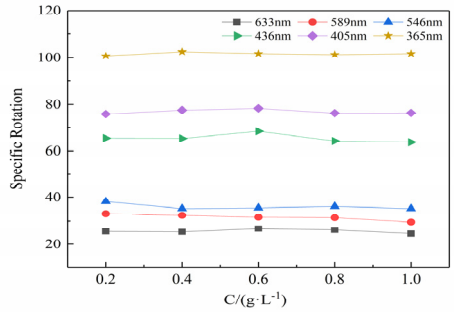


Figure 1. Dependence of specific rotation of the [BPy][L-Pro] aqueous solution at different concentration.

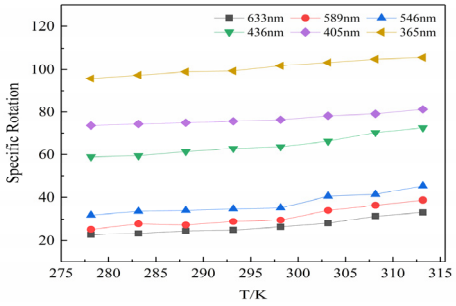


Figure 2. Dependence of specific rotation of the [BPy][L-Pro] aqueous solution at different temperature.

3.2. Refractive Index of [BPy][L-Pro]

The variation of refractive index with ILs concentration and temperature is shown on figure 3. It can be seen that the refractive index increase with ILs concentration rise and decrease linearly with temperature rise. The correlation results of the linears are presented in table 1 and obtained with satisfactory results due to above 0.99 coefficients (R^2).

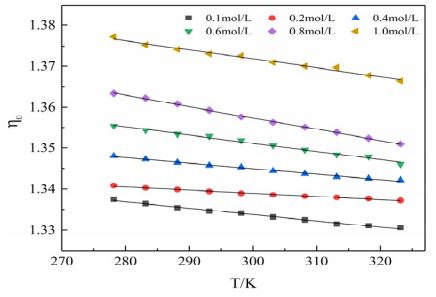


Figure 3. Linear fitting between refractive index of [BPy][L-Pro] ILs aqueous solution and temperature.

Table 1. Linear Fitting Parameters of [BPy][L-Pro] Ionic Liquid Aqueous Solution.

C (mol·L^{-1})	η_D=AT+B			
	A×10^{-4} (K^{-1})	B	R^2	RMSE×10^{-4}
0.1	1.5152	1.3792	0.9919	1.9985
0.2	0.7915	1.3626	0.9936	1.0251
0.4	1.3127	1.3843	0.9927	1.6296
0.6	2.0255	1.4119	0.9912	2.7497
0.8	2.7673	1.4404	0.9991	1.2172
1.0	2.2546	1.4394	0.9922	2.7340

3.3. Conductivity of [BPy][L-Pro]

The measurement results of conductivity are shown in figure 4. It can be seen that the conductivities of [BPy][L-Pro] aqueous solution at different concentration gradients increased lineally with the increment of temperature and can be satisfactorily correlated with R^2= 0.99 (table 2), which could be well used to illustrate that all fitting equations are suitable for the correlation of the electrical conductivities of [BPy][L-Pro] aqueous solution with temperature.

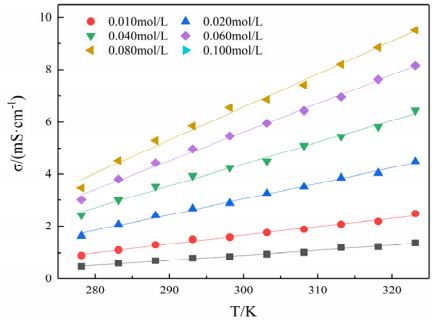


Figure 4. Linear fitting between conductivity of [BPy][L-Pro] aqueous solution and temperature.

Table 2. Linear Fitting Parameters of conductivity to temperature.

C (mol·L^{-1})	σ=A*T*+B			
	A×10^{-2} (K^{-1})	B	R^2	RMSE×10^{-4}
0.1	1.899	4.7895	0.9917	0.02219
0.2	3.276	8.1734	0.9914	0.04384
0.4	6.000	14.9596	0.9950	0.06127
0.6	8.376	20.7417	0.9931	0.10050
0.8	1.098	27.3441	0.9965	0.09425
1.0	1.267	31.4350	0.9919	0.16460

3.4. Density of [BPy][L-Pro]

From the figure 5, it could be distinctly observed that the variation in density became negative with the increasing temperature due to thermal expansion of the [BPy][L-Pro]. The variation can be well correlated as shown in table 3, which could be used to describe the temperature dependence of the density.

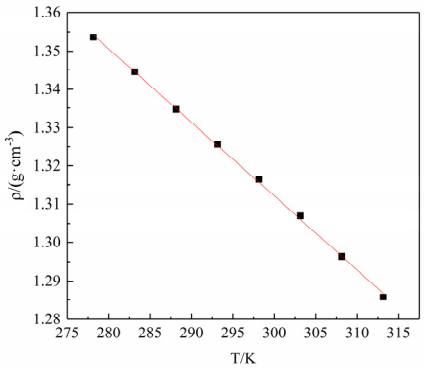


Figure 5. The fitting line of density to temperature.

Table 3. The density of [BPy][L-Pro] at different temperature

ρ=A*T*+B			
A ×10^{-3} (g·cm^{-3}·K^{-1})	B (g·cm^{-3})	R^2	RMSE×10^{-3}
1.930	1.890	0.9992	1.578

According to the expressions in the reference[8], the molecular volume, lattice energy and standard entropy of the ionic liquid at different temperatures could be calculated by the following formulas:

$$U_{POT} = 2I\alpha \times V_m^{1/3} + \beta \quad (1)$$

$$V_m = 1.66 \times 10^{-3} M_m \rho \quad (2)$$

$$S = 1246.5 V_m + 29.5 \quad (3)$$

where, U_{POT} is the lattice energy, kJ·mol^{-1}; V_m is the molecular volume, nm^3; the constants for MX with charge ratio (1:1) have the values: I=1, α=117.3 kJ·mol^{-1}·nm, and β=51.9 kJ·mol^{-1} with V_m in units of nm^3; M_m is the molar mass, 246.18g·mol^{-1}; ρ is the density, g·cm^{-3}; S is the entropy, J·K^{-1}·mol^{-1}.

And these physical parameters are caculated and listed in table 4, from which the standard entropy S_0(298.15K) could be estimated as 700.1 J·K^{-1}·mol^{-1}.

Table 4. Estimated values of physicochemical properties of [BPy][L-Pro] at different temperatures.

T / K	ρ / (g·cm^{-3})	V_m / nm^3	U_{POT} / (kJ·mol^{-1})	S / (J·K^{-1}·mol^{-1})
278.15	1.3536	0.5532	244.5	719.0
283.15	1.3445	0.5494	244.0	714.4
288.15	1.3346	0.5454	243.6	709.3
293.15	1.3256	0.5417	243.1	704.8
298.15	1.3164	0.5380	242.7	700.1
303.15	1.3069	0.5341	242.2	695.2
308.15	1.2963	0.5297	241.7	689.8
313.15	1.2857	0.5254	241.2	684.4

Compared with the alkali metal halide CsI which has the smallest lattice energy (U_{POT}=613kJ/mol^{-1}, 298.15K)[9], the [BPy][L-Pro]'s is much smaller, which is the important reason why it could exist in form of liquid at room temperature.

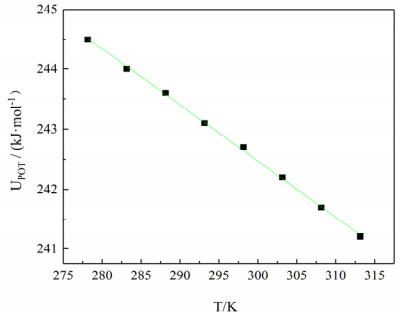


Figure 6. The fitting line of the lattice energy to temperature.

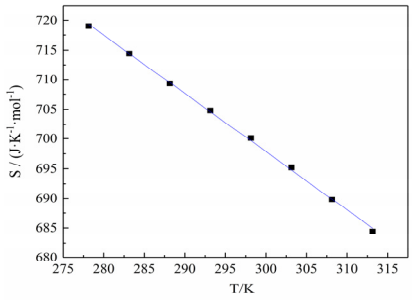


Figure 7. The fitting line of the standard entropy to temperature.

Similarly, two straight lines were applied to fit the data in the table 4, respectively, the correlation results of both linear equations were presented in table 5, and it could be seen that the coefficients of determination are all above 0.999.

Table 5. The fitting parameters of the lattice energy and standard entropy to temperature.

U_{POT}=CT+D				S=ET+F			
C / (kJ·mol^{-1}·K^{-1})	D / (kJ·mol^{-1})	R^2	RMSE	E / (J·K^{-1}·mol^{-2})	F / (J·K^{-1}·mol$^{-1)}$	R^2	RMSE
-0.09333	270.5	0.9991	0.03886	-0.9814	992.3	0.9992	0.3116

According to the definition of constant pressure thermal expansion coefficient (equation 4),

$$\alpha = -(\partial \ln\rho / \partial T)_P \quad (4)$$

a line is suitably used to fit the data, and the fitting equation is

$$\ln \rho = -0.00146T + 0.7091 \quad (5)$$

the correlation coefficient r=0.9994 and the $RMSE$=6.163×10^{-4}. Thus the coefficient of thermal expansion α could be derived as 0.00146 K^{-1}.

4. Conclusion

A pyridine-containing chiral ionic liquid [BPy][L-Pro] with an amino acid as the anion was synthesized. Some important physical properties including specific rotation, refractive index, conductivity and density have been comprehensively measured. From the results of our study, only the specific rotation of [BPy][L-Pro] in solvents is almost constant as the concentration increases, while the refractive index and conductivity change with concentration. Besides, it was confirmed that the four physical properties have temperature dependence, the refractive index, conductivity of its aqueous solution and density of pure ionic liquid change linearly with increasing temperature.

5. Appendices

Product characterization data

(1)N-n-butylpyridinium bromide

IR (KBr, cm^{-1}): 3435.76, 3079.44, 2941.46, 2859.01, 1672.87, 1606.15, 1519.50, 1346.84, 1205.35, 1105.40, 1011.86, 861.66; ^{1}H NMR (400MHz, D_2O): δ 8.78 (d, J=5.6Hz, 2H), 8.52-8.43 (m, 1H), 8.00 (t, J=6.9Hz, 2H), 4.70 (s, 3H), 4.55 (t, J=7.4Hz, 2H), 2.01-1.85 (m, 2H), 1.36-1.22 (m, 2H), 0.86 (t, J=7.4Hz, 3H); ^{13}C NMR (101 MHz, D_2O): δ 145.51, 144.24, 128.24, 61.77, 32.60, 18.76, 12.73 ppm.

(2)[BPy][L-Pro]

IR(KBr, cm^{-1}): 3441.65, 2906, 2851, 1712.94, 1599.38, 1519.1, 1343.23, 1166.39, 1078.6, 838.79, 748.06; ^{1}H NMR (400MHz, DMSO): δ 8.92 (d, J=5.5Hz, 2H), 8.78 (t, J=7.8Hz, 1H), 8.18 (t, J=7.0Hz, 2H), 4.63 (t, J=7.4Hz, 2H), 4.18-2.54 (m, 2H), 3.17 (s, 1H), 3.18-2.54 (m, 2H), 2.55-2.45 (m, 1H), 1.99-1.49 (m, 2H), 1.29 (dq, J=14.7, 7.4 Hz, 4H), 0.96-0.25 (m, 3H); ^{13}C NMR (101MHz, DMSO): δ 173.38, 145.44, 144.81.

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