

# Experimental and Modeling of Conductivity for Electrolyte Solution Systems

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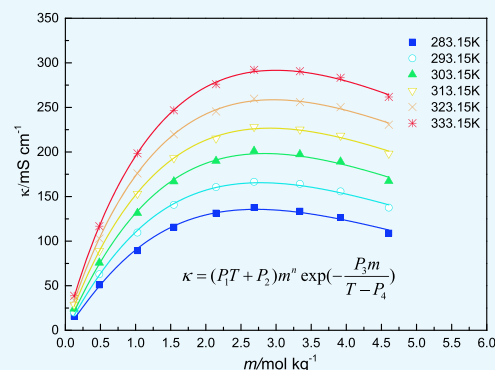
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**ABSTRACT:** Studying the concentration and temperature dependence of the conductivity of electrolyte solution is of great significance for the evaluation and improvement of the performance of the electrochemical system. In this paper, based on the influence of the number of free ions and ion mobility on the conductivity, a semiempirical conductivity model with five parameters was proposed to correlate the conductivity, concentration and temperature data of electrolyte solutions at medium and high concentrations. The conductivities of NaCl and CaCl<sub>2</sub> in propylene carbonate–H<sub>2</sub>O binary solvents were measured at temperatures varying from 283.15 to 333.15 K. The validity of the model was verified by the experimental data of this paper and the conductivity, concentration, and temperature data of 28 electrolyte solution systems in the literature. The electrolyte solutions investigated in this paper included binary organic solvent systems, pure organic solvent systems, and aqueous solution systems. The results showed that the proposed model can fit the experimental data well for both pure solvent and mixed solvents systems, which is of great value to practical engineering applications.



## 1. INTRODUCTION

The ionic conductivity of the electrolyte solution is known as a key parameter to evaluate the performance of the solution, and it has been widely used in the fields of electrochemistry, biochemistry, and environmental chemistry. When used in batteries,<sup>1</sup> supercapacitors,<sup>2</sup> electrodialysis,<sup>3</sup> and other electrochemical systems, the solvent composition of the electrolyte solution is usually fixed, and the conductivity of the solution changes with the change of the electrolyte concentration and temperature. Thus, studying the concentration and temperature dependence of electrolyte solution conductivity is of great significance to the evaluation and improvement of electrochemical system performance.<sup>4</sup>

The relationship between conductivity and the electrolyte concentration has been studied for a long time, and there exist a large number of theoretical and empirical models. The early Debye–Hückel–Onsager theory only considered the long-range electrostatic force between ions, and therefore, is only applicable to infinitely diluted solution systems.<sup>5</sup> On the basis of this theory, researchers continuously improved the model to expand its concentration range in applications. For example, using the Gurney sphere model, the Lee–Wheaton theory<sup>6,7</sup> extended the equation of conductivity to a concentration of 0.1 mol L<sup>-1</sup>. De Diego et al. adopted the concept of activity to deal with the deviation from ideality appearing at higher concentrations, and the equation fitted well for the 1:1 electrolyte aqueous solution system at a high concentration.<sup>8</sup> In the work of Chandra and Bagchi,<sup>9</sup> a theoretical formulation

was proposed based on a mode coupling theory to account for the dielectric friction during the movement of ions, which was verified by NaCl and KCl aqueous solution up to 1 mol L<sup>-1</sup>. Using the MSA (mean spherical approximation) transport theory as a basis, Bernard et al. extended the conductivity model to mixed solutions, which was further extended to weak electrolyte buffer solution systems, but the accuracy of the model depends on the selection of ion radius.<sup>10–12</sup> In recent years, Yim et al. proposed a semiempirical model based on the free volume theory, which gave a good fit over the whole concentration range.<sup>13,14</sup> Different from theoretical models, the undetermined parameters in an empirical model of the electrical conductivity can be obtained by fitting the experimental data, such as the equation developed by Villullas and Gonzalez,<sup>15</sup> polynomial models,<sup>16</sup> and the Casteel–Amis equation.<sup>17,18</sup> One of the most successful empirical models is the Casteel–Amis model, which contains four parameters and can well fit the experimental data of electrolyte solutions from infinite dilution to saturation.

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The temperature dependence of conductivity is often described by the Arrhenius equation<sup>19,20</sup> and the Vogel–Fulcher–Tammann (VFT) equation.<sup>21,22</sup> The former is widely used in aqueous solutions, while the latter can describe the temperature dependence more accurately for ionic liquids by introducing the concept of the glass transition temperature.<sup>23</sup>

For electrolyte solution systems at high concentrations, which are applied widely in practice, researchers have proposed a number of models  $\kappa = f(m, T)$  ( $\kappa$ , conductivity;  $m$ , electrolyte concentration;  $T$ , temperature). De Diego et al. modified the adjustable parameters in the Casteel–Amis equation by introducing the temperature and the conductivity in the reference state.<sup>24</sup> The modified empirical model is suitable for aqueous solution systems at high concentrations, but it is only applicable to pure solvent systems. See and White<sup>25</sup> used polynomials containing the temperature and concentration to correlate the conductivity of the KOH aqueous solution system at a high concentration and wide temperature range. The polynomial model can obtain good fitting results but lacks physical meaning, and it usually requires a large number of adjustable parameters to ensure the correlation accuracy.<sup>26</sup> Fu et al. proposed a seven-parameter quasi-Arrhenius model, which well fitted the conductivity of ionic liquids in mixed organic solvents systems, but the adoption of seven parameters increased the difficulty in solving the problem.<sup>27</sup>

In electrochemical systems, mixed solvents are commonly used to improve the performance of electrolyte solutions.<sup>28,29</sup> Although a large amount of conductivity experimental data has been reported, a model  $\kappa = f(m, T)$  for mixed solvents is still rare to be seen. Considering that propylene carbonate (PC) and H<sub>2</sub>O have good mutual solubility as polar solvents, and NaCl and CaCl<sub>2</sub> have high solubilities in PC–H<sub>2</sub>O mixed solvents, we choose NaCl–PC–H<sub>2</sub>O and CaCl<sub>2</sub>–PC–H<sub>2</sub>O systems to study the relationship between solution conductivity and the electrolyte concentration and temperature in a wide concentration range, the experimental data of which has not yet been reported. Based on the effects of the number of free ions and ion mobility on conductivity of electrolyte solution, we propose a general semiempirical model  $\kappa = f(m, T)$  with five parameters. Our experimental data of NaCl( $m$ )– $w$ PC–(1 –  $w$ )H<sub>2</sub>O and CaCl<sub>2</sub>( $m$ )– $w$ PC–(1 –  $w$ )H<sub>2</sub>O systems and data of 28 other systems from the literature are used to verify the accuracy of the developed model. The results show that our proposed model fits well with the ( $\kappa, m, T$ ) data in a wide concentration and temperature range.

## 2. MODEL DESCRIPTION

In dilute solutions, the conductivity of the electrolyte solution is the sum of the conductivities of the ions in the solution, which can be expressed by the following equation:<sup>20</sup>

$$\kappa = \sum n_i q_i \mu_i \quad (1)$$

where  $\kappa$  is conductivity,  $n_i$  is the number of ion  $i$ ,  $q_i$  is charge of ion  $i$ , and  $\mu_i$  is mobility of ion  $i$ .

It can be seen from eq 1 that the conductivity is affected by both the number of ions in the solution and the mobility of the ions. To further extend the applicability of the equation to medium and high concentrations, eq 1 needs to be revised considering the influence of the electrolyte concentration on the number of free ions and ion mobility, respectively.

In medium and high concentration solutions, the distance between anions and cations decreases, and nonconductive ion

pairs are formed by ion association, which leads to a decrease in the number of free ions participating in conduction. Specifically, this phenomenon is more obvious in mixed solvent systems.<sup>30,31</sup> Thus, the number of free ions as a function of the electrolyte concentration will deviate from the linear relationship.<sup>32</sup> The number of free ions  $n_i$  and ion concentration  $m$  can be described by the following equation:

$$n_i = am^n \quad (2)$$

where  $a$  and  $n$  are constants, and  $n$  is relevant to the species of the solvent.

Ion mobility is the average speed of ions per unit electric field strength and is the result of the combined actions of the external electric field force and ion movement resistance. Regarding the ion and its hydration layer as an entity, under the action of an external electric field, the resistance to its movement during directional migration includes ion–ion, ion–solvent, and solvent–solvent forces. The first force is a long-range interaction caused by electrostatic forces, and the latter two are short-range interactions. At low concentrations, long-range interactions dominate, and short-range interactions are usually ignored. As the electrolyte concentration in the solution increases, the distance between molecules decreases, and short-range interactions cannot be ignored, with the result that ion movement resistance increases rapidly.<sup>33</sup> Therefore, ion mobility usually decreases with the increase in the electrolyte concentration.

Based on a large amount of data of ion mobility in the literature, an empirical equation of ion mobility  $\mu_i$  and ionic strength  $I$  was proposed,<sup>34,35</sup> which is suitable for electrolyte solutions at a low concentration,  $I < 0.1 \text{ mol L}^{-1}$ .

$$\mu_i = \mu_{i0} \exp(-Cz_i^b T^c) \quad (3)$$

$$I = \frac{1}{2} \sum m_i z_i^2 \quad (4)$$

where  $\mu_{i0}$  is the mobility of ion  $i$  at infinite dilution;  $I$  is the ionic strength;  $m_i$  is the molar concentration of ion  $i$ ;  $z_i$  is the ionic valence of ion  $i$ ;  $C$ ,  $b$ ,  $c$  are constants; and  $c$  is 0.5 approximately.

To simplify eq 3 and extend it to electrolyte solutions at medium and high concentrations, we modify the expression of ion mobility  $\mu_i$  and electrolyte concentration  $m$  as

$$\mu_i = \mu_{i0} \exp(-Bm) \quad (5)$$

where  $B$  is constant.

Substituting eqs 2 and 5 into eq 1, the relationship between conductivity  $\kappa$  and concentration  $m$  can be described as follows:

$$\kappa = Am^n \exp(-Bm) \quad (6)$$

$$A = a\mu_0 \sum q_i \quad (7)$$

where  $A$  is constant.

Although eq 6 can reflect the influence of electrolyte concentration on conductivity, conductivity also changes with temperature. The degree of ion dissociation in the solution increases when the temperature increases, and the number of free ions increases. At the same time, the intermolecular force decreases with the increase in the temperature, which means that the resistance of ion movement decreases and the ion migration speed increases. To correlate the conductivity at

different temperatures, the following equations are used to describe the temperature dependence of  $A$  and  $B$ :

$$A = P_1T + P_2 \quad (8)$$

$$B = \frac{P_3}{T - P_4} \quad (9)$$

Substituting  $A$  and  $B$  in eq 4 with eqs 8 and 9, the relationship between conductivity and the temperature and electrolyte concentration are shown as eq 10:

$$\kappa = (P_1T + P_2)m^n \exp\left(-\frac{P_3m}{T - P_4}\right) \quad (10)$$

where  $P_1$ ,  $P_2$ ,  $P_3$ ,  $P_4$ , and  $n$  are constants, which are salt concentration and temperature independent but solvent-composition dependent.

Eq 10 contains five parameters, which can be obtained by fitting the ( $\kappa$ ,  $m$ ,  $T$ ) data. In the next section, the proposed model will be tested using experimental data and the data from the literature. The software tool *1stOpt* will be used to obtain the parameters based on the global optimization algorithm, with the goal of minimizing the sum of squared errors between the calculated value and the experimental data. The maximum number of iterations in the calculation is 1000, and the convergence condition is  $10^{-10}$ . The algorithm has the characteristic of initial value independence. Thus, in most cases, we can always obtain correct results starting from any random initial values.

### 3. EXPERIMENTAL SECTION

**3.1. Materials.** Anhydrous NaCl (purity,  $\geq 99.5\%$ ) was purchased from Sinopharm Chemical Reagent Co., Ltd. Anhydrous  $\text{CaCl}_2$  (purity,  $\geq 99.9\%$ ) were purchased from Aladdin Industries, Inc. NaCl and  $\text{CaCl}_2$  were dried for 24 h at 423 K before use. Propylene carbonate (PC) (purity,  $\geq 99.7\%$ ) was purchased from Aladdin Industries, Inc. and was used without any pretreatment. Distilled and deionized water (Watson Group Ltd., China) was used for the preparation of the solutions. See Table 1 for more details.

**Table 1. Material Description**

materials	CAS	source	purity (mass fraction)	analysis method
propylene carbonate	108-32-7	Aladdin Industries, Inc.	$\geq 99.7$	GC
NaCl	7647-14-5	Sinopharm Chemical Reagent Co., Ltd.	$\geq 99.5$	titration analysis
$\text{CaCl}_2$	233-140-8	Aladdin Industries, Inc.	$\geq 99.9$	titration analysis
distilled and deionized water		Watson Group, Ltd.		

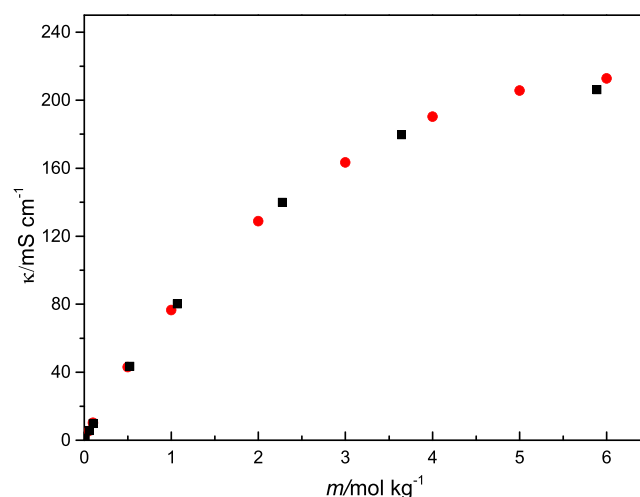
**3.2. Conductivity Measurements.** The treated NaCl/ $\text{CaCl}_2$  was added to a series of  $w\text{PC}-(1-w)\text{H}_2\text{O}$  aqueous solutions, which were prepared previously to obtain NaCl( $m$ )- $w\text{PC}-(1-w)\text{H}_2\text{O}$  and  $\text{CaCl}_2(m)$ - $w\text{PC}-(1-w)\text{H}_2\text{O}$  ternary mixed electrolyte solutions. The maximum electrolyte concentration studied in this paper was close to the solubility of the electrolyte in the mixed solvents at room temperature. Each component in the electrolytes was weighed by an

electronic balance (AL204, METTLER-TOOLEDO) with an accuracy of  $\pm 1 \times 10^{-4}$  g.

The electric conductivity measurements were carried out by a Chenhua electrochemical workstation (CHI660, CHEN-HUA) using an AC impedance method. The voltage amplitude was 10 mV, and the frequency ranged from 20 to 100 kHz.  $\kappa$  was calculated according to the  $Z''Z'$  curve. More details can be found in the reference.<sup>36</sup> The electrode in the cell was made of Pt. The temperature was controlled by a water thermostat (Polyscience) with an accuracy of  $\pm 0.01$  K. Before the measurement, the samples were kept at a constant temperature for 15 min. Each measurement was repeated three times, and average values were calculated. After the measurement of each group of samples, the cell was washed with absolute ethanol and pure water in sequence to remove contaminants. The cell constant was determined by calibration using an aqueous solution of 1 M KCl at 293 K before each sample measurement. The relative standard uncertainty for electrical conductivity was estimated to be 0.5%.

### 4. RESULTS AND DISCUSSION

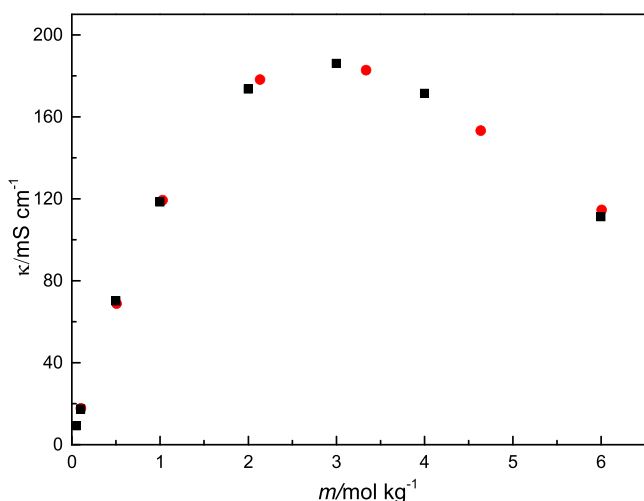
**4.1. Experimental Data.** The reliability of the measurement was verified by comparing the experimental data of NaCl- $\text{H}_2\text{O}$  and  $\text{CaCl}_2$ - $\text{H}_2\text{O}$  systems with the available literature data shown in Figures 1 and 2, respectively. In



**Figure 1.** Electrical conductivities of NaCl- $\text{H}_2\text{O}$  mixtures versus molality  $m$  at 293.15 K. The solid circle represents this work, and the solid box represents the work of Bešter-Rogač et al.<sup>30</sup>

Figure 1, the trend of our experimental data is consistent with that of the literature data. However, at  $5.89 \text{ mol kg}^{-1}$ , the fitting value of our experimental data is  $212.76 \text{ mS cm}^{-1}$ , which is 3.24% higher than that of literature data at  $206.18 \text{ mS cm}^{-1}$ . The deviation may be due to the preparation of solutions, electrode type, and so on, but it is within an acceptable range. In Figure 2, the conductivity of the solution first increases and then decreases with the increase in concentration, and there is a maximum value. The experimental data and the literature data are in good agreement.

The conductivity of NaCl in the PC- $\text{H}_2\text{O}$  mixed solvent at 283.15–328.15 K and the conductivity of  $\text{CaCl}_2$  in the PC- $\text{H}_2\text{O}$  mixed solvent at 283.15–333.15 K are plotted in Figures 3 and 4, respectively.



**Figure 2.** Electrical conductivities of  $\text{CaCl}_2\text{-H}_2\text{O}$  mixtures versus molality  $m$  at 293.15 K. The solid circle represents this work, and the solid box represents the work of Isono.<sup>37</sup>

At room temperature, the solubility of  $\text{NaCl}$  in the  $\text{PC-H}_2\text{O}$  mixed solvent decreases with the increase in  $\text{PC}$  concentration. Within the measurement range of this paper, the maximum  $\text{NaCl}$  solubility is about  $5.83 \text{ mol kg}^{-1}$  (see Figure 3a), and the minimum solubility is about  $1.31 \text{ mol kg}^{-1}$  (see Figure 3f).

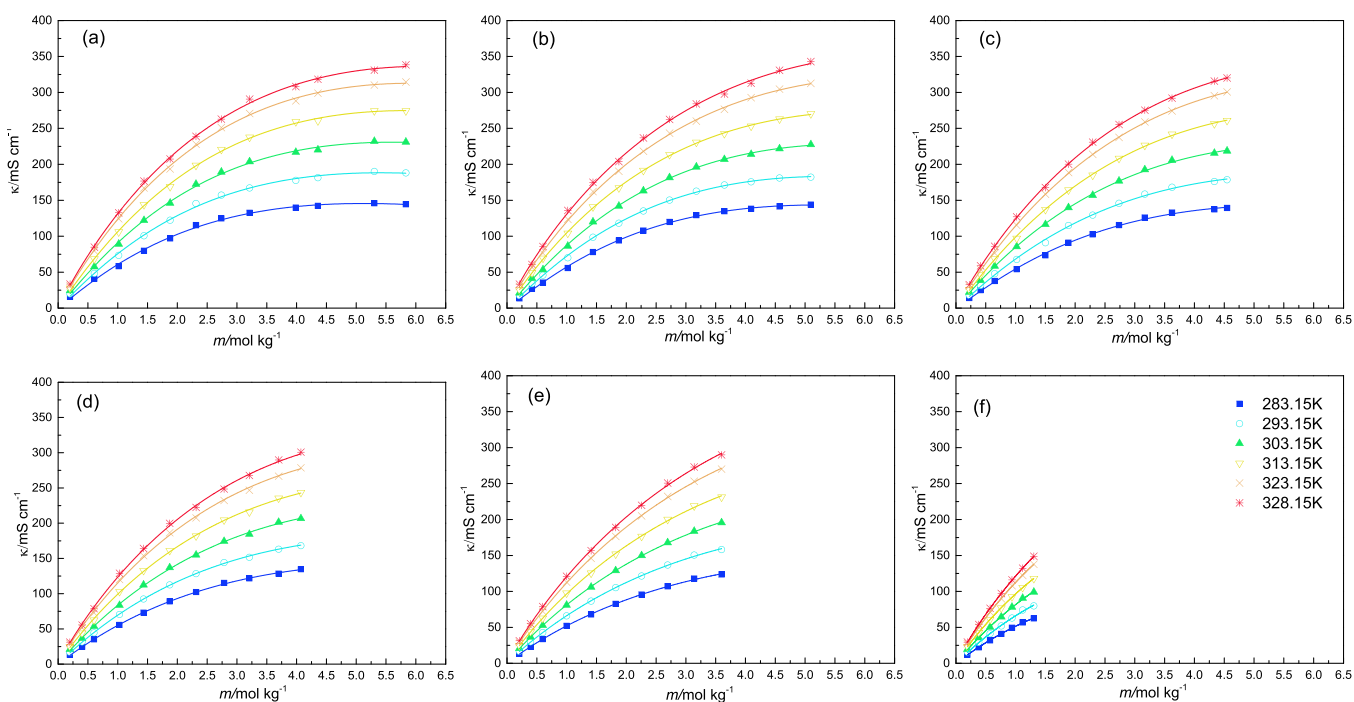
The conductivity of the  $\text{NaCl-PC-H}_2\text{O}$  system increases with the increase in the electrolyte concentration at the same temperature. It rises to a certain level, and then the trend tends to be gentle. The main reason is that as the electrolyte concentration increases, on the one hand, the distance between anions and cations in the solution decreases, as well as some anions and cations form nonconductive ion pairs, resulting in the decrease in the number of free ions participating in conduction; while on the other hand, the ion mobility

decreases with the increase in the electrolyte concentration, leading to a slow and gentle increase in the conductivity. This is consistent with the model description in this paper.

The conductivity of the solution increases with increasing temperature at the same salt concentration. In the area of low electrolyte concentration, the change of conductivity with temperature is not obvious. However, in the area of high electrolyte concentration, the conductivity changes significantly with temperature. This can be attributed to that when the concentration is high, the number of ion pairs is larger than that of the low concentration area, and the ion association weakens with increasing temperature, leading to the increase in the number of free ions. Thus, the conductivity of the high concentration area is more sensitive to temperature.

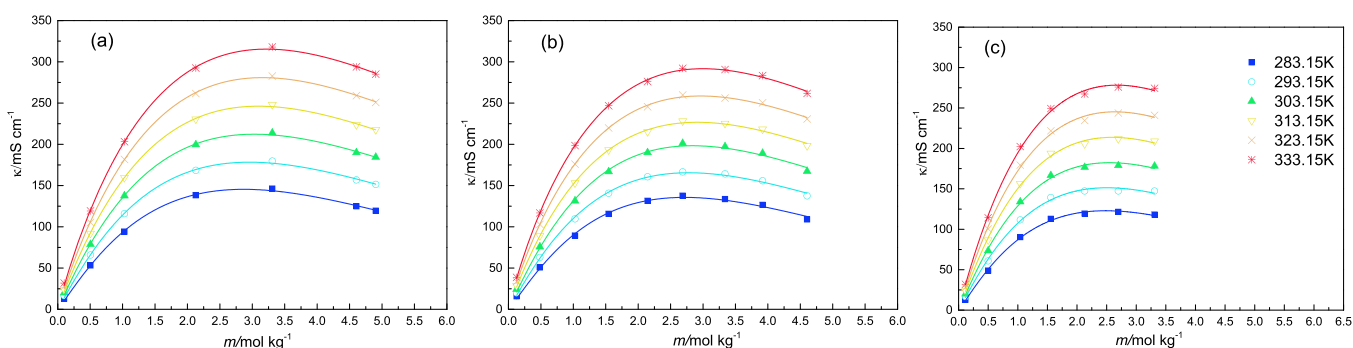
As can be seen from Figure 3a–f, at the same electrolyte concentration, the conductivity of the solution decreases with the increase in the  $\text{PC}$  concentration in the mixed solvent. This phenomenon is similar to the  $\text{NaCl-1,4-dioxane-H}_2\text{O}$  system reported by Bešter-Rogač et al.<sup>30</sup> This can be attributed to the decreasing dielectric constant of the solvent with the increase in the  $\text{PC}$  concentration. When the dielectric constant is low, it is easier to produce ionic association, leading to a decrease in electrical conductivity.

Figure 4 illustrates that the conductivity of the  $\text{CaCl}_2\text{-PC-H}_2\text{O}$  system exhibits a parabolic-like trend that increases first and then decreases as the electrolyte concentration increases, and the curve has a maximum value. This phenomenon is different from the trend of the conductivity change with the electrolyte concentration in the  $\text{NaCl-PC-H}_2\text{O}$  system. The possible reason is that  $\text{Ca}^{2+}$  is a divalent ion, which undergoes greater electrostatic forces and short-range interactions during ion migration under the action of an external electric field compared with monovalent  $\text{Na}^+$ . As a result, a rapid decrease in its mobility can be observed in the high electrolyte concentration region, and the maximum value appears. In

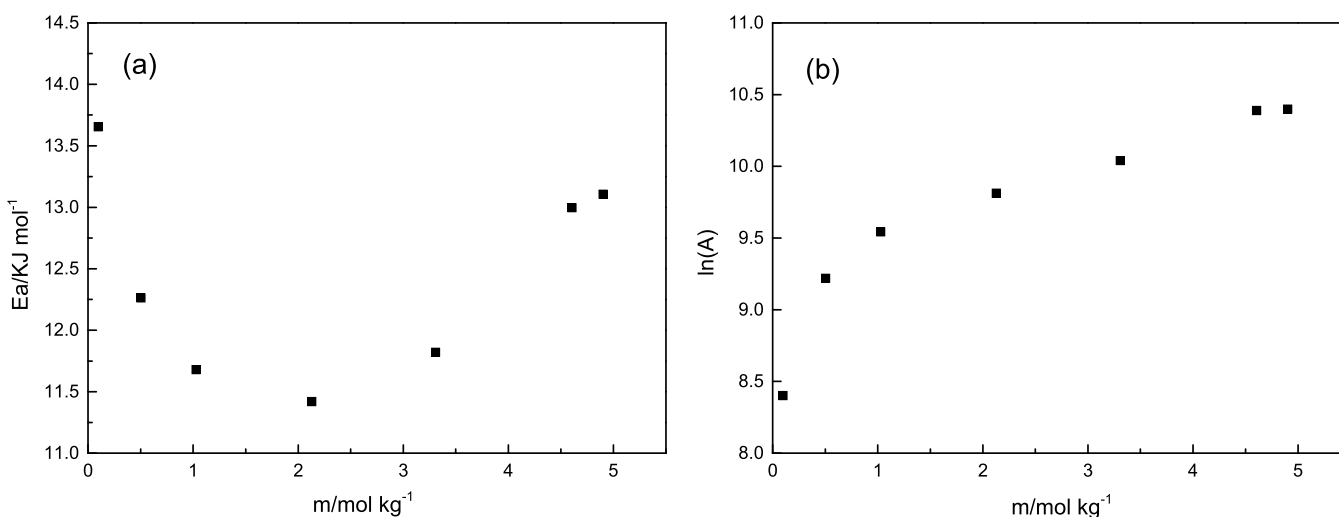


**Figure 3.** Change of conductivity  $\kappa$  with salt molality  $m$  at various temperatures  $T$  and solvent weight fractions  $w$  for  $\text{NaCl}(m)\text{-}w\text{PC}\text{-(1-w)}\text{H}_2\text{O}$  mixtures. Lines are results correlated by eq 10. (a)–(f)  $w$  are 0.0208, 0.0425, 0.0648, 0.0880, 0.112, and 0.163, respectively.





**Figure 4.** Change of conductivity  $\kappa$  with salt molality  $m$  at various temperatures  $T$  and solvent weight fractions  $w$  for  $\text{CaCl}_2(m)\text{--}w\text{PC--}(1-w)\text{H}_2\text{O}$  mixtures. Lines are results correlated by eq 10. (a)–(c):  $w$  are 0.0208, 0.0425, and 0.0880, respectively.



**Figure 5.** (a) Activation energy for  $\text{CaCl}_2\text{--}w\text{PC--}(1-w)\text{H}_2\text{O}$  as a function of concentration. (b) Pre-exponential factor for  $\text{CaCl}_2\text{--}w\text{PC--}(1-w)\text{H}_2\text{O}$  as a function of concentration,  $w$ : 0.0208.

**Table 2.** Calculated Parameters of Eq 10 of  $\text{NaCl/CaCl}_2\text{--PC--H}_2\text{O}$  and  $\text{CaCl}_2\text{--PC--H}_2\text{O}$  Solutions at Different Solvent Compositions

no.	system	$w$	$T$ (K)	$m$ (mol $\text{kg}^{-1}$ )	parameters						$dP$ (%)	$R^2$	data source
					$N_p$	$P_1$	$P_2$	$P_3$	$P_4$	$n$			
1	$\text{NaCl--}w\text{PC--H}_2\text{O}$	0.0208	283.15–328.15	0.201–5.834	72	1.818	−442.0	160.4	−616.1	1.000	2.38	0.9988	exp.
2		0.0425	283.15–328.15	0.209–5.096	78	1.747	−425.2	68.54	−132.6	0.969	1.90	0.9993	exp.
3		0.0648	283.15–328.15	0.223–4.548	72	1.743	−429.7	332.7	−1845.4	0.994	1.36	0.9993	exp.
4		0.0880	283.15–328.15	0.199–4.073	66	1.721	−423.3	558.1	−3461.9	0.956	1.61	0.9994	exp.
5		0.112	283.15–328.15	0.207–3.599	60	1.654	−411.3	58.3	−176.5	0.931	0.95	0.9998	exp.
6		0.163	283.15–328.15	0.193–1.307	42	1.876	−451.2	84.9	−178.5	0.959	1.12	0.9995	exp.
1	$\text{CaCl}_2\text{--}w\text{PC--H}_2\text{O}$	0.0208	283.15–333.15	0.100–4.903	42	2.808	−663.3	225.2	−386.2	0.995	2.35	0.9994	exp.
2		0.0425	283.15–333.15	0.125–4.605	54	2.800	−663.3	319.8	−635.4	0.977	1.81	0.9987	exp.
3		0.0648	283.15–333.15	0.117–3.309	42	3.099	−746.2	426.2	−762.4	1.029	2.18	0.9987	exp.

addition, the change trend of the conductivity of the  $\text{CaCl}_2\text{--PC--H}_2\text{O}$  system with the temperature and PC concentration in the solvent is consistent with that of the  $\text{NaCl--PC--H}_2\text{O}$  system.

Taking the system of  $\text{CaCl}_2\text{--}w\text{PC--}(1-w)\text{H}_2\text{O}$  at  $w = 0.0208 \text{ mol kg}^{-1}$  as an example, we calculated the activation energy for each solution at different concentrations and plotted it versus the concentration as shown in Figure 5. It can be seen from Figure 5a that for this specific system, with the increase in

Table 3. Calculated Parameters of Eq 8 of Reference Data in Different Concentration and Temperature Ranges<sup>a</sup>

no.	system	$w$	$T$ (K)	$m$ (mol kg <sup>-1</sup> )	$N_p$	parameters					$\epsilon$	$dP$ (%)	$R^2$	data source
						$P_1$	$P_2$	$P_3$	$P_4$	$n$				
1	C <sub>2</sub> F <sub>5</sub> Li <sub>2</sub> NO <sub>2</sub> S <sub>3</sub> -wDMC-EC	0.494	298.15–348.15	0.0547–0.735	36	0.0155	-34.25	273.5	-154.9	0.759	47.3	0.39	0.9999	38
2	C <sub>2</sub> F <sub>5</sub> LiNO <sub>2</sub> S <sub>3</sub> -wDMC-EC	0.665	298.15–368.15	0.100–1.798	64	0.02463	-50.19	250.5	-4.044	0.836	32.3	1.09	0.9991	38
3	C <sub>3</sub> F <sub>7</sub> Li <sub>2</sub> N <sub>2</sub> O <sub>8</sub> S <sub>4</sub> -wDMC-EC	0.494	298.15–348.15	0.0504–0.742	36	0.2663	-49.99	299.8	-162.8	0.794	47.2	0.78	0.9994	38
4	C <sub>4</sub> F <sub>9</sub> LiO <sub>8</sub> S <sub>3</sub> -wDMC-EC	0.494	298.15–348.15	0.0979–1.846	36	0.3366	-74.88	226.5	-120.8	0.887	47.2	0.70	0.9997	38
5	C <sub>4</sub> F <sub>9</sub> Li <sub>2</sub> NO <sub>2</sub> S <sub>3</sub> -wDMC-EC	0.665	298.15–348.15	0.0302–0.397	36	0.2617	-49.61	396.2	-95.25	0.889	32.3	0.70	0.9996	38
6	C <sub>7</sub> F <sub>13</sub> LiO <sub>6</sub> S <sub>3</sub> -wDMC-EC	0.665	298.15–348.15	0.0967–1.303	36	0.2914	-64.51	292.8	-71.33	0.876	47.8	0.44	0.9998	38
7	C <sub>9</sub> F <sub>18</sub> Li <sub>2</sub> O <sub>12</sub> S <sub>6</sub> -wDMC-EC	0.494	298.15–348.15	0.101–0.612	48	0.6756	-152.8	539.3	-120.5	0.938	47.2	1.10	0.9992	38
8	C <sub>9</sub> F <sub>18</sub> Li <sub>2</sub> O <sub>12</sub> S <sub>6</sub> -wDMC-EC	0.905	298.15–348.15	0.0779–0.6919	48	1.0524	-228.4	1206.5	-81.56	1.716	11.4	3.85	0.9976	38
9	CF <sub>3</sub> LiO <sub>3</sub> S <sub>3</sub> -wDMC-EC	0.665	298.15–368.15	0.202–1.475	64	0.0586	-12.85	140.9	-101.0	0.632	32.3	0.17	0.9998	38
10	LiPF <sub>6</sub> -wDMC-EC	0.494	298.15–358.15	0.1158–2.243	56	0.3785	-77.67	150.2	-159.9	0.932	47.2	1.63	0.9987	38
11	LiPF <sub>6</sub> -wEMC-EC	0.612	298.15–348.15	0.107–1.843	36	0.2695	-56.04	151.3	-142.0	0.911	36.5	1.12	0.9993	38
12	LiBF <sub>4</sub> -wPC-DEC	0.400	243.65–332.15	0.265–2.051	160	0.0528	-11.41	102.3	147.5	0.610	80.2	0.66	0.9999	38
13	LiBF <sub>4</sub> -wPC-DEC	0.700	243.65–332.15	0.257–2.061	160	0.1059	-23.75	132.8	152.4	0.577	72.6	1.57	0.9996	39
14	LiBF <sub>4</sub> -wPC-DEC	0.900	243.65–332.15	0.298–2.179	160	0.1382	-31.88	144.4	158.1	0.587	67.5	1.47	0.9996	38
15	LiPF <sub>6</sub> -wPC-DEC	0.300	272.95–332.15	0.259–2.316	98	0.2182	-45.04	188.3	132.3	1.058	82.7	2.19	0.9974	36
16	LiPF <sub>6</sub> -wPC-DEC	0.700	272.95–332.15	0.302–2.312	98	0.4187	-93.51	224.3	149.5	1.100	72.6	3.29	0.9984	36
17	LiPF <sub>6</sub> -wPC-DEC	0.900	282.85–332.15	0.309–2.323	84	0.4710	-108.0	227.9	160.9	1.134	67.5	2.80	0.9988	36
18	NaCl-wC <sub>4</sub> H <sub>8</sub> O <sub>2</sub> -H <sub>2</sub> O	0.298	278.15–308.15	0.0115–0.482	70	0.2781	-68.26	51.53	115.7	0.850	0.67	0.9999	30	
19	NaCl-wC <sub>4</sub> H <sub>8</sub> O <sub>2</sub> -H <sub>2</sub> O	0.110	278.15–308.15	0.0496–2.333	49	0.936	-232.2	20.81	181.3	0.959	1.84	0.9998	30	
20	C <sub>2</sub> F <sub>5</sub> LiNO <sub>2</sub> S <sub>3</sub> -DMC		298.15–368.15	0.301–2.605	49	0.0766	-5.25	378.5	17.17	2.130	4.99	0.9982	38	
21	C <sub>4</sub> F <sub>9</sub> LiO <sub>8</sub> S <sub>3</sub> -DMC		298.15–348.15	0.406–2.525	36	0.2178	-35.68	405.7	17.35	1.802	1.74	0.9975	38	
22	C <sub>7</sub> F <sub>13</sub> LiO <sub>6</sub> S <sub>3</sub> -DMC		298.15–348.15	0.204–1.773	30	0.2681	-52.06	697.7	126.6	1.876	3.16	0.9986	38	
23	LiPF <sub>6</sub> -EMC		298.15–348.15	0.510–2.889	36	0.0259	11.68	283.8	106.6	2.597	1.58	0.9993	38	
24	LiBF <sub>4</sub> -PC		243.65–332.15	0.286–2.358	160	0.1491	-34.67	144.4	164.8	0.594	1.88	0.9994	39	
25	LiPF <sub>6</sub> -PC		282.85–332.15	0.280–2.324	70	0.4900	-112.8	228.3	169.0	1.180	3.22	0.9985	36	
26	P <sub>14</sub> -PC		273.15–313.15	0.03–1 <sup>b</sup>	160	0.4902	-114.2	218.2	201.3	0.4475	4.29	0.9921	40	
27	HBF <sub>4</sub> -H <sub>2</sub> O		286.95–319.05	0.111–0.493 <sup>c</sup>	156	0.2452	-54.47	-126.4	2842.6	1.482	1.49	0.9929	41	
28	KOH-H <sub>2</sub> O		263.15–373.15	0.15–0.45 <sup>c</sup>	163	329.6	-7643	2548.8	-153.8	1.552	3.20	0.9972	25	
Average														

<sup>a</sup>DMC: Diethyl carbonate, EC: ethylene carbonate, DEC: diethyl carbonate, EMC: ethyl methyl carbonate, and P<sub>14</sub>: N-butyl-N-methylpyrrolidinium bis(trifluoromethanesulfonyl) imide. <sup>b</sup>Molar fraction of the electrolyte in the solution. <sup>c</sup>Mass fraction of the electrolyte in the solution.

the electrolyte concentration, the activation energy decreases first and then increases, ranging in 11–14 kJ mol<sup>-1</sup>. The electrolyte concentration corresponding to the lowest activation energy is about 2.3 mol kg<sup>-1</sup>, at which point the conductivity of the solution is the largest. In Figure 5b, the pre-exponential factor increases as the electrolyte concentration increases. The trends of activation energy and pre-exponential factor in this paper are very similar with those of the LiCl aqueous system reported by Yim and Abu-Lebdeh,<sup>14</sup> in which work it was believed that the enhanced ion–ion and ion–solvent interactions at high concentrations were the reason for the rapid increase in activation energy.

**4.2. Correlation of Experimental Data of NaCl/CaCl<sub>2</sub>–PC–H<sub>2</sub>O Solutions.** The conductivity model proposed in this paper is used to correlate the ( $\kappa$ ,  $m$ ,  $T$ ) data of NaCl–PC–H<sub>2</sub>O and CaCl<sub>2</sub>–PC–H<sub>2</sub>O systems. The electrolyte concentration, temperature, and model regression results are listed in Table 2.

The formula for calculating the average relative deviation is as follows:

$$dP = \frac{100\%}{Np} \sum \frac{|\kappa_{\text{exp}} - \kappa_{\text{cal}}|}{\kappa_{\text{exp}}} \quad (11)$$

where  $Np$  is the number of experimental data points.

The results show that for the NaCl–PC–H<sub>2</sub>O system, the average relative deviation of the experimental data from the calculated value of the model ( $dP$ ) is  $\leq 2.76\%$ , and  $R^2 \geq 0.9981$ . For the CaCl<sub>2</sub>–PC–H<sub>2</sub>O system,  $dP \leq 4.18\%$ , and  $R^2 \geq 0.9943$ .

It should be noted that as NaCl is a strong electrolyte in the NaCl–PC–H<sub>2</sub>O system, the relationship between the number of free ions in the solution and the electrolyte concentration is approximately linear. Thus, the value of  $n$  is approximately equal to 1, which is the same for the CaCl<sub>2</sub>–PC–H<sub>2</sub>O system. When  $n$  equals 1, eq 6 can be simplified as eq 12 under isothermal conditions, which is consistent with the model proposed by Yim et al.<sup>13</sup> based on the free volume theory.

$$\kappa = A \exp(-Bm) \quad (12)$$

In general, the error of the model proposed in this paper for the regression of ( $\kappa$ ,  $m$ ,  $T$ ) data of NaCl and CaCl<sub>2</sub> in binary PC–H<sub>2</sub>O solvents is within the acceptable range.

**4.3. Correlation of Literature Data.** Eq 10 was used to correlate the experimental ( $\kappa$ ,  $m$ ,  $T$ ) data of 28 systems reported in the literature, among which 19 are binary solvents systems, and nine are pure solvent organic or aqueous systems. The number of experimental points ( $Np$ ) for each system is no less than 36, thereby eliminating the possibility of overfitting. The system compositions, temperatures, regression results, and other data are listed in Table 3.

It can be seen from Table 3 that, under a wide concentration range and at different temperatures, the model proposed in this paper is well applicable to lithium salts in the binary organic carbonate system (nos. 1–16) and the NaCl–C<sub>4</sub>H<sub>8</sub>O<sub>2</sub>–H<sub>2</sub>O system (nos. 17 and 18), with  $dP \leq 3.29\%$  and  $R^2 \geq 0.9974$ , especially in some systems,  $R^2 \geq 0.9999$ .

For eight pure solvent organic or aqueous solution systems (nos. 19–26),  $dP \leq 4.29\%$ , which is slightly greater compared with that of the binary organic solvents systems, and  $R^2 \geq 0.9921$ . The comparison of  $dP$  and  $R^2$  illustrates that our proposed model is more suitable for the correlation of the conductivity of the binary solvent system, although the

accuracy of the model for the pure solvent system is also satisfactory.

In summary, the average  $dP$  of the proposed model is 1.87% for binary and pure solvent aqueous/organic systems. Low  $dP$  and high  $R^2$  indicate that the experimental data and the calculated value of eq 10 have good consistency. Additionally, it also indirectly proves the rationality of the assumptions adopted in this paper and the good adaptability and universality of the proposed model.

**4.4. Discussion of  $n$ .** The value of  $n$  in the proposed model is used to describe the nonlinear relationship between the concentration of free ions and the concentration of the electrolyte in the solution caused by ionic association at medium and high concentrations. If  $n = 1$ , then the relationship between them is linear; otherwise, their relationship is nonlinear. The further  $n$  deviates from 1, the more significant the nonlinear relationship is. The dielectric constant of the solvent is an important parameter that affects the association of ions, which means that for the same electrolyte, the value of  $n$  is affected by the dielectric constant of the solvent. Four electrolytes in Table 3 are used as examples to analyze the relationship between  $n$  and the dielectric constant of the solvent, including LiPF<sub>6</sub> (nos. 10, 11, 17, 23, and 25), LiBF<sub>4</sub> (nos. 12, 13, 14, and 24), C<sub>2</sub>F<sub>6</sub>LiNO<sub>4</sub>S<sub>2</sub> (nos. 2 and 20), C<sub>4</sub>F<sub>9</sub>LiO<sub>6</sub>S<sub>3</sub> (nos. 4 and 21), and C<sub>7</sub>F<sub>15</sub>LiO<sub>6</sub>S<sub>3</sub> (nos. 7 and 22).

At a certain temperature, assuming that the binary mixed solvents are an ideal solution, its dielectric constant can be calculated using the mass addition formula:<sup>42</sup>

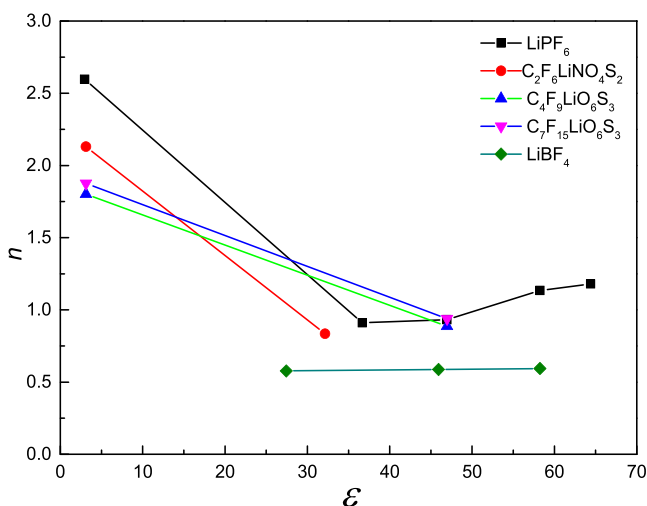
$$\epsilon = \epsilon_1 w + \epsilon_2 (1 - w) \quad (13)$$

where  $\epsilon_1$  and  $\epsilon_2$  are the dielectric constants of solvents 1 and 2 at a certain temperature, respectively, and  $w$  is the mass fraction of solvent 1 in the solution.

In this paper, eq 13 was used for a simplified calculation of the dielectric constant of binary mixed solvents by substituting the dielectric constant of a pure solvent at a certain temperature into the equation. At 298.15 K, the dielectric constants of DMC, DEC, EMC, and PC are 3.108, 2.806, 2.40, and 64.95, respectively.<sup>38</sup> The dielectric constant of EC is 90.36 (313.15 K).<sup>38</sup> The calculated dielectric constants of the mixed solvents are listed in Table 3.

Figure 6 shows the changing trend of  $n$  with the dielectric constant  $\epsilon$  of the solvent for different electrolyte systems. It can be seen from the plot that for the same electrolyte, the value of  $n$  is significantly affected by the dielectric constant of the solvent. The value of  $n$  in a solvent with a lower dielectric constant is larger, while in a solvent with a high the dielectric constant,  $n$  is smaller, between 0.5 and 1.2. This is because the electrolyte is more likely to form nonconductive ion pairs in a solvent with a lower dielectric constant, resulting in a reduction in the number of free ions participating in conduction in the solution. As a consequence, the nonlinear deviation of the relationship between the number of free ions and electrolyte concentration is significant, and the degree of deviation varies with the electrolyte. When the dielectric constant of the solvent is high, the electrolyte dissociation is relatively complete, so  $n$  fluctuates around 1.

**4.5. Comparison of Different Models.** Up to now, a general model applicable to the ( $\kappa$ ,  $m$ ,  $T$ ) data for mixed solvents has not been reported yet. Therefore, we compared the proposed model with other models for some specific systems.



**Figure 6.** Relationship between parameter  $n$  and dielectric constant  $\epsilon$  of the solvent in various electrolyte solution systems.

Lin et al.<sup>43</sup> reported the conductivity data of ionic liquids [EMIM][C<sub>2</sub>N<sub>3</sub>] and [EMIM][CF<sub>3</sub>SO<sub>3</sub>] in aqueous solutions and proposed a six-parameter empirical model that simultaneously correlated conductivity, electrolyte concentration, and temperature, as shown in eq 14.

$$\kappa = x \exp(A_1 + A_2 T^{0.5} + A_3 x^{0.5}) + A_4 + A_5 T^{0.5} + A_6 x^{0.5} \quad (14)$$

where  $A_1$ – $A_6$  are empirical parameters and can be obtained from data regression, and  $x$  is the mole fraction of the ionic liquid.

Fu et al.<sup>27</sup> proposed a seven-parameter correlation model for the conductivity of ionic liquids in binary organic solvents systems, as shown in eq 15.

$$\kappa = B_1 x^{B_2} \exp\left(-\frac{B_4 x^{0.5} + B_5 x + (B_6 x' + B_7)^2}{T - B_3}\right) \quad (15)$$

where  $B_1$ – $B_7$  are empirical parameters, and  $x'$  is related to the solvent composition.

We used six different ionic liquid systems as examples to compare the correlation results of our proposed model, Lin's model, and Fu's model. The results are listed in Table 4.

As can be seen from Table 4 for the ionic liquid aqueous solution systems, the maximum  $dP$  of our proposed five-parameter model is 2.22%, which is far smaller than the 7.8% in Lin's six-parameter model, and  $R^2$  of the proposed model is better than that of Lin's model. In Lin's model, the conductivity is related to the 0.5th power of the electrolyte concentration, while in our model,  $n$  is introduced to describe

the nonlinear deviation of the relationship between the free ion and the electrolyte concentration in the solution, which can better describe the relationship between the conductivity and the electrolyte concentration. In summary, our model can obtain better regression results with fewer parameters. In addition, it should be noted that Lin's model is only suitable for a pure solvent system, not for mixed solvents systems.

For the pure solvent system, the  $dP$  of Fu's seven-parameter model is smaller compared with our proposed model, but there is not much difference in  $R^2$ . Our proposed model can fit the experimental data well with fewer parameters. For mixed solvents systems, the  $dP$  of the Fu model is slightly better than that of the proposed model, which can be attributed to that in the mixed solvent; the resistance encountered by the ions in the directional migration is more complicated than that in a single solvent. The Fu model uses more concentration-related parameters to correct the influence of concentration on ion conductivity, which can bring better fitting effects. However, the existence of more parameters in the Fu model means that it takes longer time to solve the equation. Taking the [BMIM][TFSI]–PC–GBL system as an example, under the same hardware configuration, we compared the calculation time of different models using the software package 1stOpt. Fu's model takes 95.8 s to find the solution, while the proposed model only takes 62.8 s, which is 34.4% less.

## 5. CONCLUSIONS

In this paper, a semiempirical model with five parameters suitable for both pure and mixed solvents systems was proposed based on the influence of the electrolyte concentration and temperature on the number of free ions and ion mobility:  $\kappa = (P_1 T + P_2) m^n \exp\left(-\frac{P_3 m}{T - P_4}\right)$ . The conductivity of NaCl–PC–H<sub>2</sub>O at 283.15–328.15 K and that of the CaCl<sub>2</sub>–PC–H<sub>2</sub>O system at 283.15–333.15 K in a wide concentration range were measured. The feasibility and accuracy of the proposed model were verified by the experimental data in this paper and the  $(\kappa, m, T)$  data of 28 electrolyte solutions from the literature. The results showed that in a wide temperature and concentration range, the proposed model can fit the experimental data well for both pure and mixed solvents systems. The parameters in the proposed model are related to the type of solvent, and the value of  $n$  is closely relevant to the dielectric constant of the solvent. In a solvent with a high dielectric constant, the value of  $n$  is close to 1. In addition, compared with the conductivity model reported in the literature, the proposed model can obtain good accuracy with fewer parameters, which is of great value to practical engineering applications.

**Table 4.** Comparison of Three Different Models

system	$T$ (K)	$x$	$N_p$	Lin et al.'s model		Fu et al.'s model		this work <sup>c</sup>		data source
				$dP$ (%)	$R^2$	$dP$ (%)	$R^2$	$dP$ (%)	$R^2$	
[EMIM][C <sub>2</sub> N <sub>3</sub> ]-H <sub>2</sub> O	293.2–353.2	0.2–0.8	52	7.8	0.9994	0.96	0.9993	0.91	0.9994	43
[EMIM][CF <sub>3</sub> SO <sub>3</sub> ]-H <sub>2</sub> O	293.2–343.2	0.2–0.8	44	1.4	0.9994	0.80	0.9998	1.29	0.9994	44
[EMIM][EtSO <sub>4</sub> ]-H <sub>2</sub> O	293.2–353.2	0.2–0.8	52	2.4	0.9991	0.60	0.9999	2.22	0.9991	44
[EMIM][DCA]-PC	293.15–353.15	0.05–1	132	3.68	0.9917	2.16	0.9947	2.54	0.9930	23
[BMIM][TFSI]-PC-GBL <sup>a</sup>	293.15–353.15	0.1–1	130			1.76	0.9982	2.94	0.9952	27
[BMIM][TFSI]-EC-DMC <sup>b</sup>	293.15–333.15	0.1–1	90			1.68	0.9986	3.95	0.9921	27

<sup>a</sup>PC:GBL = 1. <sup>b</sup>EC:DMC = 1. <sup>c</sup>To simplify the calculation, mole fraction  $x$  is used in eq 10 instead of concentration  $m$ .



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## NOMENCLATURE

symbol	meaning (units)
$\kappa$	specific conductivity ( $\text{mS cm}^{-1}$ )
$m$	molality of the electrolyte ( $\text{mol kg}^{-1}$ )
$w$	mass fraction of the specific solvent in a binary solvent
$x$	molar factor of the electrolyte
$m_i$	molality of ion $i$ ( $\text{mol kg}^{-1}$ )
$n_i$	number of ion $i$
$q_i$	charge of ion $i$ (C)
$\mu_i$	mobility of ion $i$ ( $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ )
$\mu_{i0}$	mobility of ion $i$ at infinite dilution ( $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ )
$z_i$	charge number of the ion $i$
$A, B, a, n, P_1-P_4$	parameters of the model
$A_1-A_6, B_1-B_7$	parameters of the model
$I$	ionic strength ( $\text{mol L}^{-1}$ )
$N_p$	number of experimental points
$dP$	average relative error (%)
$T$	temperature (K)

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