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ARTICLE *in* JOURNAL OF CHEMICAL & ENGINEERING DATA · MARCH 2011

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# Modeling of the Ternary $\text{NH}_4\text{Cl} + \text{ROH} + \text{Water}$ Electrolyte Systems (with $\text{R} = \text{Me}$ , $\text{Et}$ , $1\text{-Pr}$ , and $2\text{-Pr}$ ) by the Pitzer–Simonson–Clegg Approach and Its Modified Forms

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**ABSTRACT:** Literature data on electrolyte modeling in nonaqueous and in mixed solvent systems are still relatively scarce. In addition, contrary to the currently used Pitzer ion-interaction approach, modeling of the ternary systems containing electrolyte, nonelectrolyte, and water by the more refined Pitzer–Simonson–Clegg (PSC) ion-interaction approach is limited only to the work of three research groups. In this context, we have recently reported the use of Pitzer and Pitzer–Simonson–Clegg (PSC) ion-interaction approaches for modeling the ternary  $\text{HCl} + \text{ROH} + \text{water}$  electrolyte systems (with  $\text{R} = \text{Me}$ ,  $\text{Et}$ ,  $1\text{-Pr}$ , and  $2\text{-Pr}$ ). The present investigation describes also the results obtained by the application of the simplified PSC, original PSC, and previously reported modified PSC, as well as another proposed modified PSC approach (presented in this work), for modeling the nonideal behavior of the ternary  $\text{NH}_4\text{Cl} + \text{ROH} + \text{water}$  mixture. The calculations were achieved based on the experimental potentiometric data previously obtained in our laboratory. Accordingly, the present calculations were performed for  $\text{NH}_4\text{Cl}$  electrolyte molalities ranging from 0.01 up to about  $4 \text{ mol} \cdot \text{kg}^{-1}$  in several alcohols ( $\text{ROH}$ ) with different percent mass fractions,  $x = (10, 20, 30, 40, \text{ and } 50) \%$ , for  $\text{R} = \text{Me}$ ,  $\text{Et}$ ,  $1\text{-Pr}$ , and up to 30 % for  $2\text{-Pr}$ , at  $(298.15 \pm 0.05) \text{ K}$ .

## INTRODUCTION

After the success of the Pitzer semiempirical virial coefficient approach,<sup>1–4</sup> Pitzer and his co-workers also developed two more refined models for the description of different electrolyte systems. In these models, the solvent is no longer considered as a continuum, but its interaction with ionic and nonionic solutes is explicitly taken into account. Effectively, Pitzer and Simonson (PS) first presented an approach with applicability over the entire concentration range for the investigation of electrolyte systems containing ions of a symmetrical charge type.<sup>5,6</sup> This model was further extended by Clegg, Pitzer, and Brimblecombe to include arbitrary charge type electrolytes and an indefinite number of ionic and neutral species and also by using an extended Debye–Hückel expression (for long-range forces including composition-dependent terms), along with a four-suffix Margules expansion (for short-range forces).<sup>7,8</sup> Unexpectedly, there are still only a limited number of reported studies concerning the application of the latter method, particularly in its complete form, for modeling electrolyte systems.<sup>9–15</sup> In addition, a survey of the literature shows that the reported results, concerning the application of both Pitzer and PSC models, are mainly concerned with electrolytes in aqueous solution, and only a few of these treatments involve electrolytes in mixed solvents.<sup>4,9–28</sup> It is worth mentioning that some authors have even used the simplified version of this second model referred to as the PSC model.<sup>17–23</sup>

This work reports the modeling results of the ternary  $\text{NH}_4\text{Cl} + \text{ROH} + \text{water}$  electrolyte systems (with  $\text{R} = \text{Me}$ ,  $\text{Et}$ ,  $1\text{-Pr}$ , and  $2\text{-Pr}$ ) by simplified PSC,<sup>17–23</sup> original PSC,<sup>7,8</sup> and a modified form of PSC by Hu and Guo<sup>9</sup> as well as by a modified PSC approach proposed in this work. The experimental potentiometric data used in this work were previously obtained in our laboratory.<sup>24–27</sup> Accordingly, the calculations were performed

over a  $\text{NH}_4\text{Cl}$  molality range of 0.01 up to about  $4 \text{ mol} \cdot \text{kg}^{-1}$  and for different alcohols with various alcohol/water percent mass fractions,  $x = (10, 20, 30, 40, \text{ and } 50) \%$ , for  $\text{R} = \text{Me}$ ,  $\text{Et}$ ,  $1\text{-Pr}$ , and up to 30 % for  $2\text{-Pr}$ , at  $(298.15 \pm 0.05) \text{ K}$ .

## METHOD

In 1992, Pitzer and co-workers extended the previous mole fraction based model of Pitzer and Simonson.<sup>5,6</sup> In this extended model known as PCS,<sup>7,8</sup> the excess Gibbs energy per mole is expressed in terms of the contribution of short-range ( $g^S$ ) and long-range ( $g^{\text{DH}}$ ) forces as

$$g^E = g^S + g^{\text{DH}} \quad (1)$$

The mean activity coefficient on the mole fraction scale ( $f_{\pm}^*$ ) is related to the excess Gibbs energy by the following relation

$$\ln(f_{\pm}^*) = \frac{1}{RT} \left( \frac{\partial}{\partial n_i} \sum_i n_i g^E \right)_{T,P} \quad (2)$$

where  $n_i$  is the number of moles of all involved ions present in the system, and other symbols have their usual meanings. The contribution of long-range forces is taken into account by an extended Debye–Hückel expression, known as the Pitzer–Debye–Hückel (PDH) term, including additional ionic strength dependent terms, and a four-suffix Margules expansion is used for the contribution of short-range forces. As a result, for a ternary

Received: July 25, 2010

Accepted: January 3, 2011

Published: January 21, 2011

**Table 1. Molalities ( $m$ ) versus the Corresponding Experimental Potentiometric Mean Activity Coefficients ( $\gamma_{\pm}$ ) for  $\text{NH}_4\text{Cl}^a$  in Various Mass Fractions ( $x$  %) of Methanol ( $x$ ) + Water ( $100 - x$ ) Mixed Solvent Systems, with  $x$  (%) = 10, 20, 30, 40, and 50, at 298.15 K, Taken from Literature<sup>24</sup>**

$m$		$m$		$m$		$m$		$m$	
$\text{mol} \cdot \text{kg}^{-1}$	$\gamma_{\pm}$	$\text{mol} \cdot \text{kg}^{-1}$	$\gamma_{\pm}$	$\text{mol} \cdot \text{kg}^{-1}$	$\gamma_{\pm}$	$\text{mol} \cdot \text{kg}^{-1}$	$\gamma_{\pm}$	$\text{mol} \cdot \text{kg}^{-1}$	$\gamma_{\pm}$
10 % MeOH		20 % MeOH		30 % MeOH		40 % MeOH		50 % MeOH	
0.0015	0.9542	0.0010	0.9592	0.0008	0.9583	0.0007	0.9564	0.000—6	0.9547
0.0035	0.9319	0.0028	0.9326	0.0023	0.9316	0.0022	0.9271	0.0019	0.9241
0.0093	0.8961	0.0074	0.8964	0.0060	0.8960	0.0060	0.8863	0.0050	0.8816
0.0193	0.8596	0.0172	0.8531	0.0148	0.8479	0.0138	0.8385	0.0112	0.8332
0.0295	0.8346	0.0269	0.8254	0.0232	0.8184	0.0213	0.8082	0.0172	0.8014
0.0784	0.7666	0.0742	0.7501	0.0650	0.7371	0.0579	0.7242	0.0472	0.7116
0.1743	0.7033	0.1644	0.6826	0.1444	0.6641	0.1287	0.6457	0.1033	0.6293
0.3570	0.6449	0.3330	0.6209	0.2924	0.5969	0.2615	0.5725	0.2040	0.5532
0.5236	0.6146	0.4882	0.5883	0.4285	0.5611	0.3838	0.5333	0.2939	0.5125
0.8245	0.5811	0.7653	0.5521	0.6725	0.5210	0.6011	0.4895	0.4414	0.4684
1.1426	0.5594	1.0613	0.5279	0.9347	0.4940	0.8312	0.4601	0.6064	0.4357
1.6509	0.5383	1.5282	0.5040	1.3538	0.4669	1.1912	0.4304	0.9366	0.3945
2.2059	0.5247	2.0274	0.4881	1.8079	0.4488	1.5700	0.4102	1.2816	0.3681
2.7177	0.5167	2.4758	0.4783	2.2212	0.4380	1.9048	0.3976	1.6023	0.3513
3.2117	0.5112	2.9031	0.4713	2.6251	0.4306	2.2193	0.3887	1.8994	0.3399
3.6119	0.5078	3.2478	0.4667	2.9476	0.4262	2.4698	0.3830	2.1364	0.3327
3.9139	0.5055	3.5079	0.4636	3.1950	0.4235	2.6569	0.3794	2.3133	0.3282
4.1071	0.5041	3.6754	0.4618	3.3528	0.4221	2.7755	0.3773	2.4249	0.3256
4.2037	0.5035	3.7017	0.4615					2.4425	0.3252

<sup>a</sup> MeOH data<sup>24</sup> were recalculated and some errors corrected.

**Table 2. Molalities ( $m$ ) versus the Corresponding Experimental Potentiometric Mean Activity Coefficients ( $\gamma_{\pm}$ ) for  $\text{NH}_4\text{Cl}$  in Various Mass Fractions ( $x$  %) of Ethanol ( $x$ ) + Water ( $100 - x$ ) Mixed Solvent Systems, with  $x$  (%) = 10, 20, 30, 40, and 50, at 298.15 K, Taken from Literature<sup>25</sup>**

$m$		$m$		$m$		$m$		$m$	
$\text{mol} \cdot \text{kg}^{-1}$	$\gamma_{\pm}$	$\text{mol} \cdot \text{kg}^{-1}$	$\gamma_{\pm}$	$\text{mol} \cdot \text{kg}^{-1}$	$\gamma_{\pm}$	$\text{mol} \cdot \text{kg}^{-1}$	$\gamma_{\pm}$	$\text{mol} \cdot \text{kg}^{-1}$	$\gamma_{\pm}$
10 % EtOH		20 % EtOH		30 % EtOH		40 % EtOH		50 % EtOH	
0.0010	0.9603	0.0008	0.9603	0.0010	0.9511	0.0009	0.9467	0.0006	0.9480
0.0030	0.9349	0.0025	0.9338	0.0027	0.9219	0.0023	0.9157	0.0017	0.9151
0.0081	0.8998	0.0064	0.8988	0.0069	0.8810	0.0059	0.8720	0.0042	0.8715
0.0177	0.8611	0.0154	0.8537	0.0145	0.8380	0.0128	0.8235	0.0097	0.8178
0.0273	0.8355	0.0243	0.8247	0.0221	0.8089	0.0196	0.7910	0.0152	0.7821
0.0747	0.7650	0.0669	0.7485	0.0603	0.7260	0.0521	0.7029	0.0419	0.6853
0.1653	0.7010	0.1526	0.6767	0.1335	0.6500	0.1173	0.6176	0.0957	0.5923
0.3358	0.6417	0.3094	0.6122	0.2758	0.5770	0.2337	0.5409	0.1940	0.5081
0.4927	0.6103	0.4538	0.5777	0.4076	0.5380	0.3379	0.4998	0.2844	0.4623
0.7701	0.5758	0.7051	0.5396	0.6428	0.4940	0.5258	0.4516	0.4412	0.4109
1.0719	0.5524	0.9710	0.5137	0.8928	0.4640	0.7254	0.4178	0.6075	0.3746
1.5397	0.5301	1.3910	0.4871	1.2821	0.4333	1.0392	0.3818	0.8627	0.3363
2.0406	0.5158	1.8367	0.4689	1.6919	0.4120	1.3699	0.3557	1.1309	0.3080
2.4903	0.5076	2.2353	0.4576	2.0559	0.3985	1.6620	0.3385	1.3671	0.2889
2.9202	0.5023	2.6138	0.4497	2.3984	0.3887	1.9364	0.3256	1.5883	0.2742
3.2649	0.4993	2.9178	0.4447	2.6715	0.3824	2.1547	0.3169	1.7639	0.2641
3.5264	0.4976	3.1465	0.4415	2.8757	0.3783	2.3179	0.3111	1.8949	0.2573
3.6928	0.4967	3.2922	0.4398	3.0055	0.3760	2.4213	0.3078	1.9779	0.2534

**Table 3.** Molalities ( $m$ ) versus the Corresponding Experimental Potentiometric Mean Activity Coefficients ( $\gamma_{\pm}$ ) for  $\text{NH}_4\text{Cl}$  in Various Mass Fractions ( $x$  %) of 1-Propanol ( $x$ ) + Water ( $100 - x$ ) Mixed Solvent Systems, with  $x$  (%) = 10, 20, 30, 40, and 50, at 298.15 K, Taken from Literature<sup>26</sup>

$m$		$m$		$m$		$m$		$m$	
mol·kg <sup>-1</sup>	$\gamma_{\pm}$	mol·kg <sup>-1</sup>	$\gamma_{\pm}$	mol·kg <sup>-1</sup>	$\gamma_{\pm}$	mol·kg <sup>-1</sup>	$\gamma_{\pm}$	mol·kg <sup>-1</sup>	$\gamma_{\pm}$
10 % 1-PrOH		20 % 1-PrOH		30 % 1-PrOH		40 % 1-PrOH		50 % 1-PrOH	
0.0009	0.9616	0.0010	0.9552	0.0009	0.9475	0.0008	0.9427	0.0007	0.9335
0.0028	0.9359	0.0029	0.9251	0.0027	0.9143	0.0022	0.9057	0.0020	0.8894
0.0078	0.8990	0.0075	0.8859	0.0071	0.8694	0.0060	0.8542	0.0052	0.8311
0.0178	0.8578	0.0167	0.8409	0.0158	0.8184	0.0136	0.7958	0.0118	0.7649
0.0277	0.8309	0.0259	0.8111	0.0245	0.7848	0.0212	0.7575	0.0183	0.7221
0.0768	0.7573	0.0720	0.7284	0.0674	0.6928	0.0598	0.6513	0.0506	0.6059
0.1713	0.6904	0.1622	0.6522	0.1510	0.6082	0.1340	0.5567	0.1131	0.5027
0.3480	0.6286	0.3315	0.5814	0.3090	0.5288	0.2726	0.4700	0.2283	0.4105
0.5067	0.5961	0.4876	0.5432	0.4550	0.4856	0.3998	0.4234	0.3362	0.3607
0.7920	0.5589	0.7645	0.4994	0.7172	0.4354	0.6254	0.3701	0.5270	0.3048
1.0966	0.5334	1.0592	0.4687	0.8252	0.4201	0.8600	0.3332	0.7279	0.2664
1.5789	0.5075	1.5232	0.4360	1.3125	0.3707	1.2290	0.2932	1.0428	0.2256
2.0946	0.4898	2.0075	0.4124	1.8319	0.3365	1.6200	0.2635	1.3806	0.1954
2.5574	0.4791	2.4444	0.3962	2.2863	0.3147			1.6735	0.1756
3.0053	0.4715	2.8617	0.3836	2.7092	0.2984			1.9542	0.1603
3.3634	0.4669	3.1963	0.3750	3.0433	0.2875			2.1733	0.1501
3.6320	0.4641	3.4467	0.3691	3.2914	0.2802			2.3403	0.1431
3.8012	0.4625			3.4482	0.2759				

**Table 4.** Molalities ( $m$ ) versus the Corresponding Experimental Potentiometric Mean Activity Coefficients ( $\gamma_{\pm}$ ) for  $\text{NH}_4\text{Cl}$  in Various Mass Fractions ( $x$  %) of 2-Propanol ( $x$ ) + Water ( $100 - x$ ) Mixed Solvent Systems, with  $x$  (%) = 10, 20, and 30, at 298.15 K, Taken from Literature<sup>27</sup>

$m$		$m$		$m$	
mol·kg <sup>-1</sup>	$\gamma_{\pm}$	mol·kg <sup>-1</sup>	$\gamma_{\pm}$	mol·kg <sup>-1</sup>	$\gamma_{\pm}$
10 % 1-PrOH		20 % 1-PrOH		30 % 1-PrOH	
0.0009	0.9611	0.0009	0.9555	0.0009	0.9478
0.0027	0.9361	0.0028	0.9248	0.0026	0.9136
0.0068	0.9035	0.0072	0.8858	0.0070	0.8671
0.0162	0.8614	0.0164	0.8390	0.0153	0.8166
0.0256	0.8339	0.0256	0.8085	0.0236	0.7832
0.0718	0.7595	0.0676	0.7295	0.0667	0.6876
0.1593	0.6924	0.1513	0.6533	0.1485	0.6021
0.3242	0.6292	0.3048	0.5830	0.3060	0.5205
0.4780	0.5946	0.4468	0.5440	0.4453	0.4777
0.7504	0.5556	0.6972	0.4990	0.7185	0.4237
1.0487	0.5282	0.9693	0.4661	1.0049	0.3869
1.5125	0.5004	1.3995	0.4302	1.4459	0.3489
1.9831	0.4819	1.8642	0.4029	1.9099	0.3218
2.4218	0.4698	2.2865	0.3838	2.3195	0.3044
2.8249	0.4614	2.6853	0.3689		
3.1743	0.4557	3.0218	0.3580		

system containing one electrolyte (MX), neutral solute (n), and water (1), the final PSC model equation for  $\ln(f_{\pm}^*)$  is obtained by summing the contribution of both long-range and short-range

contributions<sup>7-9</sup>

$$\begin{aligned} \ln(f_{\pm}^*) = & -A_X \left[ \frac{2}{\rho} \ln(1 + \rho I_X^{1/2}) + I_X^{1/2}((1 - 2I_X) \right. \\ & \left. / (1 + \rho I_X^{1/2})) \right] + (I_X/2) B_{MX} [g(\alpha I_X^{1/2}) \\ & + \exp(-\alpha I_X^{1/2})(1 - x_1)] + (1 - x_1)(x_1 W_{IMX} \\ & + x_n W_{IMX}) + 2x_1(1 - x_1)\{x_1 U_{IMX} + x_n U_{IMX}\} \\ & + x_1(2 - 3x_1)\{x_1^2 V_{IMX} + x_n^2 V_{IMX}\} \\ & + x_1 x_n(1 - 2x_1) Y_{InMX} - x_1 x_n [w_{1n} \\ & + 2(x_1 - x_n) u_{1n}] - W_{IMX} \end{aligned} \quad (3)$$

with

$$g(\alpha I_X^{1/2}) = 2[1 - (1 + \alpha I_X^{1/2}) \exp(-\alpha I_X^{1/2})] / (\alpha^2 I_X) \quad (4)$$

In eq 3,  $A_X = 2.9168$  is the Debye–Hückel parameter,  $\rho = 14.0292$  is the empirical “closest approach” distance parameter (fixed to a constant value without units),  $I_X$  is the ionic strength, and  $\alpha = 13$  is a Pitzer constant parameter. In this equation, all parameters are defined on the mole-fraction basis,<sup>7,8</sup> and  $B_{MX}$  is a Pitzer–Debye–Hückel (PDH) parameter for a MX electrolyte.

The other parameters are:

- $x_1$ ,  $x_n$ , and  $x_n$ : total ion mole fraction, water mole fraction, and neutral species mole fraction, respectively.
- $W_{IMX}$ ,  $V_{IMX}$ , and  $U_{IMX}$ : different ternary short-range PSC interaction parameters related to the electrolyte MX in water (1).
- $W_{IMX}$ ,  $V_{IMX}$ ,  $U_{IMX}$ , and  $Y_{InMX}$ : different ternary and quaternary short-range PSC interaction parameters involving also the neutral species (n).

**Table 5. Evaluated Short-Range Parameters for the Simplified PSC, Original PSC, Modified Hu and Guo PSC (Including  $b$  and  $c$  Parameters<sup>9</sup>), and Proposed PSC in Modeling the Ternary  $\text{NH}_4\text{Cl} + \text{MeOH} + \text{H}_2\text{O}$  System with Various MeOH Percent Mass Fractions:  $x$  (%) = 10, 20, 30, 40, and 50, at 298.15 K**

model	$W_{\text{nMX}}$	$U_{\text{nMX}}$	$V_{\text{nMX}}$	$b$	$c$	$Y_{\text{1nMX}}^{(0)}$	$Y_{\text{1nMX}}^{(1)}$	$\sigma$ (rmsd)
simplified PSC	3.5723	-3.3176	-38.3797					0.0345 <sup>a</sup>
PSC	3.1844	-3.9931	-34.0201			0.5472		0.0340 <sup>b</sup>
modified PSC	3.8541	-12.4055	63.1805	1.25	1/2	-71.8771	92.8181	0.0070 <sup>c</sup>
proposed PSC	2.4443	-0.2337	-9.6743			2.0059		0.0105 <sup>d</sup>

<sup>a</sup> Simplified PSC model:  $Y_{\text{1nMX}} = Y_{\text{1nMX}}^{(0)} = Y_{\text{1nMX}}^{(1)} = 0$ . <sup>b</sup> PSC model:  $Y_{\text{1nMX}} = Y_{\text{1nMX}}^{(0)}$  and  $Y_{\text{1nMX}}^{(1)} = 0$ . <sup>c</sup> Modified PSC model:  $Y_{\text{1nMX}} = X_{\text{n}}^{1.25} - I_{\text{X}}^{1/2} Y_{\text{1nMX}}^{(0)} + I_{\text{X}}^2 Y_{\text{1nMX}}^{(1)}$ . <sup>d</sup> Proposed PSC model:  $Y_{\text{1nMX}} = \exp(-\alpha I_{\text{X}}^{1/2}) Y_{\text{1nMX}}^{(0)}$ .

**Table 6. Evaluated Short-Range Parameters for the Simplified PSC, Original PSC, Modified Hu and Guo PSC (Including  $b$  and  $c$  Parameters<sup>9</sup>), and Proposed PSC in Modeling the Ternary  $\text{NH}_4\text{Cl} + \text{EtOH} + \text{H}_2\text{O}$  System with Various EtOH Percent Mass Fractions:  $x$  (%) = 10, 20, 30, 40, and 50, at 298.15 K**

model	$W_{\text{nMX}}$	$U_{\text{nMX}}$	$V_{\text{nMX}}$	$b$	$c$	$Y_{\text{1nMX}}^{(0)}$	$Y_{\text{1nMX}}^{(1)}$	$\sigma$ (rmsd)
simplified PSC	4.2952	2.2905	-155.1304					0.0340 <sup>a</sup>
PSC	3.0792	-0.3352	-136.4967			1.5952		0.0332 <sup>b</sup>
modified PSC	5.0507	-22.7824	24.7589	1	1/4	-28.6455	343.4602	0.0051 <sup>c</sup>
proposed PSC	2.3930	1.1874	-52.1772			3.0744		0.0071 <sup>d</sup>

<sup>a</sup> Simplified PSC model:  $Y_{\text{1nMX}} = Y_{\text{1nMX}}^{(0)} = Y_{\text{1nMX}}^{(1)} = 0$ . <sup>b</sup> PSC model:  $Y_{\text{1nMX}} = Y_{\text{1nMX}}^{(0)}$  and  $Y_{\text{1nMX}}^{(1)} = 0$ . <sup>c</sup> Modified PSC model:  $Y_{\text{1nMX}} = X_{\text{n}}^{1.25} - I_{\text{X}}^{1/2} Y_{\text{1nMX}}^{(0)} + I_{\text{X}}^2 Y_{\text{1nMX}}^{(1)}$ . <sup>d</sup> Proposed PSC model:  $Y_{\text{1nMX}} = \exp(-\alpha I_{\text{X}}^{1/2}) Y_{\text{1nMX}}^{(0)}$ .

**Table 7. Evaluated Short-Range Parameters for the Simplified PSC, Original PSC, Modified Hu and Guo PSC (Including  $b$  and  $c$  Parameters<sup>9</sup>), and Proposed PSC in Modeling the Ternary  $\text{NH}_4\text{Cl} + 1\text{-PrOH} + \text{H}_2\text{O}$  System with Various 1-PrOH Percent Mass Fractions:  $x$  (%) = 10, 20, 30, 40, and 50, at 298.15 K**

model	$W_{\text{nMX}}$	$U_{\text{nMX}}$	$V_{\text{nMX}}$	$b$	$c$	$Y_{\text{1nMX}}^{(0)}$	$Y_{\text{1nMX}}^{(1)}$	$\sigma$ (rmsd)
simplified PSC	5.2785	-26.3499	-115.3581					0.0519 <sup>a</sup>
PSC	2.1060	-28.7373	-80.0296			3.8948		0.0495 <sup>b</sup>
modified PSC	6.4620	-67.2150	352.5755	3/4	1/4	-38.0369	543.0395	0.0323 <sup>c</sup>
proposed PSC	2.0445	-27.6934	175.1956			4.7734		0.0332 <sup>d</sup>

<sup>a</sup> Simplified PSC model:  $Y_{\text{1nMX}} = Y_{\text{1nMX}}^{(0)} = Y_{\text{1nMX}}^{(1)} = 0$ . <sup>b</sup> PSC model:  $Y_{\text{1nMX}} = Y_{\text{1nMX}}^{(0)}$  and  $Y_{\text{1nMX}}^{(1)} = 0$ . <sup>c</sup> Modified PSC model:  $Y_{\text{1nMX}} = X_{\text{n}}^{1.25} - I_{\text{X}}^{1/2} Y_{\text{1nMX}}^{(0)} + I_{\text{X}}^2 Y_{\text{1nMX}}^{(1)}$ . <sup>d</sup> Proposed PSC model:  $Y_{\text{1nMX}} = \exp(-\alpha I_{\text{X}}^{1/2}) Y_{\text{1nMX}}^{(0)}$ .

- $w_{\text{1n}}$  and  $u_{\text{1n}}$ : binary interaction parameters related to the Margules coefficients for the system containing water (1) and neutral species (n).

The standard state associated with the solvent (water) is its pure state (e.g.,  $\gamma_1 \rightarrow 1$  as  $x_1 \rightarrow 1$ ), and the standard state taken for neutral and ionic solutes (i) are their infinitely dilute aqueous solutions (e.g.,  $\gamma_i \rightarrow 1$  as  $x_i \rightarrow 0$ ), both states considered at the system temperature and pressure.<sup>5-9</sup> To convert the mole fraction based activity coefficient  $f_i^*$  to the molal-based activity coefficient ( $\gamma_i$ ), the following relation was used

$$f_i^* = \gamma_i (1 + (M_1/1000) \sum_i m_i) \quad (5)$$

where  $\gamma_i$ ,  $M_1$ , and  $m_i$  are the molal activity coefficient, the molar mass of the solvent (water), and the molal concentration of the solute ionic species  $i$ , respectively.

In this work, the simplified PSC, original PSC, and modified form of PSC reported by Hu and Guo,<sup>9</sup> as well as another modified PSC approach proposed herein, were all used for modeling the mixture of  $\text{NH}_4\text{Cl}$  (as ionic solute), ROH (as neutral solute), and water (as solvent). The final model parametrization was each time achieved by fitting the potentiometric

experimental data to the related PSC model equation. Finally, the following relation (or the root of mean square deviation) was used for the estimation of the regression quality of the corresponding fit

$$\sigma = \left[ \frac{1}{N-1} \sum_N (\gamma_{\pm, \text{Th}} - \gamma_{\pm, \text{exp}})^2 \right]^{1/2} \quad (6)$$

where  $N$  is the number of experimental data.

## RESULTS

The determination of the long and short-range interaction parameters for the binary  $\text{NH}_4\text{Cl} + \text{water}$  system was based on the available experimental published data.<sup>28</sup> On the basis of a regression up to  $4 \text{ mol} \cdot \text{kg}^{-1}$ , the resulting parameter values were found to be  $B_{\text{MX}} = 5.6958$ ,  $W_{\text{1MX}} = 3.6514$ ,  $U_{\text{1MX}} = 12.3340$ , and  $V_{\text{1MX}} = -7.8314$  (with  $\sigma = 3.10^{-4}$ ), respectively. The binary interaction parameters ( $w_{\text{1n}}$  and  $u_{\text{1n}}$ ) related to the Margules coefficients for the system containing water (1) and alcohol ( $n = \text{MeOH}$ , and  $\text{EtOH}$ ,<sup>29</sup>  $n = 1\text{-PrOH}$ ,<sup>30</sup> and  $n = 2\text{-PrOH}$ <sup>31</sup>) were also taken from the literature. Using these binary parameters, the ternary short-range PSC interaction parameters ( $W_{\text{1MX}}$ ,  $V_{\text{1MX}}$ ,



**Table 8. Evaluated Short-Range Parameters for the Simplified PSC, Original PSC, Modified Hu and Guo PSC (Including  $b$  and  $c$  Parameters<sup>9</sup>), and Proposed PSC in Modeling the Ternary  $\text{NH}_4\text{Cl} + 2\text{-PrOH} + \text{H}_2\text{O}$  System with Various 2-PrOH Percent Mass Fractions:  $x$  (%) = 10, 20, and 30, at 298.15 K**

model	$W_{\text{nMX}}$	$U_{\text{nMX}}$	$V_{\text{nMX}}$	$b$	$c$	$Y_{\text{InMX}}^{(0)}$	$Y_{\text{InMX}}^{(1)}$	$\sigma$ (rmsd)
simplified PSC	5.21151	-30.1249	-222.763					0.0259 <sup>a</sup>
PSC	2.445752	-29.8507	-192.414			3.06028		0.0257 <sup>b</sup>
modified PSC	6.389052	-42.8722	129.5624	1/2	1/4	-26.6893	255.8691	0.0037 <sup>c</sup>
proposed PSC	2.49705	-20.0778	-45.2697			3.791541		0.0042 <sup>d</sup>

<sup>a</sup> Simplified PSC model:  $Y_{\text{InMX}} = Y_{\text{InMX}}^{(0)} = Y_{\text{InMX}}^{(1)} = 0$ . <sup>b</sup> PSC model:  $Y_{\text{InMX}} = Y_{\text{InMX}}^{(0)}$  and  $Y_{\text{InMX}}^{(1)} = 0$ . <sup>c</sup> Modified PSC model:  $Y_{\text{InMX}} = X_{\text{n}}^{1.25} \cdot I_{\text{X}}^{1/2} Y_{\text{InMX}}^{(0)} + I_{\text{X}}^2 Y_{\text{InMX}}^{(1)}$ . <sup>d</sup> Proposed PSC model:  $Y_{\text{InMX}} = \exp(-\alpha I_{\text{X}}^{1/2}) Y_{\text{InMX}}^{(0)}$ .

$U_{\text{InMX}}$  and  $Y_{\text{InMX}} = Y_{\text{InMX}}^{(0)}$  were then calculated in this work by regression for each series of experimental data containing different alcohols (with ROH/water mass fraction content  $x = (10 \text{ to } 50) \%$  for  $R = \text{Me, Et, and } 1\text{-Pr}$  and  $x = (10 \text{ to } 30) \%$  for  $R = 2\text{-Pr}$ ), as reported in Tables 1 to 4. The same calculations were also repeated by using the modified composition dependent form of the  $Y_{\text{InMX}}$  parameter proposed by Hu and Guo<sup>9</sup> ( $Y_{\text{InMX}} = Y_{\text{InMX}}^{(0)} x_{\text{n}}^b I_{\text{x}}^c + Y_{\text{InMX}}^{(1)} I_{\text{x}}^2$ , where  $b$  and  $c$  are the related constant parameters), as well as by using a modified composition-dependent form of the  $Y_{\text{InMX}}$  parameter proposed in this work ( $Y_{\text{InMX}} = e^{(-\alpha I_{\text{x}}^{0.5})} Y_{\text{InMX}}^{(0)}$ ). Tables 5 to 8 contain all calculated model parameters corresponding to the simplified PSC ( $Y_{\text{InMX}} = 0$ ), original PSC ( $Y_{\text{InMX}} = Y_{\text{InMX}}^{(0)}$ ), modified Hu and Guo PSC, and modified PSC proposed in this work ( $Y_{\text{InMX}} = e^{(-\alpha I_{\text{x}}^{0.5})} Y_{\text{InMX}}^{(0)}$ ).

## CONCLUSION

In this work, the resulting value of the binary and ternary model parameters associated with the simplified PSC, original PSC, Hu and Guo modified PSC (involving a composition-dependent form of the  $Y_{\text{InMX}}$  parameter), and a proposed PSC concerning the ternary  $\text{NH}_4\text{Cl} + \text{ROH} + \text{water}$  electrolyte system were determined and compared. As a result, the evaluated values of the simplified PSC parameters ( $W_{\text{nMX}}$ ,  $V_{\text{nMX}}$ ,  $U_{\text{nMX}}$ , and  $Y_{\text{InMX}} = 0$ ), original PSC parameters ( $W_{\text{nMX}}$ ,  $V_{\text{nMX}}$ ,  $U_{\text{nMX}}$ , and  $Y_{\text{InMX}} = Y_{\text{InMX}}^{(0)}$ ), modified PSC interactions parameters ( $W_{\text{nMX}}$ ,  $V_{\text{nMX}}$ ,  $U_{\text{nMX}}$ , and  $Y_{\text{InMX}} = Y_{\text{InMX}}^{(0)} x_{\text{n}}^b I_{\text{x}}^c + Y_{\text{InMX}}^{(1)} I_{\text{x}}^2$ ), and proposed PSC parameters ( $W_{\text{nMX}}$ ,  $V_{\text{nMX}}$ ,  $U_{\text{nMX}}$ , and  $Y_{\text{InMX}} = e^{(-\alpha I_{\text{x}}^{0.5})} Y_{\text{InMX}}^{(0)}$ ) for the ternary electrolyte system containing different ROH and various mass fractions were reported at 298.15 K.

The comparison of the results presented in Tables 5 to 8 shows that the best results (with lowest  $\sigma$  values) are obtained by the Hu and Guo modified PSC (involving additional  $b$  and  $c$  parameters). The second-best results are those obtained by the modified PSC approach proposed in this work. However, it is interesting to note that these slightly higher  $\sigma$  values are obtained in the absence of any additional parameters in the  $Y_{\text{InMX}}$  form proposed in this work. It should also be noted that the results obtained by Hu and Guo,<sup>9</sup> Ferreira et al.,<sup>10,11</sup> and our recently reported results,<sup>12–15</sup> as well as those obtained in this work, all confirm the necessity of using a modified composition-dependent  $Y_{\text{InMX}}$  form, to obtain a better quality of fit of the experimental data. Finally, it can be concluded that both the PSC and the modified PSC models (proposed in this work) are able to correlate conveniently the experimental data with less parameters than the currently used Pitzer model.<sup>24–27</sup> Accordingly, for each series of investigated  $\text{NH}_4\text{Cl} + \text{ROH}$  ( $x \%$ ) + water [(100 -  $x$ ) %] electrolyte system, five PSC parameters compared to

15 Pitzer parameters [ $\beta^{(0)}$ ,  $\beta^{(1)}$ , and  $C^{(\phi)}$  for all percent mass fractions  $x = (10, 20, 30, 40, \text{ and } 50) \%$ ], are needed, respectively, for their modeling at (298.15  $\pm$  0.05) K.

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### Funding Sources

The author acknowledges and is grateful to the Research Vice-Presidency of Shahid Beheshti University for financial support.

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