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Electrical Conductivity of Solutions of Ionic Liquids with Methanol, Ethanol, Acetonitrile, and Propylene Carbonate

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Ⓢ *Supporting Information*

ABSTRACT: A series of solutions composed of air- and water-stable hydrophobic ionic liquids (ILs) [Etpy][Tf_2N], [Bupy][Tf_2N], [Pepy][Tf_2N], [EtM_4py][Tf_2N], and [BuM_4py][Tf_2N] were prepared. The electrical conductivity of the solutions was investigated at T = 298.15 K, respectively. Then the electrical conductivity of solutions of [Bupy][Tf_2N] and [Hepy][Tf_2N] in acetonitrile/propylene carbonate were investigated at temperature range from (283.15 to 313.15) K. The correlation of concentration and electrical conductivity was fitted according to the empirical Casteel−Amis (CA) equation. The maximum electrical conductivity was extrapolated by the fitted result. The influence of the successive methylene ($-CH_2-$) group and the organic solvent to the electrical conductivity was discussed. The temperature dependence of the electrical conductivity of the solutions, ILs [Bupy][Tf_2N] and [Hepy][Tf_2N] in acetonitrile/propylene carbonate, was fitted by the empirical Vogel−Fulcher−Tamman (VFT) equation at a volume ratio of 50 %.

INTRODUCTION

Ionic liquids (ILs) are organic salts that exhibit outstanding physicochemical properties like low melting temperature, good solvation, negligible vapor pressure, high electrical conductivity, and high thermal stability. ILs have been paid more and more attention as green solvents from industrial and scientific communities.[1−4] However, ILs have a significant disavantage due to their high viscosities compared to traditional organic solvents.[5] Therefore, the use of the pure ILs is still limited to applications which are independent of the viscosity of the used solvent. To increase the potential application of ILs in industry and academia, it is essential that the physicochemical properties of the binary mixtures be studied in more detail. Recently, more and more data about physicochemical properties of binary mixtures have been published.[6−12]

In this regard the anion bis(trifluoromethylsulfonyl)imide [Tf_2N]$^-$, an anion mostly used to create hydrophobic ILs, has attracted increased attention in some fields.[13−16] ILs with the [Tf_2N]$^-$ anion were investigated intensively due to their relativity low viscosity, wide electrochemical stable window, and high conductivity, which makes them suitable candidates for electrochemical devices.[17−23] Although the electrical conductivity of this type of ILs is high, it is still lower than traditional organic electrolytes that are currently used in electrochemical devices.[24] Therefore, more physicochemical property data of their solutions with organic solvents are required.

To gain further understanding and extend the range of applications of [NTf_2]$^-$ anion-based ILs, the concentration dependence of the electrical conductivity of *N*-alkylpyridinium bis(trifluoromethylsulfonyl)imide ([Rpy], R = ethyl (Et), butyl (Bu), pentyl (Pe)) and *N*-alkyl-4-methylpyridinium bis(trifluoromethylsulfonyl)imide ([RM_4py], R = ethyl (Et), butyl (Bu)) with methanol and ethanol was studied at 298.15 K. The temperature dependence and concentration dependence on electrical conductivity of *N*-alkylpyridinium bis(trifluoromethylsulfonyl)imide ([Rpy], R = butyl (Bu), hexyl (He)) with acetonitrile (AN) and propylene carbonate (PC) were also discussed.

EXPERIMENTAL SECTION

Chemicals. The ILs *N*-alkylpyridinium bis(trifluoromethylsulfonyl)imide ([Rpy], R = ethyl (Et), butyl (Bu), pentyl (Pe), hexyl (He)) and *N*-alkyl-4-methylpyridinium bis(trifluoromethylsulfonyl)imide ([RM_4py], *R* = ethyl (Et), butyl (Bu)) were synthesized according to the literature.[25] Their structure was determined by ^{1}H NMR and ^{13}C NMR. No impurities could be found by NMR. The remaining Br content, tested by $AgNO_3$/HNO_3 solution, was below the detection limit of approximately 50 ppm. The prepared ILs were further dried for 24 h at 353.15 K under high vacuum before being used. Since trace water still exists in the ILs after drying by common methods, the presence of water becomes the most problematic impurity and needs to be confirmed before measurement. The mass fractions of remaining water were determined by three measurements with a Cou-Lo

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Aquamax Karl Fischer moisture meter. The average water mass fraction in the ILs was found to be less than 0.02 %. The final purity of the ILs was estimated to be better than 99 % in mass. Methanol (≥ 99.9 %) purchased from J&K Chemica Co., ethanol (≥ 99.8 %) purchased from Tianjin Tianli Chemical Reagent Co., acetonitrile (99.9 %) purchased from Sigma-Aldrich Co., and propylene carbonate (99.5 %) purchased from Aladdin Co. were stored over freshly activated molecular sieves of type 4 Å until being used for the experiments.

Electrical Conductivity. The electrical conductivity of the solution was measured by a MP522 conductivity instrument with the cell constants of 1 cm^{-1} (the cell was calibrated with the aqueous KCl solution) under high purity argon gas at the different temperatures. Each sample was placed in a cell with a jacket for measurement. The temperature was controlled by a thermostat with an uncertainty of ± 0.05 K. The attaining thermal equilibrium time was 30 min. The results are listed in Tables S1 to S7 of the Supporting Information. The uncertainties of the experimental values were estimated to be ± 1 %. All measurements were carried out in the entire mole fraction range from $x_{\mathrm{IL}} = 0$ to 1.

RESULTS AND DISCUSSION

As shown in Tables S1 to S7 of the Supporting Information, the data of the electrical conductivity of the investigated solution covered the entire concentration. The solution exhibit a substantially higher electrical conductivity than the pure ILs. The electrical conductivity of the pure IL $[\mathrm{Bupy}][\mathrm{Tf_2N}]$ was compared with literature,[26,27] and the values are listed in Table 1.

Table 1. Comparison of the Electrical Conductivity of the Pure IL $[\mathrm{Bupy}][\mathrm{Tf_2N}]$ Resulting from This Investigation with Selected Literature Data

T/K	313.15	303.15	298.15	293.15	283.15
k/ $\mathrm{mS \cdot cm^{-1}}$	5.41[a]	3.78[a]	3.07[a]	2.46[a]	1.50[a]
	5.8[b]	4.0[b]	3.3[b]	2.6[b]	1.6[b]
			3.245[c]		

[a] This work. [b] Reference 26. [c] Reference 27. The deviations of this work values with ref 26 are less than 7.5 %.

To describe the relationship of the electrical conductivity with concentration, the empirical Castell–Amis equation was used.[28,29] The empirical equation is:

$$k = k_{\max}\left(\frac{x}{x_{\max}}\right)^{a} \exp\left[b(x - x_{\max})^{2} - \frac{a}{x_{\max}}(x - x_{\max})\right] \qquad (1)$$

where $k_{\max}$ is the maximum value of the electrical conductivity at the mole fraction scale $x_{\max}$. a and b are the empirical parameters. The fitted values, $k_{\max}$, $x_{\max}$, a, and b, and the standard deviation, s, are listed in Tables 2, 3, and 4. From the standard deviation, the four-parameter empirical equation shows excellent agreement with the experimental results of the IL solutions.

At 298.15 K, the concentration dependence on experimental values, calculated values and deviations of ILs with methanol or ethanol are presented in Figures 1 to 4. The concentration dependence on experimental values of ILs with AN or PC at the different temperatures are presented in Figures 5 to 8.

From Figures 1 to 8, the curves can be divided into two parts separated by the maximum of the graph. The increasing and decreasing parts depended on the added amount of the ILs. The electrical conductivity increased with the increase of the IL concentration at low IL concentrations. However, the incremental electrical conductivity did not follow the anticipated linear behavior. The increasing rate of the electrical conductivity slowly followed the concentration increase of the ILs until the maximum values appeared. There are two aspects leading to the results: (1) the mobility of the charge carriers was reduced with increasing viscosity; (2) the number of the charge carriers was reduced due to the aggregate formation. The aggregation formation becomes the dominant factor for the change of the increasing conductivity.[30−32] Hence, the curve of the low concentration region of the ILs indicated the aggregation formation. At the high concentration region of the ILs, the electrical conductivity decreased with the increasing IL concentration. The electrical conductivity has a relationship with ion mobility and number of charge carriers:[33,34]

$$k = \sum n_i q_i \mu_i \qquad (2)$$

Table 2. Fitted Values of the Empirical Parameters, $k_{\max}$, $x_{\max}$, a, b, and s, According to the Empirical Casteel–Amis Equation at 298.15 K

	$k_{\max}$				s
	$\mathrm{mS \cdot cm^{-1}}$	$x_{\max}$	a	b	$\mathrm{mS \cdot cm^{-1}}$
$[\mathrm{Etpy}][\mathrm{Tf_2N}]$ + methanol	32.0	0.1352	0.666	1.797	0.58
$[\mathrm{Bupy}][\mathrm{Tf_2N}]$ + methanol	24.1	0.1153	0.680	2.255	0.65
$[\mathrm{Pepy}][\mathrm{Tf_2N}]$ + methanol	21.4	0.1027	0.671	2.630	0.59
$[\mathrm{EtM_4py}][\mathrm{Tf_2N}]$ + methanol	33.1	0.1454	0.692	1.827	0.70
$[\mathrm{BuM_4py}][\mathrm{Tf_2N}]$ + methanol	23.3	0.1146	0.653	2.225	0.70
$[\mathrm{Etpy}][\mathrm{Tf_2N}]$ + ethanol	17.35	0.2559	0.816	0.458	0.07
$[\mathrm{Bupy}][\mathrm{Tf_2N}]$ + ethanol	11.97	0.2011	0.800	0.872	0.12
$[\mathrm{Pepy}][\mathrm{Tf_2N}]$ + ethanol	10.16	0.1782	0.770	1.036	0.11
$[\mathrm{EtM_4py}][\mathrm{Tf_2N}]$ + ethanol	18.97	0.2625	0.895	0.782	0.11
$[\mathrm{BM_4py}][\mathrm{Tf_2N}]$ + ethanol	12.48	0.2019	0.848	1.098	0.12
$[\mathrm{Bupy}][\mathrm{Tf_2N}]$ + AN	40.12	0.0747	0.447	2.133	0.35
$[\mathrm{Bupy}][\mathrm{Tf_2N}]$ + PC	10.26	0.1733	0.775	1.679	0.09
$[\mathrm{Hepy}][\mathrm{Tf_2N}]$ + AN	33.99	0.0611	0.411	2.452	0.64
$[\mathrm{Hepy}][\mathrm{Tf_2N}]$ + PC	8.45	0.1447	0.815	2.217	0.10

Table 3. Fitted Values of the Empirical Parameters, k_{max}, x_{max}, a, b, and s, of [Bupy][Tf_2N] in Acetonitrile or Propylene Carbonate According to the Empirical Casteel−Amis Equation from (283.15 to 313.15) K

T	k_{max}				s
K	$mS \cdot cm^{-1}$	x_{max}	a	b	$mS \cdot cm^{-1}$
		[Bupy][Tf_2N] + AN			
313.15	46.4	0.0819	0.434	1.953	0.41
303.15	42.4	0.0767	0.439	2.066	0.38
298.15	40.1	0.0747	0.447	2.133	0.35
293.15	38.1	0.0720	0.446	2.144	0.34
283.15	34.1	0.0682	0.471	2.397	0.30
		[Bupy][Tf_2N] + PC			
313.15	14.12	0.1933	0.768	1.533	0.13
303.15	11.53	0.1803	0.774	1.628	0.10
298.15	10.26	0.1733	0.775	1.679	0.09
293.15	9.11	0.1667	0.776	1.726	0.08
283.15	7.01	0.1527	0.792	1.928	0.06

Table 4. Fitted Values of the Empirical Parameters, k_{max}, x_{max}, a, b, and s, of [Hepy][Tf_2N] in Acetonitrile or Propylene Carbonate According to the Empirical Casteel−Amis Equation from 283.15 to 313.15 K

T	k_{max}				s
K	$mS \cdot cm^{-1}$	x_{max}	a	b	$mS \cdot cm^{-1}$
		[Hepy][Tf_2N] + AN			
313.15	39.3	0.0699	0.422	2.269	0.62
303.15	35.8	0.0646	0.420	2.398	0.61
298.15	34.0	0.0611	0.411	2.452	0.64
293.15	32.3	0.0585	0.410	2.525	0.61
283.15	28.9	0.0543	0.420	2.753	0.52
		[Hepy][Tf_2N] + PC			
313.15	11.72	0.1602	0.811	2.061	0.14
303.15	9.51	0.1503	0.812	2.136	0.11
298.15	8.45	0.1447	0.815	2.217	0.10
293.15	7.51	0.1390	0.819	2.323	0.08
283.15	5.73	0.1282	0.818	2.460	0.06

where n_i is the number of charge carriers of species i, q_i is the charge, and μ_i is the ion mobility. It can be explained that decrease of the organic solvents enhanced the interaction force among ions and weakened the movement of ions.

From Figures 1 to 4, the electrical conductivity decreases with the extension of the alkyl side chain of the cation over the entire concentration for the same organic solvent in this work: [Etpy][Tf_2N] > [Bupy][Tf_2N] > [Pepy][Tf_2N]; [EtM_4py][Tf_2N] > [BuM_4py][Tf_2N]. It indicated that the ion mobility decreases with the increase of the alkyl side chain at the same concentration. From Figures 5 to 8, the electrical conductivity increases with the temperature increase. It indicated that the increase in temperature leads to an increase in the ion mobility.

From Table 2, the maximum values appeared in the range of the mole fractions from 0.06 to 0.27 for these solution at 298.15 K.

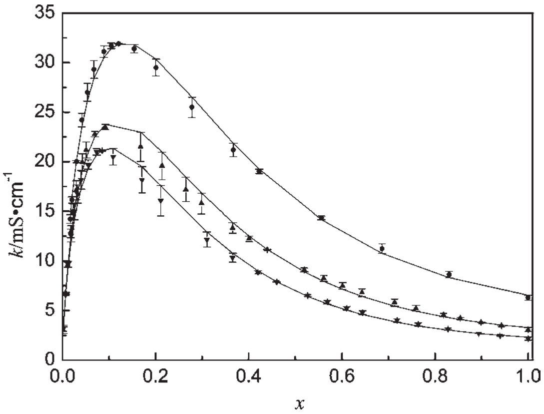

Figure 1. Concentration dependence on the electrical conductivity of IL [Rpy][Tf_2N] in methanol at 298.15 K. [Etpy][Tf_2N]: ●, exptl; —, calcd. [Bupy][Tf_2N]: ▲, exptl; —, calcd. [Pepy][Tf_2N]: ▼, exptl; —, calcd.

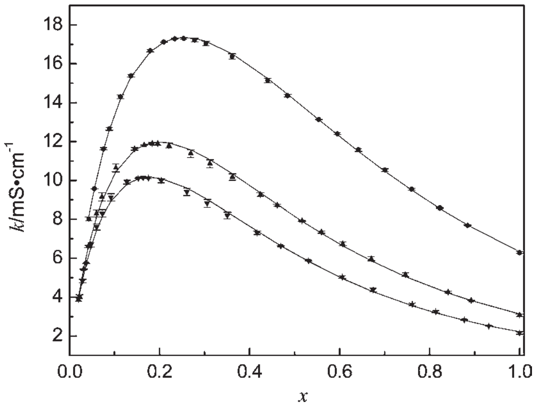

Figure 2. Concentration dependence on the electrical conductivity of IL [Rpy][Tf_2N] in ethanol at 298.15 K. [Etpy][Tf_2N]: ●, exptl; —, calcd. [Bupy][Tf_2N]: ▲, exptl; —, calcd. [Pepy][Tf_2N]: ▼, exptl; —, calcd.

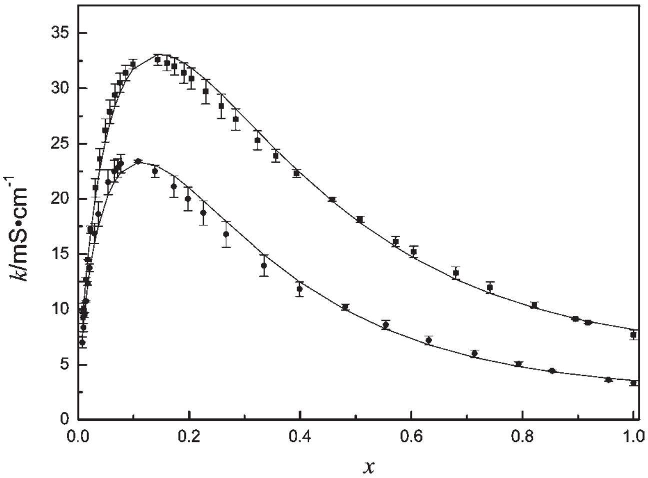

Figure 3. Concentration dependence on the electrical conductivity of IL [RM_4py][Tf_2N] in methanol at 298.15 K. [EtM_4py][Tf_2N]: ■, exptl; —, calcd. [BuM_4py][Tf_2N]: ●, exptl; —, calcd.

The fitted maximum value orders for the same ILs are: methanol > ethanol; AN > PC; AN > methanol > ethanol > PC from Table 2. For the pure ILs, the electrical conductivity increases with the

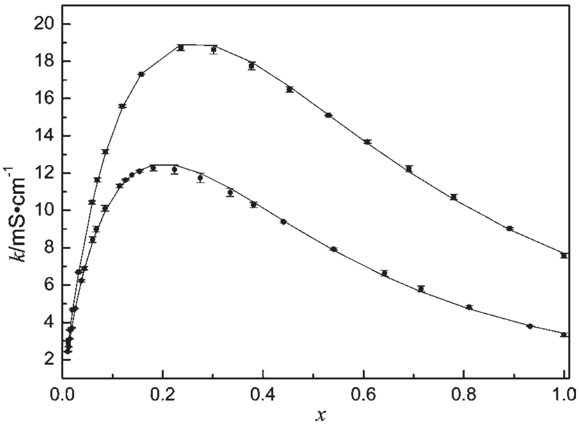

Figure 4. Concentration dependence on the electrical conductivity of IL [RM$_4$py][Tf$_2$N] in ethanol at 298.15 K. [EtM$_4$py][Tf$_2$N]: ■, exptl; —, calcd. [BuM$_4$py][Tf$_2$N]: ●, exptl; —, calcd.

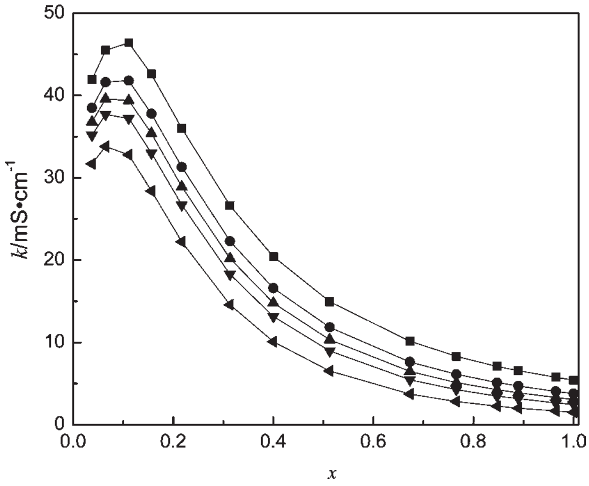

Figure 5. Concentration dependence on the electrical conductivity of IL [Bupy][Tf$_2$N] in AN from (283.15 to 313.15) K. ■, 313.15 K; ●, 303.15 K; ▲, 298.15 K; ▼, 293.15 K; ◀, 283.15 K.

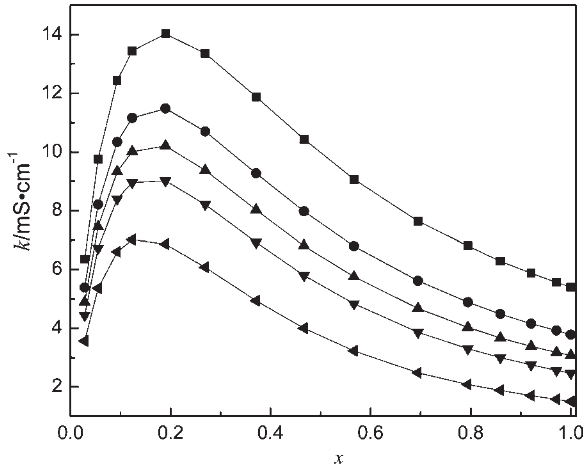

Figure 6. Concentration dependence on the electrical conductivity of IL [Bupy][Tf$_2$N] in PC from (283.15 to 313.15) K. ■, 313.15 K; ●, 303.15 K; ▲, 298.15 K; ▼, 293.15 K; ◀, 283.15 K.

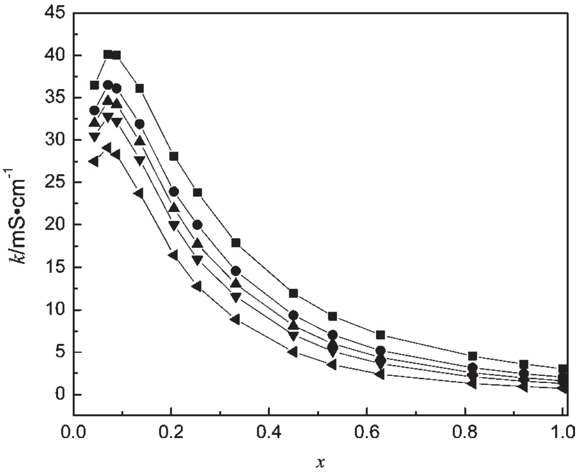

Figure 7. Concentration dependence on the electrical conductivity of IL [Hepy][Tf$_2$N] in AN from (283.15 to 313.15) K. ■, 313.15 K; ●, 303.15 K; ▲, 298.15 K; ▼, 293.15 K; ◀, 283.15 K.

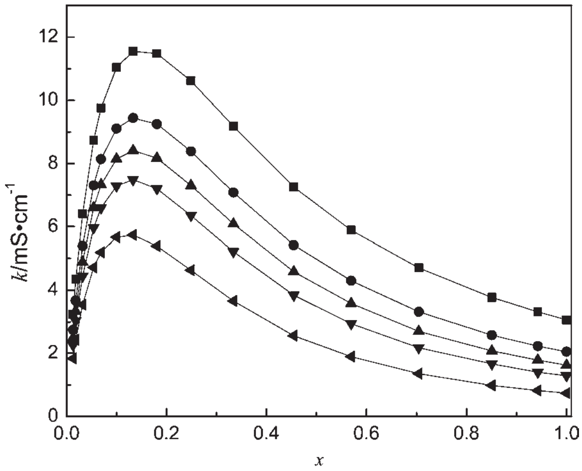

Figure 8. Concentration dependence on the electrical conductivity of IL [Hepy][Tf$_2$N] in PC from (283.15 to 313.15) K. ■, 313.15 K; ◀, 303.15 K; ●, 298.15 K;▲, 293.15 K; ▼, 283.15 K.

Table 5. Fitted Values of the Empirical Parameters, k_0, B, and T_0, of [Rpy][Tf$_2$N] (R = Butyl (Bu), Hexyl (He)) in Acetonitrile or Propylene Carbonate According to the VFT Equation

		k_0		T_0	
	x	S·cm^{-1}	B	K	R
[Bupy][Tf$_2$N] + AN	0.1566	0.37	405.8	149.5	0.99998
[Hepy][Tf$_2$N] + AN	0.1355	0.32	408.4	146.2	0.99997
[Bupy][Tf$_2$N] + PC	0.2690	0.32	474.9	110.1	0.9999
[Hepy][Tf$_2$N] + PC	0.2489	0.35	547.2	116.4	0.9999

cation change from [Rpy]$^+$ to [RM$_4$py]$^+$. For the solution, most of the fitted maximum values increase with the cation change from [Rpy]$^+$ to [RM$_4$py]$^+$ except for [BuM$_4$py][Tf$_2$N] + methanol < [Bupy][Tf$_2$N] + methanol from Table 2. The result of the wrong order cannot be simply for any reason. The maximum value order for the isomer is: [BuM_4py][Tf_2N] > [Pepy][Tf_2N]. From the above results, it is a effective method that introduces a methyl group into the contraposition of the pyridinium ring for increasing the electrical conductivity.

Recently, Guerfi et al.[35] performed an experiment on the flammability and electrical conductivity test. We look at the nonflammability and the high electrical conductivity when the volume ratio of IL 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide to solvent is in the range of 3:2 to 2:3. Herein, the temperature dependence on electrical conductivity of ILs with AN or PC was discussed by the Vogel−Fulcher−Tamman (VFT) equation at a volume about 50 % of the ILs. The VFT equation is as follows:[36]

$$k = k_0 \exp(-B/(T - T_0)) \tag{3}$$

where k_0, B, and T_0 are the empirical constants. The best fit values of k_0, B, T_0, and the correlation coefficient, R, are listed in Table 5. From Table 5, we see that the R are 0.9999 or better. It indicated that the VFT equation is excellent for this solution.

■ CONCLUSIONS

The concentration dependence on the electrical conductivity of air- and water-stable hydrophobic ILs [Etpy][Tf_2N], [Bupy][Tf_2N], [Pepy][Tf_2N], [EtM_4py][Tf_2N], and [BuM_4py][Tf_2N] with methanol and ethanol was studied at T = 298.15 K. The concentration dependence on the electrical conductivity of ILs [Bupy][Tf_2N] and [Hepy][Tf_2N] with AN or PC was studied in the range of (283.15 to 313.15) K. The values were fitted according to the empirical Casteel−Amis (CA) equation. The fitted maximum value orders for the same ILs are: methanol > ethanol; AN > PC; AN > methanol > ethanol > PC in this work. The values of the electrical conductivity decrease with the extension of the alkyl side chain of the cation over the entire concentration for the same organic solvent in this work. For the pure ILs, it is a effective method to introduce a methyl group on the pyridinium ring to increase the electrical conductivity

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Experimental values of electrical conductivity, k, corresponding to molar concentration, x, of the studied systems (Tables S1 to S7). This material is available free of charge via the Internet at http://pubs.acs.org.

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