

# Experimental Measurement and Modeling of Aniline Hydrochloride Solubility in Water, Methanol, Ethanol, Propan-1-ol, and Their Mixed Systems

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**ABSTRACT:** The solubilities of aniline hydrochloride ([HAE]Cl) in different aqueous solutions of methanol, ethanol, propan-1-ol, and their mixed solvent solutions were determined using the dynamic method in the temperature range between 288 K and 328 K. With the purpose of improving AspenPlus's prediction capability, in regards to [HAE]Cl solubilities in the CH<sub>3</sub>OH–C<sub>2</sub>H<sub>5</sub>OH–C<sub>3</sub>H<sub>7</sub>OH–H<sub>2</sub>O system at various temperatures, new interaction energy parameters  $\tau_{[\text{HAE}]^+-\text{Cl}^-, \text{CH}_3\text{OH}}$ ,  $\tau_{[\text{HAE}]^+-\text{Cl}^-, \text{C}_2\text{H}_5\text{OH}}$ ,  $\tau_{[\text{HAE}]^+-\text{Cl}^-, \text{C}_3\text{H}_7\text{OH}}$ ,  $\tau_{[\text{HAE}]^+-\text{Cl}^-, \text{CH}_3\text{OH}, [\text{HAE}]^+-\text{Cl}^-}$ ,  $\tau_{[\text{HAE}]^+-\text{Cl}^-, \text{C}_2\text{H}_5\text{OH}, [\text{HAE}]^+-\text{Cl}^-}$ , and  $\tau_{[\text{HAE}]^+-\text{Cl}^-, \text{C}_3\text{H}_7\text{OH}, [\text{HAE}]^+-\text{Cl}^-}$  were obtained via regression of the experimental solubility of [HAE]Cl in binary mixed solvent systems with the maximum-likelihood principle. With the newly obtained electrolyte nonrandom two-liquid (NRTL) interaction parameters, a self-consistent model was established for the calculation of [HAE]Cl solubility in the system of CH<sub>3</sub>OH–C<sub>2</sub>H<sub>5</sub>OH–C<sub>3</sub>H<sub>7</sub>OH–H<sub>2</sub>O as a function of temperature and the composition of solvents. The maximum relative deviation between experimental and predicted solubility data is 2.3 %, and the average relative deviation is 1.8 %.

## INTRODUCTION

High-quality anhydrous magnesium chloride is the main precursor of magnesium metal produced by electrochemical methods. With the development of the past few decades, many methods, for example, HCl gas protective heating,<sup>1–3</sup> organic solvent distillation, or molecular sieve absorption<sup>4,5</sup> and decomposition of the complex,<sup>6–10</sup> have been tested or even commercialized to prepare anhydrous magnesium chloride from magnesium chloride hydrate. Nevertheless, further improvement is still explored to reduce energy costs and satisfy stricter environmental requirements. The thermal decomposition of complex [HAE]Cl·MgCl<sub>2</sub>·6H<sub>2</sub>O may be an effective way to produce high-purity anhydrous magnesium chloride.<sup>8,11</sup> In a previous work, the solid–liquid equilibria for the binary [HAE]Cl–H<sub>2</sub>O system and the ternary [HAE]Cl–MgCl<sub>2</sub>–H<sub>2</sub>O system have been investigated and modeled with good results.<sup>12</sup> To synthesize the complex [HAE]Cl·MgCl<sub>2</sub>·6H<sub>2</sub>O with good crystalline form, the anti-solvent crystallization method was proposed. In this process, the solubility of aniline hydrochloride in mixed solvent system is the key problem.

To estimate the solubility of [HAE]Cl in a mixed solvent system accurately, the key problem is to calculate the mean activity coefficients precisely. In this respect, a number of electrolyte models have been proposed in literature.<sup>13–18</sup> Among those models, their applicabilities only were proposed to calculate the vapor–liquid equilibrium or liquid–liquid equilibrium behavior.<sup>19–21</sup> Up to now, the models used for the prediction of solid–liquid equilibrium in mixed solvent systems are rather limited.<sup>22–24</sup> Chen<sup>25</sup> proposed the electrolyte nonrandom two-liquid (NRTL) model for the representation of solid–liquid equilibrium of aqueous electrolyte systems with successful results. Later, Chen and his partners<sup>26</sup> developed this model and provided a thermodynamic representation of phase equilibria of mixed solvent electrolyte systems.

Barata and Serrano<sup>27</sup> described the solubility of potassium dihydrogen phosphate in aqueous ethanol, propan-1-ol, and propan-2-ol mixtures via calculated ionic mean activity coefficients with the electrolyte NRTL model. Kim et al.<sup>28</sup> described the phase equilibrium conditions of L-ornithine–L-aspartate + water + methanol with the electrolyte NRTL model successfully. Requiring only binary interaction parameters, the electrolyte NRTL activity coefficient model has been one of the most widely thermodynamic models for both aqueous and nonaqueous electrolyte systems.<sup>29–31</sup> Recent industrial applications of the electrolyte NRTL model include thermodynamic modeling of the sulfuric acid–sulfur trioxide–water system,<sup>32</sup> CO<sub>2</sub> capture with amines,<sup>33</sup> and the salting-out effect of CO<sub>2</sub> with brine solutions.<sup>34</sup>

The purpose of this study is to investigate the effects of temperature and alcohol content on the solubility of [HAE]Cl. The solubility of [HAE]Cl in absolute alcohols and in aqueous solutions of mixed solvent were measured over a wide temperature range. In addition, a thermodynamic description of the solubility of [HAE]Cl was also developed. From the models based on the local composition concept, the electrolyte NRTL model was used to describe the activity coefficients in the mixed solvent systems [HAE]Cl–alcohols–water, mainly for the following reasons: (i) it accounts for the interactions of all species in solution (ion–ion, molecule–ion, and molecule–molecule); (ii) the short-range contributions are accounted for by the NRTL expressions, which are adequate for electrolyte solutions; (iii) it is based on mole fraction, and no specific area or volume data are needed; and (iv) only binary parameters are needed.

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## EXPERIMENTAL SECTION

**Materials.** The chemicals used in the experiments include aniline hydrochloride (mass fraction purity >0.990, Sinopharm Chemical Reagent Co., Ltd.), methanol (mass fraction purity >0.995, Beijing Chemical Plant), ethanol (mass fraction purity >0.997, Beijing Chemical Plant), and propan-1-ol (mass fraction purity >0.990, Xilong Chemical Plant). All were analytical grade without further purification. A series of mixed solvents, concentrations in mass fraction ranging from 10 % to 80 %, were prepared by dissolving alcohols in double-distilled water (conductivity <0.1  $\mu\text{S}\cdot\text{cm}^{-1}$ ).

**Apparatus and Procedure.** The solubilities of [HAE]Cl in mixed solvent solutions were determined using a dynamic method.<sup>35</sup> A jacketed glass vessel with a volume of 250 mL was used in this system. The mixed solvent of known composition was put into the vessel, and the system was maintained at a certain temperature using a water bath. A known mass of [HAE]Cl was added into the solvent. A magnetic stirrer was used to provide vigorous agitation to the sample. Some time later, more weighted [HAE]Cl was added if the last trace of salts was observed to disappear. The mixture of solute and solvent was heated very slowly (<2  $\text{K}\cdot\text{h}^{-1}$  near the equilibrium temperature) with continuous stirring. The temperature at which crystals disappeared, detected visually, was measured with a thermometer. The temperature precision was 0.1 K. All chemical reagents were prepared by weighting the pure components with an uncertainty of 0.001 g.

## THERMODYNAMIC MODELING FRAMEWORK

**Prediction Model of the Solubility of Ternary Systems.** The thermodynamic description of solid–liquid equilibrium is an important step in precipitation studies, which requires the knowledge of the activity coefficients of the electrolyte species in the temperature and the concentration ranges studied. Electrolyte thermodynamics enables the calculation of the activity coefficients, and thus a description of the nonideality of the system is possible. The electrolyte NRTL model is a versatile model for the calculation of activity coefficients. The electrolyte NRTL model contains two contributions: one contribution for the long-range ion–ion interactions is represented by the Pitzer–Debye–Hückel model, and the other related to the local interactions is represented by the NRTL theory.<sup>36</sup> The main mathematical equation of the model can be expressed as follows:

$$\frac{G_m^{*E}}{RT} = \frac{G_m^{*E,PDH}}{RT} + \frac{G_m^{*E,lc}}{RT} \quad (1)$$

This leads to

$$\ln \gamma_i^* = \ln \gamma_i^{*PDH} + \ln \gamma_i^{*lc} \quad (2)$$

where  $G_m^{*E}$  is the molar excess Gibbs energy,  $R$  is the universal gas constant,  $T$  is absolute temperature, and  $\gamma_i$  is the activity coefficient of species  $i$  in the liquid phase. The asterisk is used to denote an unsymmetrical reference state, and PDH and lc mean Pitzer–Debye–Hückel and local composition, respectively. The first and second terms on the right side of the above equation are the activity coefficients introduced by the Pitzer–Debye–Hückel and NRTL models, respectively. The expression for the Pitzer–Debye–Hückel equation is given in the following equation.

$$\ln \gamma_i^{*PDH} = - \left( \frac{1000}{M_B} \right)^{1/2} A_\phi \left[ \left( \frac{2Z_i^2}{\rho} \right) \ln(1 + \rho I_x^{1/2}) + \frac{Z_i^2 I_x^{1/2} - 2I_x^{3/2}}{1 + \rho I_x^{1/2}} \right] \quad (3)$$

where  $M_B$  is the molecular weight of the solvent B,  $A_\phi$  is the Debye–Hückel parameter,  $Z_i$  is the charge number of ion  $i$ ,  $\rho$  is the “closest approach” parameter, and  $I_x$  is ionic strength (mole fraction scale). The local composition activity coefficient equation for cation, anion, and molecular components in a multicomponent solution were given by the following expressions:

$$\begin{aligned} \frac{1}{Z_c} \ln \gamma_c^{*lc} = & \sum_{a'} \left( \frac{X_{a'}}{\sum_{a''} X_{a''}} \right) \frac{\sum_k X_k G_{kc, a'c} \tau_{kc, a'c}}{\sum_k X_k G_{kc, a'c}} \\ & + \sum_{B'} \frac{X_B G_{cB}}{\sum_k X_k G_{kB}} \left( \tau_{cB} - \frac{\sum_k X_k G_{kB} \tau_{kB}}{\sum_k X_k G_{kB}} \right) \\ & + \sum_a \sum_{c'} \left( \frac{X_{c'}}{\sum_{c''} X_{c''}} \right) \frac{X_a G_{ca, c'a}}{\sum_k X_k G_{ka, c'a}} \left( \tau_{ca, c'a} - \frac{\sum_k X_k G_{ka, c'a} \tau_{ka, c'a}}{\sum_k X_k G_{ka, c'a}} \right) \end{aligned} \quad (4)$$

$$\begin{aligned} \frac{1}{Z_c} \ln \gamma_c^{*lc} = & \sum_{a'} \left( \frac{X_{a'}}{\sum_{a''} X_{a''}} \right) \frac{\sum_k X_k G_{kc, a'c} \tau_{kc, a'c}}{\sum_k X_k G_{kc, a'c}} \\ & + \sum_{B'} \frac{X_B G_{cB}}{\sum_k X_k G_{kB}} \left( \tau_{cB} - \frac{\sum_k X_k G_{kB} \tau_{kB}}{\sum_k X_k G_{kB}} \right) \\ & + \sum_a \sum_{c'} \left( \frac{X_{c'}}{\sum_{c''} X_{c''}} \right) \frac{X_a G_{ca, c'a}}{\sum_k X_k G_{ka, c'a}} \left( \tau_{ca, c'a} - \frac{\sum_k X_k G_{ka, c'a} \tau_{ka, c'a}}{\sum_k X_k G_{ka, c'a}} \right) \end{aligned} \quad (5)$$

$$\begin{aligned} \ln \gamma_B^{lc} = & \frac{\sum_j X_j G_{jB} \tau_{jB}}{\sum_k X_k G_{kB}} + \sum_{B'} \frac{X_{B'} G_{BB'}}{\sum_k X_k G_{kB'}} \left( \tau_{BB'} - \frac{\sum_k X_k G_{kB'} \tau_{kB'}}{\sum_k X_k G_{kB'}} \right) \\ & + \sum_c \sum_{a'} \left( \frac{X_{a'}}{\sum_{a''} X_{a''}} \right) \frac{X_c G_{Bc, a'c}}{\sum_k X_k G_{kc, a'c}} \left( \tau_{Bc, a'c} - \frac{\sum_k X_k G_{kc, a'c} \tau_{kc, a'c}}{\sum_k X_k G_{kc, a'c}} \right) \\ & + \sum_a \sum_{c'} \left( \frac{X_{c'}}{\sum_{c''} X_{c''}} \right) \frac{X_a G_{Ba, c'a}}{\sum_k X_k G_{ka, c'a}} \left( \tau_{Ba, c'a} - \frac{\sum_k X_k G_{ka, c'a} \tau_{ka, c'a}}{\sum_k X_k G_{ka, c'a}} \right) \end{aligned} \quad (6)$$

where a means anion, c means cation, B means solvent,  $j$  and  $k$  can be any species (a, c, or B), and  $X_j = x_j Z_j$  is the effective mole fraction of species  $j$ . The other variables are written as

$$\ln G_{ka, c'a} = - \tau_{ka, c'a} \alpha \quad (7)$$

**Table 1.** Experimental Molality  $m$  and Mole Fraction Solubilities  $x$  of [HAE]Cl in Different Solvents at Temperature  $T$ 

$T/K$	$\text{CH}_3\text{OH}$		$\text{C}_2\text{H}_5\text{OH}$		$\text{C}_3\text{H}_7\text{OH}$	
	$m/\text{mol}\cdot\text{kg}^{-1}$	$x$	$m/\text{mol}\cdot\text{kg}^{-1}$	$x$	$m/\text{mol}\cdot\text{kg}^{-1}$	$x$
288.15	5.26	0.144	1.95	0.082	0.82	0.047
298.15	6.17	0.165	2.35	0.098	1.00	0.057
308.15	7.21	0.188	2.81	0.115	1.25	0.070
318.15	8.21	0.208	3.36	0.134	1.50	0.083
328.15	9.33	0.230	3.98	0.155	1.81	0.098

$$\begin{aligned}\tau_{cB} &= \tau_{aB} = \tau_{ca,B}; \\ \tau_{Bc} &= \tau_{Ba} = \tau_{B,ca}; \quad \tau_{Bc,ac} = \tau_{Ba,ca} = \tau_{B,ca}\end{aligned}\quad (8)$$

In this work, for a multicomponent mixed solvent electrolyte system, the electrolyte NRTL parameters consist of both the non-randomness factor  $\alpha$  and energy parameter  $\tau$ . In practice, the value of  $\alpha$  usually is 0.2 for molecule–electrolyte and 0.3 for molecule–molecule,<sup>26</sup> and the energy parameters  $\tau$  are written in terms of temperature as follows.

Molecule–molecule binary parameters:

$$\tau_{B,B'} = C_{B,B'} + \frac{D_{B,B'}}{T} \quad (9)$$

$$\tau_{B',B} = C_{B',B} + \frac{D_{B',B}}{T} \quad (10)$$

Electrolyte–molecule pair parameters:

$$\tau_{ca,B} = C_{ca,B} + \frac{D_{ca,B}}{T} + E_{ca,B} \left[ \frac{(T_r - T)}{T} + \ln \left( \frac{T}{T_r} \right) \right] \quad (11)$$

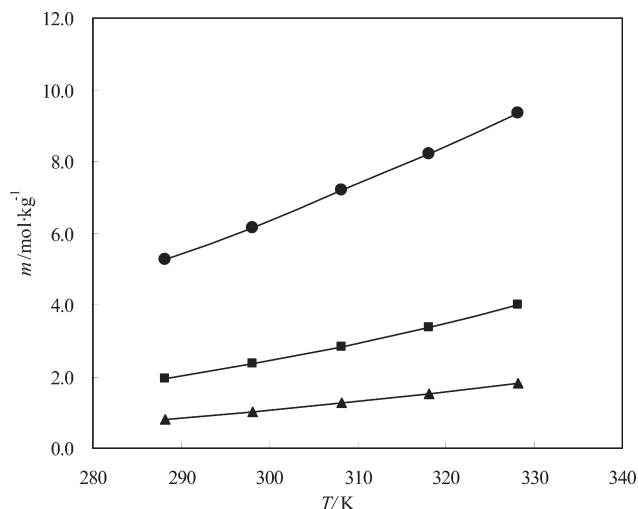
$$\tau_{B,ca} = C_{B,ca} + \frac{D_{B,ca}}{T} + E_{B,ca} \left[ \frac{(T_r - T)}{T} + \ln \left( \frac{T}{T_r} \right) \right] \quad (12)$$

where ca means electrolyte (cation–anion) and  $T_r$  means the reference temperature. Therefore, for each interaction energy parameter  $\tau$ , three adjustable parameters  $C$ ,  $D$ , and  $E$  should be calculated over the whole range of temperature.

**Compilation and Reduction of Experimental Data.** To use the Aspen regression property analysis, molality  $m_i$  should be transformed to mole fraction  $x_i$ . Therefore, the following relation for aqueous multicomponent solutions was used for the conversion:

$$x_i = \frac{m_i}{\sum_j v_j m_j + 55.508} \quad (13)$$

where  $v_i$  is the stoichiometric number of an ion  $i$  in solutions with one mole salt dissolution. Based on the maximum-likelihood principle,<sup>36</sup> the following general objective function was used to

**Figure 1.** Molality solubility  $m$  of [HAE]Cl as a function of temperature  $T$  in  $\bullet$ ,  $\text{CH}_3\text{OH}$ ;  $\blacksquare$ ,  $\text{C}_2\text{H}_5\text{OH}$ ; and  $\blacktriangle$ ,  $\text{C}_3\text{H}_7\text{OH}$ , respectively.

optimize the solubility data:

$$\begin{aligned}\text{OBF} = \min \sum_i & \left[ f_1 \left( \frac{T_i^{\text{exp}} - T_i^{\text{cal}}}{\sigma_T} \right)^2 + f_2 \left( \frac{P_i^{\text{exp}} - P_i^{\text{cal}}}{\sigma_P} \right)^2 \right. \\ & \left. + f_3 \left( \frac{x_i^{\text{exp}} - x_i^{\text{cal}}}{\sigma_x} \right)^2 \right] \quad (14)\end{aligned}$$

where  $\sigma$  is the standard deviation,  $f_i$  is the weight factor, and exp and cal mean experimental data and calculated results, respectively.

## RESULTS AND DISCUSSION

**Experimental Results. [HAE]Cl in Pure Solvent.** The solubilities of [HAE]Cl in absolute  $\text{CH}_3\text{OH}$ ,  $\text{C}_2\text{H}_5\text{OH}$ , and  $\text{C}_3\text{H}_7\text{OH}$  were measured in the temperature range from 288 K to 328 K, respectively, and the results are listed in Table 1. In this table, the solubility of [HAE]Cl was expressed both in molality ( $m$ ,  $\text{mol}\cdot\text{kg}^{-1}$ ) and mole fraction ( $x$ ) for convenient practical and thermodynamic reference. Figure 1 shows the experimental solubility of [HAE]Cl in absolute  $\text{CH}_3\text{OH}$ ,  $\text{C}_2\text{H}_5\text{OH}$ , and  $\text{C}_3\text{H}_7\text{OH}$  as a function of temperature. The results show that the solubility of [HAE]Cl increases with an increase of the temperature but decreases with increasing the length of carbon chain of alcohols.

**[HAE]Cl in Binary Mixed Solvent Systems.** The solubilities of [HAE]Cl in  $\text{CH}_3\text{OH}-\text{H}_2\text{O}$ ,  $\text{C}_2\text{H}_5\text{OH}-\text{H}_2\text{O}$ , and  $\text{C}_3\text{H}_7\text{OH}-\text{H}_2\text{O}$  binary mixed solvent systems were measured between 288 K and 348 K, concentration in the mass fraction range from 10 % to 80 %, and are listed in Tables 2 to 4. Figures 2 to 4 show the experimental solubility of [HAE]Cl in different alcohol solutions as a function of the composition of solvents. The results show that the solubility of [HAE]Cl increases with an increase of the temperature but decreases with increasing alcohol concentration when the concentration of solvents was over 20 % (mass fraction). This phenomenon was the most obvious in propan-1-ol solution. However, when alcohol concentration was less than 20 % (mass fraction), the solubility of [HAE]Cl increases slightly with an increase of the solvent concentration.

**Table 2.** Experimental SLE Data for the System [HAE]Cl (1)–CH<sub>3</sub>OH (2)–H<sub>2</sub>O (3) for Molality  $m$  and Mole Fraction  $x$  at Temperature  $T$ 

$T/K$	$m/\text{mol}\cdot\text{kg}^{-1}$	$x_1$	$x_2$	$m/\text{mol}\cdot\text{kg}^{-1}$	$x_1$	$x_2$
288.15	7.28	0.121	0.052	7.32	0.126	0.107
298.15	9.06	0.146	0.051	9.08	0.152	0.103
308.15	10.94	0.171	0.049	10.86	0.176	0.100
318.15	13.04	0.197	0.048	12.92	0.203	0.097
328.15	15.18	0.222	0.046	14.99	0.228	0.094
288.15	7.77	0.145	0.236	7.64	0.157	0.379
298.15	9.29	0.169	0.230	8.96	0.179	0.369
308.15	11.02	0.194	0.223	10.40	0.202	0.359
318.15	12.87	0.220	0.216	12.14	0.228	0.347
328.15	14.75	0.244	0.209	13.96	0.253	0.336
288.15	6.71	0.157	0.580			
298.15	7.94	0.180	0.564			
308.15	9.30	0.205	0.547			
318.15	10.54	0.226	0.533			
328.15	11.99	0.249	0.517			

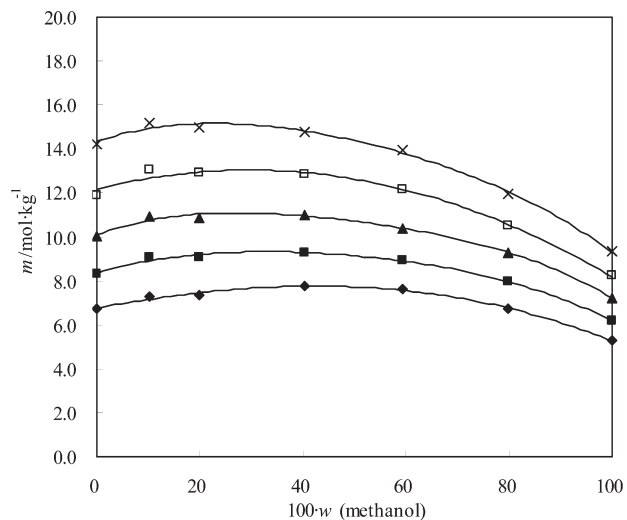
**Table 3.** Experimental SLE Data for the System [HAE]Cl (1)–C<sub>2</sub>H<sub>5</sub>OH (2)–H<sub>2</sub>O (3) for Molality  $m$  and Mole Fraction  $x$  at Temperature  $T$ 

$T/K$	$m/\text{mol}\cdot\text{kg}^{-1}$	$x_1$	$x_2$	$m/\text{mol}\cdot\text{kg}^{-1}$	$x_1$	$x_2$
288.15	7.08	0.120	0.037	7.57	0.136	0.080
298.15	8.71	0.143	0.036	9.15	0.160	0.078
308.15	10.49	0.167	0.035	10.91	0.185	0.075
318.15	12.36	0.192	0.034	12.79	0.210	0.073
328.15	14.54	0.218	0.032	14.84	0.235	0.071
338.15	16.88	0.244	0.031	17.30	0.264	0.068
348.15	19.79	0.275	0.030	20.09	0.294	0.065
288.15	7.24	0.138	0.124	7.17	0.147	0.184
298.15	8.79	0.162	0.120	8.66	0.172	0.178
308.15	10.40	0.186	0.117	10.18	0.197	0.173
318.15	12.28	0.213	0.113	11.81	0.221	0.168
328.15	14.23	0.239	0.109	13.49	0.245	0.163
338.15	16.46	0.266	0.105	15.56	0.272	0.157
348.15	19.20	0.297	0.101	17.85	0.300	0.151
288.15	6.29	0.149	0.301	4.68	0.140	0.517
298.15	7.42	0.172	0.293	5.56	0.163	0.504
308.15	8.75	0.196	0.284	6.44	0.183	0.491
318.15	10.25	0.222	0.275	7.50	0.207	0.477
328.15	11.77	0.247	0.266	8.60	0.231	0.463
338.15	13.55	0.274	0.256	9.99	0.258	0.446
348.15	15.48	0.302	0.247	11.42	0.285	0.430

[HAE]Cl in Ternary Mixed Solvent Systems. In the present work, the solubility of [HAE]Cl in CH<sub>3</sub>OH–C<sub>2</sub>H<sub>5</sub>OH–H<sub>2</sub>O, C<sub>2</sub>H<sub>5</sub>OH–C<sub>3</sub>H<sub>7</sub>OH–H<sub>2</sub>O, and CH<sub>3</sub>OH–C<sub>3</sub>H<sub>7</sub>OH–H<sub>2</sub>O ternary mixed solvent systems were measured over the temperature range from 288 K to 328 K. Table 5 and Figure 6 summarize the experimental data for [HAE]Cl in these systems. The results show that the solubility of [HAE]Cl is linearly proportional to temperature and increases with the temperature.

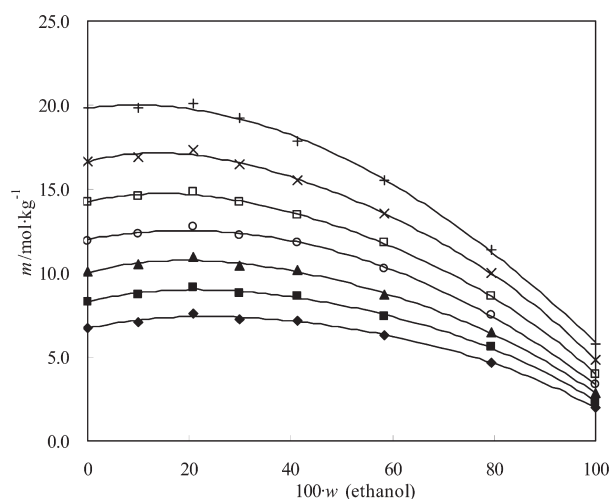
**Table 4.** Experimental SLE Data for the System [HAE]Cl (1)–C<sub>3</sub>H<sub>7</sub>OH (2)–H<sub>2</sub>O (3) for Molality  $m$  and Mole Fraction  $x$  at Temperature  $T$ 

$T/K$	$m/\text{mol}\cdot\text{kg}^{-1}$	$x_1$	$x_2$	$m/\text{mol}\cdot\text{kg}^{-1}$	$x_1$	$x_2$
288.15	7.49	0.127	0.028	7.64	0.137	0.059
298.15	9.22	0.152	0.027	9.39	0.164	0.057
308.15	11.08	0.177	0.027	11.06	0.187	0.055
318.15	13.11	0.202	0.026	13.09	0.214	0.053
328.15	15.26	0.228	0.025	15.05	0.239	0.052
288.15	7.04	0.140	0.104	6.91	0.148	0.144
298.15	8.95	0.171	0.101	8.43	0.175	0.140
308.15	10.57	0.196	0.098	9.92	0.200	0.135
318.15	12.29	0.221	0.095	11.50	0.224	0.131
328.15	14.11	0.246	0.092	13.12	0.248	0.127
288.15	5.94	0.154	0.255	4.30	0.144	0.427
298.15	7.05	0.178	0.248	5.01	0.163	0.417
308.15	8.20	0.201	0.241	5.81	0.185	0.406
318.15	9.46	0.225	0.233	6.69	0.207	0.395
328.15	10.79	0.249	0.226	7.60	0.228	0.384

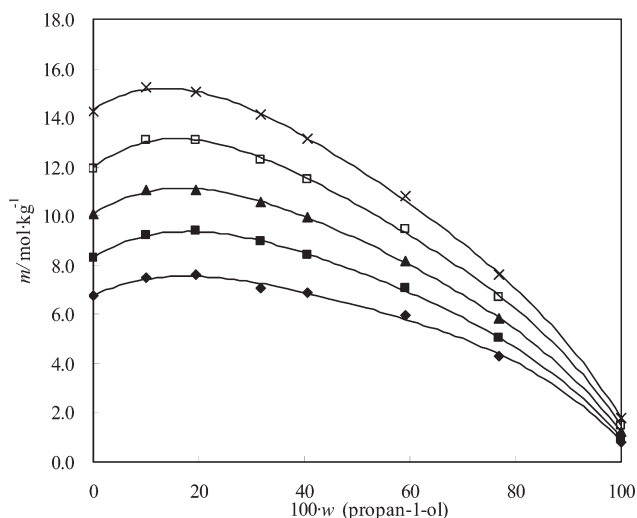
**Figure 2.** Molality solubility  $m$  of [HAE]Cl against the composition of solvent in mass fraction  $w$  in the ternary [HAE]Cl–CH<sub>3</sub>OH–H<sub>2</sub>O system. Points, experimental data in this work  $\blacklozenge$ , 288.15 K;  $\blacksquare$ , 298.15 K;  $\blacktriangle$ , 308.15 K;  $\square$ , 318.15 K;  $\times$ , 328.15 K; lines, calculated results.

[HAE]Cl in the Quaternary Mixed Solvent System. The solubility of [HAE]Cl in a mixture of CH<sub>3</sub>OH–C<sub>2</sub>H<sub>5</sub>OH–C<sub>3</sub>H<sub>7</sub>OH–H<sub>2</sub>O was obtained in the temperature range from 288 K to 328 K with an interval of 10 K. The results of experimentally determined solubility are listed in Table 6. Figure 7 shows the solubility of [HAE]Cl as a function of temperature in a mixed solvent system. It can be observed that the solubility of [HAE]Cl increases with the increase of temperature.

**Estimation of Model Parameters.** Interaction between [HAE]Cl and Methanol. To describe the system of [HAE]Cl–CH<sub>3</sub>OH–H<sub>2</sub>O, three interactions [HAE]Cl–H<sub>2</sub>O, CH<sub>3</sub>OH–H<sub>2</sub>O, and [HAE]Cl–CH<sub>3</sub>OH, need to be determined. The interaction energy parameters  $\tau_{[\text{HAE}]\text{Cl}-\text{H}_2\text{O}}$  and  $\tau_{\text{H}_2\text{O},[\text{HAE}]\text{Cl}}$  have been determined in a previous work.<sup>12</sup> The binary parameters between ethanol and water which were regressed from



**Figure 3.** Molality solubility  $m$  of [HAE]Cl against the composition of solvent in mass fraction  $w$  in the ternary [HAE]Cl–C<sub>2</sub>H<sub>5</sub>OH–H<sub>2</sub>O system. Points, experimental data in this work  $\blacklozenge$ , 288.15 K;  $\blacksquare$ , 298.15 K;  $\blacktriangle$ , 308.15 K;  $\circ$ , 318.15 K;  $\square$ , 328.15 K;  $\times$ , 338.15 K;  $+$ , 348.15 K; lines, calculated results.



**Figure 4.** Molality solubility  $m$  of [HAE]Cl against the composition of solvent in mass fraction  $w$  in the ternary [HAE]Cl–C<sub>3</sub>H<sub>7</sub>OH–H<sub>2</sub>O system. Points, experimental data in this work  $\blacklozenge$ , 288.15 K;  $\blacksquare$ , 298.15 K;  $\blacktriangle$ , 308.15 K;  $\square$ , 318.15 K;  $\times$ , 328.15 K; lines, calculated results.

vapor–liquid equilibrium data of the CH<sub>3</sub>OH–H<sub>2</sub>O system can be obtained from AspenPlus's default database. All of the parameters needed are listed in Table 7. New interaction energy parameters  $\tau_{[\text{HAE}]^+\text{-Cl}^-\text{-CH}_3\text{OH}}$  and  $\tau_{\text{CH}_3\text{OH},[\text{HAE}]^+\text{-Cl}^-}$  were regressed with the experimental solubilities of aniline hydrochloride in the ternary [HAE]Cl–CH<sub>3</sub>OH–H<sub>2</sub>O system by the electrolyte NRTL model embedded in the AspenPlus platform. The resulting parameters are also listed in Table 7. Figure 2 shows the comparison of the calculated and experimental solubility for the ternary system over the temperature range from 288 K to 328 K. As shown in Figure 2, the calculated solubility data agree well with the experimental values with the average relative deviation (ARD) of 1.2 % and the maximum relative deviation (MRD) 3.2 %. Figure 5 shows the relative deviations between experimental and

**Table 5.** Experimental SLE Data for [HAE]Cl (1) in Ternary Mixed Solvent Systems for Molality  $m$  and Mole Fraction  $x$  at Temperature  $T$

$T/\text{K}$	$m/\text{mol}\cdot\text{kg}^{-1}$	$x_1$	$x_2$	$x_3$
CH <sub>3</sub> OH (2)–C <sub>2</sub> H <sub>5</sub> OH (3)–H <sub>2</sub> O (4)				
288.15	5.82	0.153	0.328	0.227
298.15	6.85	0.175	0.320	0.221
308.15	7.80	0.195	0.312	0.216
318.15	9.01	0.218	0.303	0.210
328.15	10.25	0.241	0.294	0.204
CH <sub>3</sub> OH (2)–C <sub>3</sub> H <sub>7</sub> OH (3)–H <sub>2</sub> O (4)				
288.15	5.42	0.152	0.352	0.187
298.15	6.33	0.173	0.343	0.183
308.15	7.23	0.193	0.335	0.178
318.15	8.32	0.216	0.325	0.173
328.15	9.47	0.239	0.316	0.168
C <sub>2</sub> H <sub>5</sub> OH (2)–C <sub>3</sub> H <sub>7</sub> OH (3)–H <sub>2</sub> O (4)				
288.15	5.106	0.162	0.275	0.212
298.15	5.935	0.183	0.268	0.206
308.15	6.605	0.200	0.263	0.202
318.15	7.541	0.222	0.256	0.196
328.15	8.565	0.245	0.248	0.191

**Table 6.** Experimental SLE Data for the System [HAE]Cl (1)–CH<sub>3</sub>OH (2)–C<sub>2</sub>H<sub>5</sub>OH (3)–C<sub>3</sub>H<sub>7</sub>OH (4)–H<sub>2</sub>O (5) for Molality  $m$  and Mole Fraction  $x$  at Temperature  $T$

$T/\text{K}$	$m/\text{mol}\cdot\text{kg}^{-1}$	$x_1$	$x_2$	$x_3$	$x_4$
288.15	6.66	0.155	0.144	0.100	0.077
298.15	7.85	0.178	0.140	0.098	0.075
308.15	8.98	0.198	0.137	0.095	0.073
318.15	10.37	0.222	0.133	0.092	0.071
328.15	11.82	0.246	0.129	0.090	0.069

calculated values. The results show that the excellent performance of the electrolyte NRTL model is evident for the [HAE]Cl–CH<sub>3</sub>OH–H<sub>2</sub>O system.

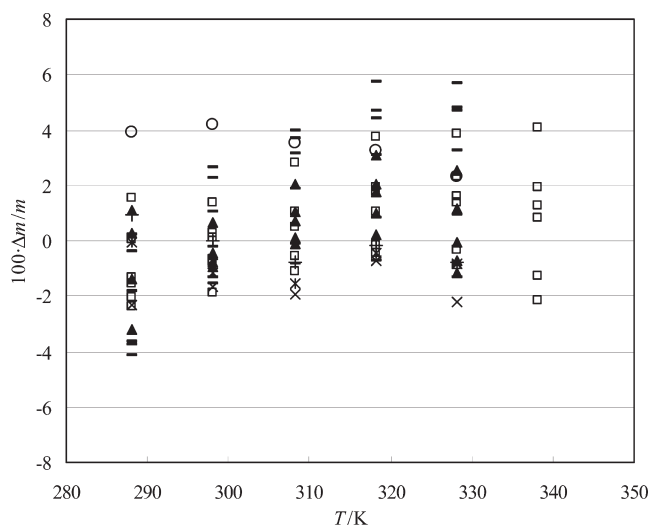
*Interaction between [HAE]Cl and Ethanol.* To allow for a more precise estimation of the chemistry of this system, the interaction parameters for ionic pairs [HAE]<sup>+</sup>:Cl<sup>−</sup>–C<sub>2</sub>H<sub>5</sub>OH and C<sub>2</sub>H<sub>5</sub>OH–[HAE]<sup>+</sup>:Cl<sup>−</sup> were regressed with the experimental solubility data of [HAE]Cl in different concentrations of ethanol solutions. Because the interaction between ethanol and water has been intensively investigated, the interaction parameters for C<sub>2</sub>H<sub>5</sub>OH–H<sub>2</sub>O and H<sub>2</sub>O–C<sub>2</sub>H<sub>5</sub>OH in the AspenPlus's default database were retained. The regressed model results for the solubility of [HAE]Cl in the ternary system are shown in Figure 3. It can be seen that the effect of temperature and ethanol concentration on the solubility of [HAE]Cl can be well depicted by the model with ARD 1.4 % and MRD 3.9 %. The relative deviations between experimental and calculated values were shown in Figure 5. The default and resulting interaction parameters are listed in Table 7.

*Interaction between [HAE]Cl and Propan-1-ol.* The experimental solubility data of [HAE]Cl in propan-1-ol solution were used to regress the interaction parameters for ionic pairs

Table 7. Binary Electrolyte NRTL Interaction Parameters for Different Ionic Pairs

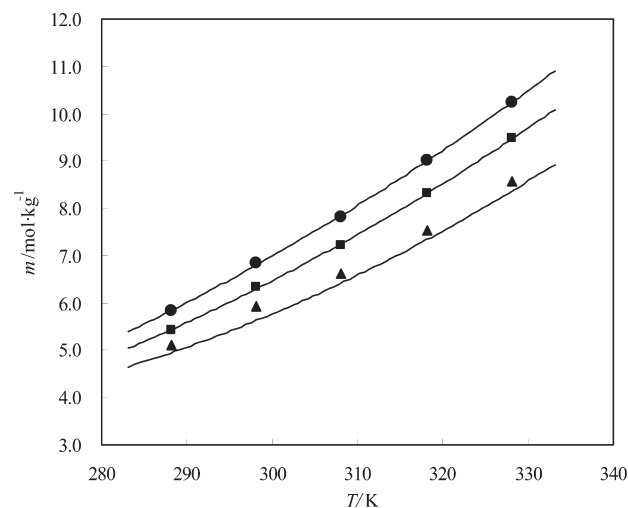
parameter no. <sup>a</sup>	component <i>i</i>	component <i>j</i>	<i>C</i>	<i>D</i>	<i>E</i>	$\alpha_{ij}$
1	[HAE] <sup>+</sup> , Cl <sup>-</sup>	H <sub>2</sub> O	-4.829	130.682	40.625	0.2
2	H <sub>2</sub> O	[HAE] <sup>+</sup> , Cl <sup>-</sup>	14.028	-1852.460	-181.273	0.2
3	[HAE] <sup>+</sup> , Cl <sup>-</sup>	CH <sub>3</sub> OH	-3.713	480.986	683.732	0.2
4	CH <sub>3</sub> OH	[HAE] <sup>+</sup> , Cl <sup>-</sup>	-2.356	589.125	-234.565	0.2
5	[HAE] <sup>+</sup> , Cl <sup>-</sup>	C <sub>2</sub> H <sub>5</sub> OH	-0.356	389.269	461.136	0.2
6	C <sub>2</sub> H <sub>5</sub> OH	[HAE] <sup>+</sup> , Cl <sup>-</sup>	-4.428	831.864	-68.468	0.2
7	[HAE] <sup>+</sup> , Cl <sup>-</sup>	C <sub>3</sub> H <sub>7</sub> OH	3.683	0.084	-0.613	0.2
8	C <sub>3</sub> H <sub>7</sub> OH	[HAE] <sup>+</sup> , Cl <sup>-</sup>	-2.424	0.143	-1.264	0.2
9	CH <sub>3</sub> OH	H <sub>2</sub> O	-2.626	828.387		0.3
10	H <sub>2</sub> O	CH <sub>3</sub> OH	4.824	-1329.544		0.3
11	C <sub>2</sub> H <sub>5</sub> OH	H <sub>2</sub> O	-0.922	284.286		0.3
12	H <sub>2</sub> O	C <sub>2</sub> H <sub>5</sub> OH	3.622	-636.726		0.3
13	C <sub>3</sub> H <sub>7</sub> OH	H <sub>2</sub> O	-1.810	596.958		0.3
14	H <sub>2</sub> O	C <sub>3</sub> H <sub>7</sub> OH	5.509	-879.538		0.3
15	CH <sub>3</sub> OH	C <sub>2</sub> H <sub>5</sub> OH	-3.059	1328.872		0.3
16	C <sub>2</sub> H <sub>5</sub> OH	CH <sub>3</sub> OH	1.939	-877.049		0.3
17	CH <sub>3</sub> OH	C <sub>3</sub> H <sub>7</sub> OH	0.000	91.716		0.3
18	C <sub>3</sub> H <sub>7</sub> OH	CH <sub>4</sub> O	0.000	-72.332		0.3
19	C <sub>2</sub> H <sub>5</sub> OH	C <sub>3</sub> H <sub>7</sub> OH	8.207	-2827.706		0.3
20	C <sub>3</sub> H <sub>7</sub> OH	C <sub>2</sub> H <sub>5</sub> OH	-9.609	3371.329		0.3

<sup>a</sup> Parameters (nos. 1, 2) from literature (ref 12), (nos. 9–20) from the AspenPlus default data bank, and (nos. 3–8) obtained in this work.



**Figure 5.** Relative differences  $\Delta m/m = \{m(\text{exp}) - m(\text{cal})\}/m(\text{cal})$  of the experimental molality solubility  $m$  of [HAE]Cl in different mixed solvent systems, from the value obtained from electrolyte NRTL model (cal) as a function of temperature  $T$ .  $\blacktriangle$ , CH<sub>3</sub>OH–H<sub>2</sub>O;  $\square$ , C<sub>2</sub>H<sub>5</sub>OH–H<sub>2</sub>O;  $-$ , C<sub>3</sub>H<sub>7</sub>OH–H<sub>2</sub>O;  $+$ , CH<sub>3</sub>OH–C<sub>2</sub>H<sub>5</sub>OH–H<sub>2</sub>O;  $*$ , CH<sub>3</sub>OH–C<sub>3</sub>H<sub>7</sub>OH–H<sub>2</sub>O;  $\circ$ , C<sub>2</sub>H<sub>5</sub>OH–C<sub>3</sub>H<sub>7</sub>OH–H<sub>2</sub>O;  $\times$ , CH<sub>3</sub>OH–C<sub>2</sub>H<sub>5</sub>OH–C<sub>3</sub>H<sub>7</sub>OH–H<sub>2</sub>O.

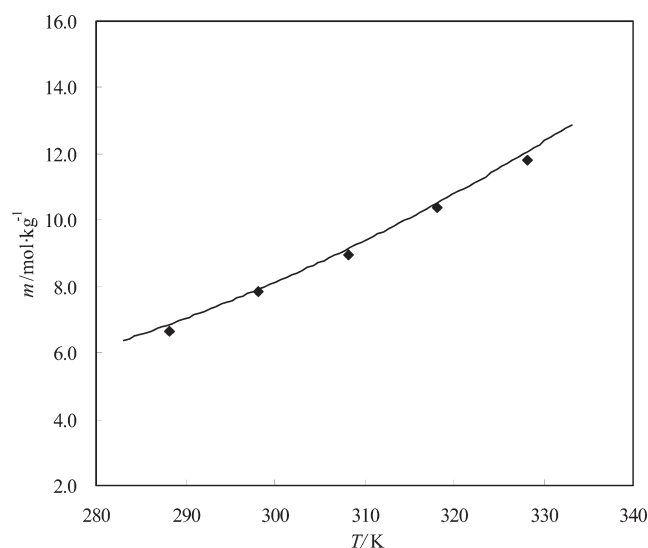
[HAE]<sup>+</sup>:Cl<sup>-</sup>–C<sub>3</sub>H<sub>7</sub>OH and C<sub>3</sub>H<sub>7</sub>OH–[HAE]<sup>+</sup>:Cl<sup>-</sup> to allow for a more precise estimation of the chemistry of this system. The interaction parameters for C<sub>3</sub>H<sub>7</sub>OH–H<sub>2</sub>O and H<sub>2</sub>O–C<sub>3</sub>H<sub>7</sub>OH in the AspenPlus's default database were adopted. The regressed model results for the solubility of [HAE]Cl in the ternary system are shown in Figure 4. It can be seen that the influence of temperature and propan-1-ol concentration



**Figure 6.** Molality solubility  $m$  of [HAE]Cl as a function of temperature  $T$  in different ternary mixed solvent systems:  $\bullet$ , CH<sub>3</sub>OH–C<sub>2</sub>H<sub>5</sub>OH–H<sub>2</sub>O;  $\blacksquare$ , CH<sub>3</sub>OH–C<sub>3</sub>H<sub>7</sub>OH–H<sub>2</sub>O;  $\blacktriangle$ , C<sub>2</sub>H<sub>5</sub>OH–C<sub>3</sub>H<sub>7</sub>OH–H<sub>2</sub>O. Points, experimental data in this work; lines, calculated results.

on the solubility of [HAE]Cl can be well-depicted by the model. The overall ARD is 2.6 %, and the MRD is 5.7 %. The relative deviations between experimental and calculated values are shown in Figure 5. The resulting interaction parameters are listed in Table 7 as well.

**Verification of Parameters.** [HAE]Cl in Ternary Mixed Solvent Systems. To test whether the model parameters obtained perform equally well in a ternary mixed solvent system (not used in model parametrization process), the solubility data of [HAE]Cl in three ternary systems CH<sub>3</sub>OH–C<sub>2</sub>H<sub>5</sub>OH–H<sub>2</sub>O,



**Figure 7.** Comparison of predicted and experimental molality solubility  $m$  of [HAE]Cl in the  $\text{CH}_3\text{OH}-\text{C}_2\text{H}_5\text{OH}-\text{C}_3\text{H}_7\text{OH}-\text{H}_2\text{O}$  system at different temperatures  $T$ . Points, experimental data in this work; lines, predicted results.

$\text{C}_2\text{H}_5\text{OH}-\text{C}_3\text{H}_7\text{OH}-\text{H}_2\text{O}$ , and  $\text{CH}_3\text{OH}-\text{C}_3\text{H}_7\text{OH}-\text{H}_2\text{O}$  were predicted in the temperature range of 288 K to 328 K. The binary interaction parameters for any two different alcohols obtained from AspenPlus's default database are listed in Table 7. The compositions of the predicted ternary mixed solvent systems are the same with experimental systems. To show the overall prediction performance, the predicted and the experimental solubilities are compared and plotted in Figure 6. For systems  $\text{CH}_3\text{OH}-\text{C}_2\text{H}_5\text{OH}-\text{H}_2\text{O}$ ,  $\text{C}_2\text{H}_5\text{OH}-\text{C}_3\text{H}_7\text{OH}-\text{H}_2\text{O}$ , and  $\text{CH}_3\text{OH}-\text{C}_3\text{H}_7\text{OH}-\text{H}_2\text{O}$ , the MRD is 0.9 %, 1.2 %, and 4.2 %, and the ARD is 0.5 %, 0.8 %, and 3.4 %, respectively. The relative deviations between experimental and calculated values are shown in Figure 5. The results indicate that the electrolyte NRTL model is applicable for the systems studied, since the deviation is basically evenly occurred in all systems and no data points show extra deviations in Figure 5. The good agreement obtained is an indication that the new parameters can represent the solubility of [HAE]Cl in ternary mixed solvent systems over the temperature range well.

[HAE]Cl in the Quaternary Mixed Solvent System. With the electrolyte NRTL interaction energy parameters newly obtained and previously listed in Table 7, a self-consistent model for the system [HAE]Cl- $\text{CH}_3\text{OH}-\text{C}_2\text{H}_5\text{OH}-\text{C}_3\text{H}_7\text{OH}-\text{H}_2\text{O}$  was totally established. To verify its reliability, the solubility of [HAE]Cl in the  $\text{CH}_3\text{OH}-\text{C}_2\text{H}_5\text{OH}-\text{C}_3\text{H}_7\text{OH}-\text{H}_2\text{O}$  mixed system was predicted out of parametrization without introducing any new parameters. The predicted results were compared with experimental values and are shown in Figure 7. As shown in Figure 7, the MRD was 2.3 %, and the ARD was 1.8 %. The relative deviations between experimental and calculated values are also shown in Figure 5. The good agreement obtained is an indication that the new parameters can represent the solubility of [HAE]Cl in aqueous mixed alcohols containing solutions well.

## CONCLUSIONS

In this work, the solubility of [HAE]Cl was measured in absolute methanol, ethanol, propan-1-ol, and three binary and

ternary mixed solvent systems and one quaternary mixed solvent system  $\text{CH}_3\text{OH}-\text{C}_2\text{H}_5\text{OH}-\text{C}_3\text{H}_7\text{OH}-\text{H}_2\text{O}$  over the temperature range from 288 K to 328 K. New interaction energy parameters  $\tau_{[\text{HAE}]^+-\text{Cl}^-, \text{CH}_3\text{OH}} \tau_{\text{CH}_3\text{OH}, [\text{HAE}]^+-\text{Cl}^-}$ ,  $\tau_{[\text{HAE}]^+-\text{Cl}^-, \text{C}_2\text{H}_5\text{OH}} \tau_{\text{C}_2\text{H}_5\text{OH}, [\text{HAE}]^+-\text{Cl}^-}$  and  $\tau_{[\text{HAE}]^+-\text{Cl}^-, \text{C}_3\text{H}_7\text{OH}} \tau_{\text{C}_3\text{H}_7\text{OH}, [\text{HAE}]^+-\text{Cl}^-}$  were determined with the solubility of [HAE]Cl in the [HAE]Cl- $\text{CH}_3\text{OH}-\text{H}_2\text{O}$ , [HAE]Cl- $\text{C}_2\text{H}_5\text{OH}-\text{H}_2\text{O}$ , and [HAE]Cl- $\text{C}_3\text{H}_7\text{OH}-\text{H}_2\text{O}$  systems by using the electrolyte NRTL model embedded in the AspenPlus platform. With these parameters, a self-consistent model for the system of [HAE]Cl- $\text{CH}_3\text{OH}-\text{C}_2\text{H}_5\text{OH}-\text{C}_3\text{H}_7\text{OH}-\text{H}_2\text{O}$  was totally established. The model could represent the solubilities of [HAE]Cl in the quaternary mixed solvent system  $\text{CH}_3\text{OH}-\text{C}_2\text{H}_5\text{OH}-\text{C}_3\text{H}_7\text{OH}-\text{H}_2\text{O}$  very well. The established self-consistent model proved to be an accurate model for describing the solubility of [HAE]Cl in aqueous mixed alcohols solutions and will provide a thermodynamic basis for the synthesis of complex [HAE]Cl· $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  with the antisolvent crystallization method.

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