



The Conductivity of EmimCl and BmimPF₆ Ionic Liquids for Limited Range of Temperature (25 to 75 °C) Under Optimal Electrolyte Combination Conditions

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Abstract

The purpose of this study was to evaluate the ionic conductivity as a function of temperature, range (25 to 75°C) in the imidazolium-based ionic liquids 1-ethyl-3-methylimidazolium chloride (EmimCl) and 1-butyl-3-methyl imidazolium hexafluorophosphate (BmimPF₆) of different volume percentages under optimal electrolyte combination conditions. The findings revealed that when 1% EmimCl or 1% BmimPF₆ was applied, conductivity decreased significantly in relation to the Kohlrausch relationship. When 1% EmimCl or 2% BmimPF₆ was added, the study showed the highest coefficient of alpha (α), while beta (β) was the lowest coefficient for temperature. In conclusion, the influence of the change in volume percentage on the conductivity is weakened by temperature control.

Keywords: EmimCl, BmimPF₆, Conductivity, Temperature coefficient.

Introduction

Room temperature ionic liquids (RTILs) that can be abbreviated as ionic liquids (ILs) present at low temperatures. ILs is one of the green solvent systems following water and supercritical carbon dioxide [1].

Compared to the commonly used conventional solvents, ILs exhibit unique physicochemical properties and their unique functions [2]. Usually, the ILs consist of organic cations and inorganic or organic anions, which possess the desirable characteristics of a wide range of liquid temperatures, thermal stability, low vapor pressure and no volatilization, reusable, high conductivity, preferably chemical stability and large electrochemical windows, etc. [3-5]. ILs

are thus considered to be an effective replacement for organic solvent in the reaction-separation coupling system [6].

Many ILs can be used as green solvents because they do not have the characteristics of volatilization [7]. The solubility of ILs is closely related to the properties of their cations and anions.

As a new type of green solvent, called ILs have been widely used in many fields and rapidly developed into a research and gain popularity. The application fields of ILs mainly include organic synthesis [8], catalytic reaction [9], electrochemical extension [10], extraction separation [11], biochemistry [12]

and material engineering [6]. But so far, there have been few studies on the deposition of metals by ILs as additives [13]. Some research shows that ILs considerably amend the properties like density, viscosity, polarity and conductivity by addition of polar solvents [14].

Conductivity results for a range of 1-alkyl-3-methylimidazolium tetrafluoroborates extending to significantly lower temperatures have been reported. The general picture given by reported studies is that the ionic mobilities which are primarily related to the values of electrical conductivity that are highly affected by the exact existence of the anion-cation interaction. The Coulombic interaction between the charges of the ions and the van der Waals interaction between the induced charges of the ions builds up this interaction. The precise essence of this interaction then relies on characteristics such as the composition of the ions, their polarizability and the hydrogen bonding possibilities [15].

When choosing an ILs for an electrochemical application, conductivity (k) is of vital importance. One impediment to the use of ILs is the lack of accurate data for conductivity. Few or no data has been released for many ILs. An example of such a case is 1-ethyl-3-methylimidazolium chloride, abbreviated herein as [Emim Cl] for which the only available data are ($25^{\circ}\text{C} \pm 2$ to $45^{\circ}\text{C} \pm 2$) conductivity [16].

ILs are highly promising in pure form or either in mixtures with proton conductors as electrolytes in electrochemical devices [17]. Conductivity is used to describe the extent to which electrons move in a substance. The type of ions in the solution and the ion concentration of the solution all have an effect on the conductivity of the solution [18]. There has been a surge of significance on this topic and a considerable number of researches on

the physiochemical properties of IL like conductivity. Although, physiochemical properties are the apparent sign of infinitesimal stage of interactive features, therefore detail analysis of properties can present the extensive explanation about interactions with the variation in temperature in binary system [19].

Similarly, in ILs the conductivity is critical and if the IL has high conductivity and a high current density, the current efficiency will be high [5,20]. Studying the conductivity of ILs and their variations in a variety of different situations are critical to introducing ILs into the electrolyte to promote electrolysis [20]. In this paper, the conductivity of different volume percentages of ILs in solution was determined, and the law of variation was studied.

Materials and Methods

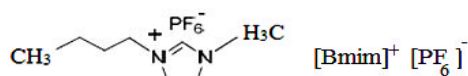
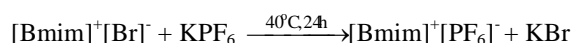
Reagent

1-(3-Aminopropyl) imidazole ($\geq 97\%$), purchased from Aldrich Chemicals; methyl isothiocyanate (97%); 1-ethylimidazole Chloride ($\geq 97\%$) and 1-butylimidazole (97%), purchased from Suiyuan Chemical Technology (Shanghai) Ltd; 1-bromooctane (99%), 1-bromohexane (99%), 1-bromobutane (99%), from Shanghai Civic Chemical Technology Co., Ltd; Acetonitrile (HPLC grade) from Labing Chemical; Carbon tetrachloride, purchased from Aladdin Chemical Company. Multi-parameter Conductivity instrument Model Multi 3320, purchased from Xylem Analytics Germany. Copper sulphate, Sodium chloride and Sulfuric acid was purchased from Aladdin Chemicals (Shanghai). 1-ethyl-3-methylimidazolium chloride (EmimCl) ionic liquid purchased from Aldrich Chemicals and 1-butyl-3-methyl imidazolium hexafluorophosphate (BmimPF₆) was synthesized.

Structure of Ionic Liquids

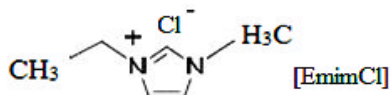
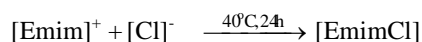
1-Butyl-3-methylimidazolium hexafluorophosphate, [BmimPF₆] was synthesized using previously published literature [21].

The chemical structure of butyl imidazolium ionic liquid is shown in scheme 1;



Scheme 1. 1-Butyl-3-methylimidazolium hexafluorophosphate ionic Liquid

The chemical structure of ethyl chloride ionic liquid is shown in scheme 2;



Scheme 2. 1-Ethyl-3-methylimidazolium chloride ionic Liquid

Physical Measurements

In the range of 25°C~75°C, used the German made Multi 3320 conductivity meter to measure the optimal conditions of the electrolyte ratio by respectively adding 0%, 1%, 2%, 3%, 4%, and 5% of EmimCl IL and the conductivity of the BmimPF₆ IL with mixed solution Fig. 1.

In the assessment, CuSO₄ concentration: 30 g/L; NaCl concentration: 40 g/L; H₂SO₄ concentration: 150 g/L of 12 parts, 10 mL each was prepared. 0%, 1%, 2%, 3%, 4%, and 5% of EmimCl and BmimPF₆ were added to each of 12 solutions.

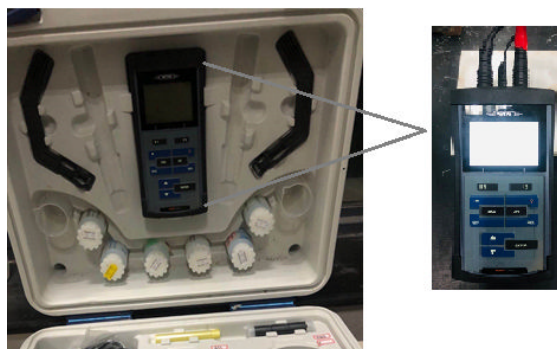


Figure 1. Multi instrument conductivity meter

The specific measurement process is as follows:

(1) Turned on the conductivity operation switch and preheated it for 30 min to slowly enter the steady-state and selected the best standard solution at a specific electrode constant.

(2) Connected the conductivity electrode and set the instrument temperature at 25°C. Rinsed the conductivity electrode with distilled water, immerse the conductivity electrode in a standard solution, and read the conductivity Ka. Calculated the electrode constant $J=K/K_a$ according to the standard solution conductivity.

(3) Performed electrode constant setting according to the electrode used and then washed the conductivity electrode with distilled water and then added the EmimCl and BmimPF₆ ions with volume percentages of 0%, 1%, 2%, 3%, 4%, and 5%, respectively under the optimum conditions of the electrolyte solution. The liquid (mixed solution) rinsed the conductivity electrode and then inserted it into the sample to be tested. Pressed the "TDS" button and waited for stable the readings on conductivity instrument screen. After the reading is stable then read the test display results.

(4) After the examination, the conductivity electrode is sufficiently cleaned and stored in distilled water.

Results and Discussion

Effect of Volume Percentage of EmimCl and BmimPF₆ on Conductivity

The relationship between the volume percentage of EmimCl and BmimPF₆ and the conductivity of the sample is shown in Fig. 2. The variation of conductivity of pure ILs at different temperatures is shown in Table 1 and also compared the data with previously published work.

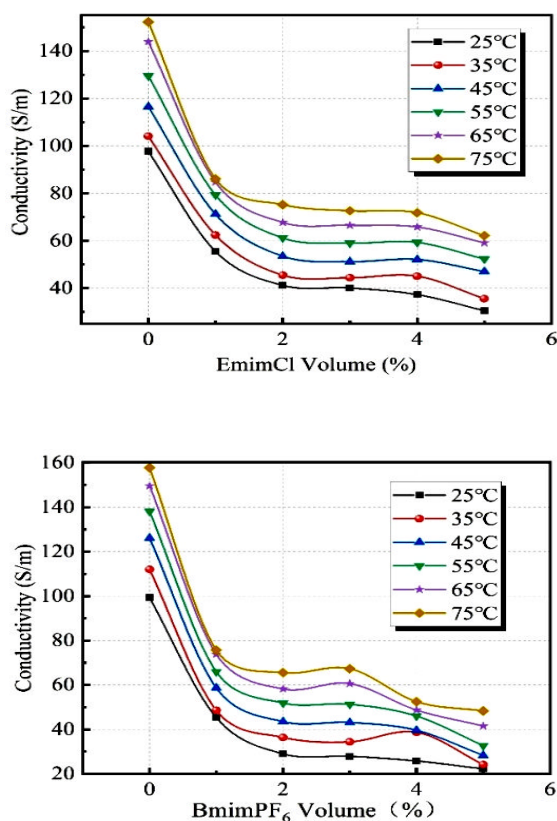


Figure 2. Relationship between volume fraction of EmimCl and BmimPF₆ conductivity of the solution

It can be seen from Fig. 2 that when the temperature was fixed, the conductivity decreases with the increase of the volume percentage of the IL. When the volume percentage was more than 1%, the change was

stable, which may be due to the conductivity of the solution. The conductivity of mixed solution attained and at the same time obtained high viscosity of IL. When the IL is added into the solution, the overall viscosity and density of the solution was swiftly increased and when increased the volume percentage of IL more than 1% then the conductivity stands weakened. At the same time its effect on the conductivity of the solution that was not obvious. The conductivity is related to the mobility of the load carriers, which can be explained by the higher viscosity caused by stronger van der Waals interactions between the longer alkyl chains and the larger cation size. In addition, the longer alkyl chain results in a greater volume fraction of the neutral hydrocarbon component of the organic cation.

It can be concluded from Table 1 that the conductivity of the two pure ILs differs significantly from the conductivity of the electrolyte used in the test. The conductivity of the two pure ILs was relatively low and the viscosity of EmimCl and BmimPF₆ was high. In the large group the anion was inactive and the transition speed was slow, which makes the conductivity of the whole mixed sample system significantly reduced.

Table 1. Conductivity of pure EmimCl and BmimPF₆ at different temperatures.

Ionic Liquids	Temperature	This Work	Literature	Reference
EmimCl	25°C	1.3	0.9	[16, 22]
	35°C	1.9	1.5	[16]
	45°C	2.4	2.46	[16]
	55°C	3.2	3.59	NA
	65°C	4.1	4.54	NA
	75°C	4.7	5.04	NA
BmimPF ₆	25°C	0.7	0.304	[23-26]
	35°C	0.8	0.518	[23-26]
	45°C	0.9	0.820	[23-25]
	55°C	1.3	1.222	[23, 25]
	65°C	1.4	1.735	[24, 25]
	75°C	1.5	1.102	[25]

NA=Not available

From previous studies (literature) it has been shown that the conductivity κ of the mixed solution confirms to the following formula:

$$\kappa = F \sum_j |z_j| u_j c_j \quad (1)$$

κ is the conductivity S/m; F is the Faraday constant usually 96.5 kC/mol; $|z_j|$ is the charge number; c_j is the molar concentration, mol/m³; u_j is the twist, m²/(s•V).

From equation (1) the conductivity of the mixed sample is the sum of the conductance of the individual components in the sample and is related to the concentration change and the twist. The twist was determined by the solution diffusion coefficient, such as the Einstein relation (2)

$$D_i = \frac{u_i RT}{z_i F} \quad (2)$$

Where: D_i is the diffusion coefficient which is affected by the u_i degree. Moreover, according to previous studies (literature) there was a corresponding linear relationship between the u_i degree u_i and the viscosity η and the u_i degree u_i decreases as the viscosity η increases and the specific relationship was as shown in the formula (3).

$$u_i = \frac{|z_i| e}{6\pi\eta r} \quad (3)$$

Where e is the electron charge 1.6022×10^{-19} C; u_i is the twist, m²/(s•V); η represents the viscosity of the medium; r represents the radius of the charged body m ; π is the pi. It is known from the formula (3) that u_i degree u_i is negatively correlated with the charged body radius r and the medium viscosity η . The conductivity of the mixed solution is the result of the interaction of the individual ions contained in the solution and the magnitude of the twist can affect the

conductivity. The twist was positively correlated with D_i . When D_i was large, the resistance of the ion motion was small and the twist becomes large which resulting in high conductivity. Since the cation group radius of EmimCl and BmimPF₆ is large, the diffusion coefficient of the solution was small resulting in a small degree of twist so that the conductivity of the entire solution was lowered. Among them BmimPF₆ has a larger ionic radius so its conductivity was smaller.

Effect of temperature on conductivity

The conductivity of the solution is easily affected by temperature. Therefore, in the test the law of conductivity changes with temperature under different ILs and different addition amounts was determined as shown in Fig. 3.

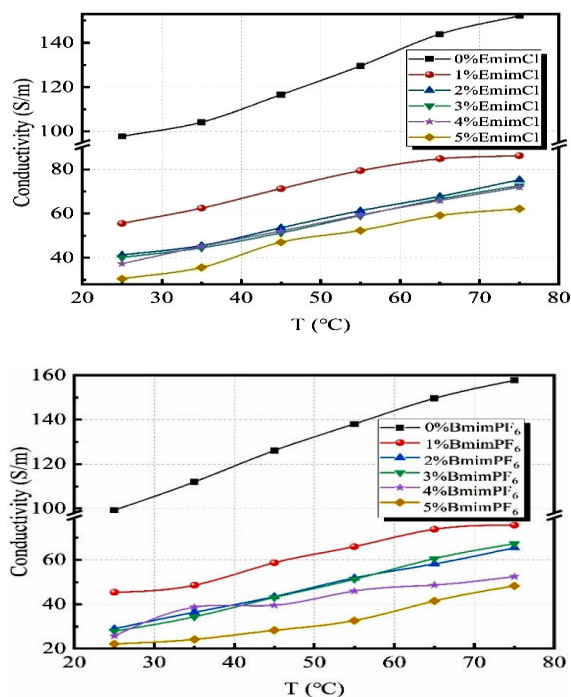


Figure 3. The influence of temperature on conductivity of electrolyte

Conductivity of Electrolyte

As seen in Fig. 3, the conductivity of the test sample was positively correlated with

temperature. This is because of ions in the solution increase with the temperature and the diffusion coefficient becomes more substantial. According to the equations (1) and (2) the viscosity of the solution was negatively correlated and the viscosity decreases causing the particles to accelerate migration and become active that was responsible for increasing the conductivity.

There are many factors that affect particle motion which can be divided into:

(1) Ion radius: The motion resistance in the solution was positively correlated with the ionic radius. The larger the radius becomes greater resistance. The positive ion radii of both ILs was large so the resistance of the solution was also increased.

(2) Ion valence state: the valence state was high; the electric field force was obvious and the movement speed was large.

(3) The concentration of a mixed solution: The concentration increases the spacing between the ions was reduced and the mutual influence between the ions becomes strong so that the movement was difficult.

(4) Temperature: Group was active by increasing the temperature increases and the reaction transition speeds up which resulting an increase in haste.

(5) Solution viscosity: positively correlated with motion resistance. When the viscosity enhanced then resistance increased and the swiftness slowed down.

For further study the data of the conductivity of the two different ILs with temperature in different additions the polynomial fitting of the results and explore the correlation can get Fig. 4.

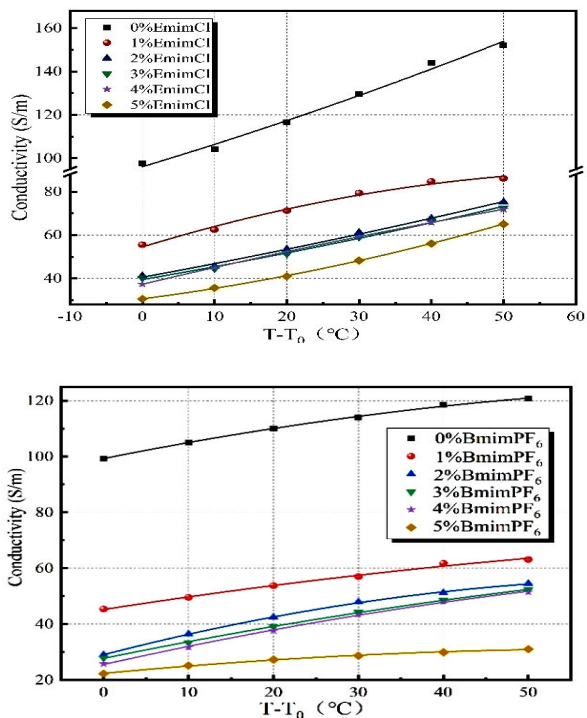


Figure 4. Regression relationship between temperature and conductivity of electrolyte

The data is shown in Table 2. According to the analysis of data the experimental data was in accordance with the *Kohlrausch* relationship:

Table 2. Correlation parameters of solution conductivity and temperature regression equation.

Type	Volume ratio%	Equation type	Intercept A	B ₁	B ₂
EmimCl	0	Y=A+B ₁ *X+B ₂ *X ²	96.10357	1.00061	0.00313
	1		54.46786	1.01839	-0.00734
	2		40.52857	0.60871	0.00179
	3		39.44857	0.57066	0.0021
	4		37.30714	0.78907	-0.00196
	5		30.56071	0.43104	0.0052
BmimPF ₆	0	99.27143	0.60814	-0.0035	
	1	45.23214	0.47132	-0.00209	
	2	29.03214	0.78961	-0.00566	
	3	27.72143	0.62407	-0.00261	
	4	25.53214	0.68261	-0.00316	
	5	22.35357	0.28696	-0.00234	

$$k = k_0 \left[1 + \alpha(t - t_0) + \beta(t - t_0)^2 \right] \quad (4)$$

Where: k_0 : the conductivity when $t=t_0$, S/m; α , β are temperature coefficients; t is temperature °C; $t_0=25^\circ\text{C}$. The calculated and α , β are listed in Table 3.

Table 3. Coefficient parameters of solution conductivity and temperature in Kohlrausch.

Types	Volume percentage	k_0 ($S \cdot m^{-1}$)	Temperature Coefficient (α)	Temperature Coefficient ($10^4\beta$)	Correlation coefficient r
Emim Cl	0%	96.10357	0.010411788	0.32569	0.9917
	1%	54.46786	0.018697081	-1.34758	0.9908
	2%	40.52857	0.015019281	0.441664	0.9967
	3%	39.44857	0.014465924	0.532339	0.9963
	4%	37.30714	0.017150643	-0.52537	0.9999
	5%	30.56071	0.014104384	1.701531	0.9998
Bmim PF ₆	0%	99.27143	0.006126032	-0.35257	0.9981
	1%	45.23214	0.010420024	-0.46206	0.9931
	2%	29.03214	0.027197788	-1.94956	0.9995
	3%	27.72143	0.022512186	-0.94151	0.9996
	4%	25.53214	0.026735323	-1.23766	0.9988
	5%	22.35357	0.012837323	-1.04681	0.9946

The temperature coefficients α and β was plotted on the ordinate and the volume percentages of EmimCl and BmimPF₆ was plotted on the abscissa as shown in Fig. 5 and 6.

As can be seen from the Fig. 5 the temperature coefficient α was the largest when the volume fraction of EmimCl in the solution was 1%. It indicates that the influence of temperature on the conductivity of the sample system was gradually weakened when the volume percentage of EmimCl exceeds 1%.

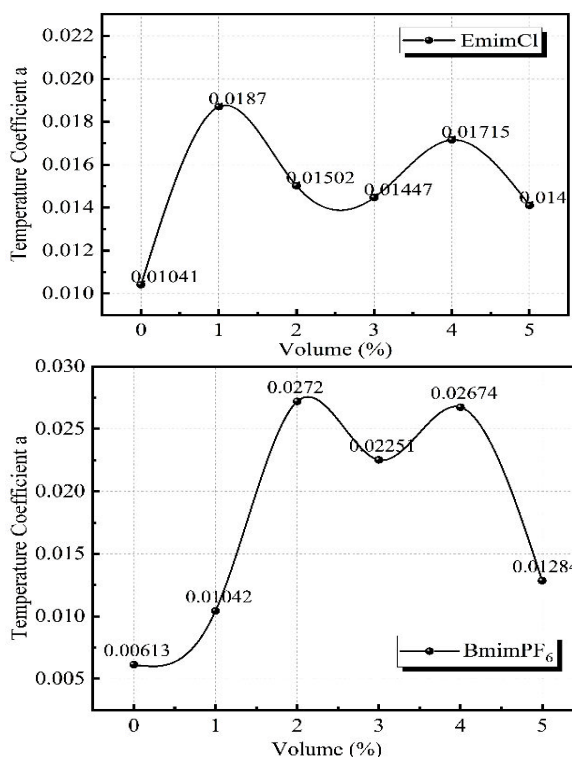


Figure 5. Relationship between EmimCl, BmimPF₆ volume percentage and temperature coefficient (α)

With the increase of BmimPF₆ volume percentage α reached at maximum when the volume fraction of BmimPF₆ was 2% in solution and the temperature coefficient α decreased with the change of BmimPF₆ volume percentage. It shows that the increase of the volume percentage of BmimPF₆ to 2% that effect the temperature which getting lower and the temperature coefficient α decreases with the volume percentage of BmimPF₆.

It can be concluded from Fig. 6 that when 1% EmimCl was added to the solution, the temperature coefficient β reaches the minimum peak and then the volume fraction of EmimCl changes. The temperature coefficient β does not fall below to the minimum peak because the effect of the coefficient β was relatively small.

Similarly, when the volume fraction of BmimPF₆ is 2% the temperature coefficient β

was the smallest and then with the change of the volume fraction of BmimPF₆ β increases gradually which shows the influence of β on relatively small content.

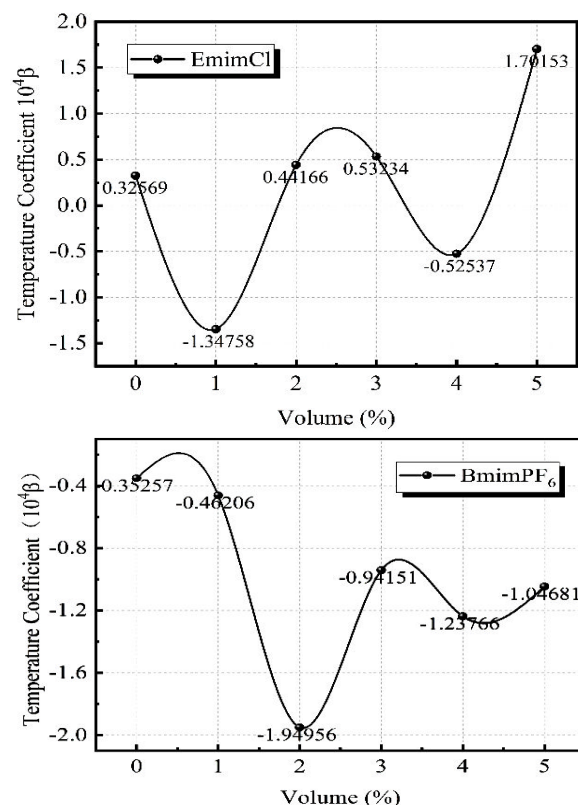


Figure 6. Relationship between EmimCl, BmimPF₆ volume percentage and temperature coefficient (β)

Conclusions

Through the experimental study on the conductivity of the best ILs and the optimal electrolyte system, it is revealed that the volume percentage of EmimCl and BmimPF₆ is inversely proportional to the conductivity of the test sample, and the conductivity is significantly reduced when 1% IL is added. Conductivity is positively correlated with temperature and is in accordance with Kohlrausch. When the volume fraction of EmimCl is 1% or when the content of BmimPF₆ is 2%, the temperature coefficient α is the largest, and β is the smallest. Therefore,

when more than 1% EmimCl or more than 2% BmimPF₆ is added, the effect of the change in IL content on the conductivity is weakened by temperature control.

Conflict of Interest

The authors declare that there is no conflict of interest regarding the publication of this article

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