

# Measurement and Prediction of Vapor-Liquid Equilibrium of Aqueous 1-Ethyl-3-methylimidazolium-Based Ionic Liquid Systems

Luke D. Simoni, Lindsay E. Ficke, Caitlin A. Lambert, Mark A. Stadtherr, and Joan F. Brennecke\*

Department of Chemical and Biomolecular Engineering, University of Notre Dame, Notre Dame, IN 46556

\* Corresponding author. Telephone: (574)631-5847. Fax: (574)631-8366. E-mail: jfb@nd.edu.

## Supporting Information

Supporting information includes detailed expressions for the NRTL, UNIQUAC and eNRTL models.

## Molecular Models (NRTL and UNIQUAC)

Two of the models used in this work to represent the nonideality of the IL (1) + water (2) solutions are molecular models that assume the salts present are completely associated. In other words, each cation is completely paired with an anion, and that pair is considered a single molecular species in the solution. If the reference states are pure liquids of both components at system  $T$  and  $P$ , then for the NRTL model the  $H^E$  and  $\gamma_2^\infty$  expressions for a binary system of IL (1) + water (2) are:

$$H^E = x_1 x_2 \left( \frac{\Delta g_{21} G_{21} (x_1 + x_2 G_{21} - x_1 \alpha_{21} \tau_{21})}{(x_1 + x_2 G_{21})^2} + \frac{\Delta g_{12} G_{12} (x_2 + x_1 G_{12} - x_2 \alpha_{12} \tau_{12})}{(x_2 + x_1 G_{12})^2} \right), \quad (\text{SI1})$$

$$\ln \gamma_2^\infty = \tau_{12} + \tau_{21} G_{21}, \quad (\text{SI2})$$

$$G_{ij} = \exp(-\alpha_{ij} \tau_{ij}) \quad (\text{SI3})$$

and

$$\tau_{ij} = \frac{g_{ij} - g_{jj}}{RT} = \frac{\Delta g_{ij}}{RT}. \quad (\text{SI4})$$

$\Delta g_{ij}$  is an energy parameter characterizing the energetic interaction of species  $i$  and  $j$ , and  $\alpha_{12} = \alpha_{21} = \alpha$  is a constant related to the nonrandomness of the mixture. In this work we use the common value of  $\alpha = 0.3$  for VLE.<sup>1</sup> The binary interaction parameters  $\Delta g_{ij} = \Delta \theta_{ij}$  are estimated from experimental data using eq 1. For the VLE predictions, the activity coefficient of water (2) is

$$\ln \gamma_2 = x_1^2 \left[ \tau_{12} \left( \frac{G_{12}}{x_2 + x_1 G_{12}} \right)^2 + \frac{\tau_{21} G_{21}}{(x_1 + x_2 G_{21})^2} \right]. \quad (\text{SI5})$$

For the UNIQUAC model, the expressions for  $H^E$  and  $\gamma_2^\infty$  are:

$$H^E = H_{\text{comb}}^E + H_{\text{res}}^E, \quad (\text{SI6})$$

$$\ln \gamma_2^\infty = \ln \gamma_{2,\text{comb}}^\infty + \ln \gamma_{2,\text{res}}^\infty, \quad (\text{SI7})$$

$$H_{\text{res}}^E = \frac{q_1 x_1 \theta_2 \Delta u_{21} \tau_{21}}{\theta_1 + \theta_2 \tau_{21}} + \frac{q_2 x_2 \theta_1 \Delta u_{12} \tau_{12}}{\theta_1 \tau_{12} + \theta_2}, \quad (\text{SI8})$$

$$\ln \gamma_{2,\text{comb}}^\infty = \ln \frac{r_2}{r_1} + 5q_2 \ln \frac{q_2 r_1}{q_1 r_2} + s_2 - s_1 \frac{r_2}{r_1}, \quad (\text{SI9})$$

$$\ln \gamma_{2,\text{res}}^\infty = q_2 [1 - \ln \tau_{12} - \tau_{21}], \quad (\text{SI10})$$

$$\theta_i = \frac{q_i x_i}{q_1 x_1 + q_2 x_2}, \quad i \in \{1, 2\}, \quad (\text{SI11})$$

$$s_i = 5(r_i - q_i) + 1 - r_i, \quad i \in \{1, 2\} \quad (\text{SI12})$$

and

$$\tau_{ij} = \exp \left( \frac{-\Delta u_{ij}}{RT} \right). \quad (\text{SI13})$$

Here,  $q_i$  represents the dimensionless surface area for component  $i$ ,  $r_i$  is the dimensionless volume of component  $i$  and  $H_{\text{comb}}^E = 0$  since there is no temperature dependence in the combinatorial contribution. The dimensionless size ( $r_i$ ) and shape ( $q_i$ ) of the ILs were estimated using the methods described in recent publications.<sup>2-4</sup> Table S1 contains the values of  $r_i$  and  $q_i$  used for the systems studied here. The binary interaction parameters  $\Delta u_{ij} = \Delta \theta_{ij}$  were estimated from experimental data using eq 1. For the VLE predictions, the activity coefficient of water is:

$$\ln \gamma_2 = \ln \gamma_{2,\text{comb}} + \ln \gamma_{2,\text{res}}, \quad (\text{SI14})$$

$$\ln \gamma_{2,\text{comb}} = \ln \frac{\phi_2}{x_2} + 5q_2 \ln \frac{\theta_2}{\phi_2} + s_2 - \frac{\phi_2}{x_2} (x_1 s_1 + x_2 s_2), \quad (\text{SI15})$$

$$\ln \gamma_{2,\text{res}} = q_2 \left[ 1 - \ln(\theta_1 \tau_{12} + \theta_2) - \left( \frac{\theta_1 \tau_{21}}{\theta_1 + \theta_2 \tau_{21}} + \frac{\theta_2}{\theta_1 \tau_{12} + \theta_2} \right) \right] \quad (\text{SI16})$$

and

$$\phi_i = \frac{r_i x_i}{r_1 x_1 + r_2 x_2}, \quad i \in \{1, 2\}. \quad (\text{SI17})$$

### Electrolyte Model (eNRTL)

Chen et al. originally formulated the eNRTL model consisting of a Pitzer extended Debye-Hückel expression,  $G_{\text{PDH}}^{\text{E}*}$ , for the long range electrostatic contribution<sup>5</sup> and an NRTL-type local composition contribution,  $G_{\text{LC}}^{\text{E}*}$ , for the short range interactions,<sup>6</sup> such that  $G^{\text{E}*} = G_{\text{PDH}}^{\text{E}*} + G_{\text{LC}}^{\text{E}*}$ . The asterisks in the previous expression denote an unsymmetric reference state for the salt components. Furthermore, this model operates under the assumption that all electrolyte components are completely dissociated in solution, such that

$$\text{Salt}_i \rightarrow \nu_{i,+} \text{Cation}_i^{z_{i,+}} + \nu_{i,-} \text{Anion}_i^{z_{i,-}}. \quad (\text{SI18})$$

If salt  $i$  is an IL, then the stoichiometric coefficients and valencies of the ions are  $\nu_{i,+} = 1$ ,  $\nu_{i,-} = 1$ ,  $z_{i,+} = 1$  and  $z_{i,-} = 1$  respectively.

Previously, we renormalized the eNRTL model so that the electrolyte reference states were dissociated salts as pure liquids at the  $T$  and  $P$  of the system in question, which is a symmetric reference state ( $G^{\text{E}} = G_{\text{PDH}}^{\text{E}} + G_{\text{LC}}^{\text{E}}$ ).<sup>1,7</sup> Clearly, this is more practical for systems containing electrolytes that are liquid (pure fused salt) at the  $T$  and  $P$  of the systems in question, like ILs. Therefore, from eqs 2 and 3,

$$H^{\text{E}} = H_{\text{PDH}}^{\text{E}} + H_{\text{LC}}^{\text{E}} \quad (\text{SI19})$$

and

$$\ln \gamma_2^\infty = \ln \gamma_{2,\text{PDH}}^\infty + \ln \gamma_{2,\text{LC}}^\infty. \quad (\text{SI20})$$

For each contribution, we obtain  $H^E$  and  $\gamma_2^\infty$  for a 1:1 valence electrolyte (IL) as follows.

$$H_{\text{PDH}}^E = \frac{40RT^2}{\rho} \sqrt{\frac{10}{M_2}} y_\pm \ln \left( \frac{1 + \rho \sqrt{y_\pm}}{1 + \rho/\sqrt{2}} \right) \left( \frac{\partial A_\phi}{\partial T} \right)_{P,x}, \quad (\text{SI21})$$

$$A_\phi = \frac{1}{3} \sqrt{\frac{2\pi N_A d_2}{1000}} \left( \frac{e^2}{\epsilon_0 \epsilon_2 k_B T} \right)^{3/2}, \quad (\text{SI22})$$

$$H_{\text{LC}}^E = 2y_\pm y_2 \left[ \frac{y_2 \alpha_{21} \Delta g_{21} \tau_{21} G_{21}^2 - (\alpha_{21} \Delta g_{21} \tau_{21} G_{21} - \Delta g_{21} G_{21})(y_\pm + y_2 G_{21})}{(y_\pm + y_2 G_{21})^2} \right. \\ \left. \dots + \frac{2y_\pm \alpha_{12} \Delta g_{12} \tau_{12} G_{12}^2 - (\alpha_{12} \Delta g_{12} \tau_{12} G_{12} - \Delta g_{12} G_{12})(2y_\pm G_{12} + y_2)}{(2y_\pm G_{12} + y_2)^2} \right], \quad (\text{SI23})$$

$$\ln \gamma_{2,\text{PDH}}^\infty = \frac{2\sqrt{1000/M_2} A_\phi \left( \frac{1}{2} \right)^{3/2}}{1 + \rho \sqrt{1/2}} \quad (\text{SI24})$$

and

$$\ln \gamma_{2,\text{LC}}^\infty = 2\tau_{21} G_{21} + \tau_{12}, \quad (\text{SI25})$$

where  $y_i$  denotes the *actual* mole fraction of species  $i$  in the hypothetical solution assuming complete ionic dissociation. On the other hand,  $x_i$  is the *observable* (apparent) mole fraction of component  $i$ . For a quantity associated with salt  $i$  ( $\zeta_i$ ) the corresponding mean ionic quantity is given by  $\zeta_{\pm,i} = (\zeta_{+,i}^{\nu_{+,i}} \zeta_{-,i}^{\nu_{-,i}})^{1/\nu_i}$ , where  $\nu_i = \nu_{+,i} + \nu_{-,i}$ .<sup>8</sup> The actual mole fractions in eqs SI21 and SI23 for an IL (1) + water (2) system are related to observable mole fractions by:<sup>7</sup>

$$y_\pm = \frac{x_1}{1 + x_1}, \quad (\text{SI26})$$

and

$$y_2 = \frac{1 - x_1}{1 + x_1}. \quad (\text{SI27})$$

Like the NRTL model, the binary interaction parameters  $\Delta g_{ij} = \Delta \theta_{ij}$  are estimated from experimental data using eq 1, using  $\alpha_{12} = \alpha_{21} = \alpha = 0.3$  and eqs SI3 and SI4 apply.  $N_A$  is

Avogadro's number,  $M_2$  is the molecular weight of water,  $d_2$  is the density of water in  $\text{kg/m}^3$ ,<sup>9</sup>  $e$  is the elementary charge,  $\varepsilon_0$  is the permittivity of free space,  $\varepsilon_2$  is the dielectric constant (relative permittivity) of water<sup>9</sup> and  $k_B$  is Boltzmann's constant.  $\rho$ , a parameter related to the distance of closest ionic approach, is a fixed constant whose value is set to 25, consistent with previous publications<sup>1,7</sup> For the VLE predictions, the activity coefficient of water is:

$$\ln \gamma_2 = \ln \gamma_{2,\text{PDH}} + \ln \gamma_{2,\text{LC}}, \quad (\text{SI28})$$

$$\ln \gamma_{2,\text{PDH}} = \frac{2\sqrt{1000/M_2} A_\phi y_\pm^{3/2}}{1 + \rho\sqrt{y_\pm}} \quad (\text{SI29})$$

and

$$\ln \gamma_{2,\text{LC}} = 2 \left( \frac{y_\pm^2 G_{21} \tau_{21}}{(y_\pm + y_2 G_{21})^2} - \frac{y_\pm y_2 G_{12} \tau_{12}}{(2y_\pm G_{12} + y_2)^2} + \frac{y_\pm G_{12} \tau_{12}}{2y_\pm G_{12} + y_2} \right). \quad (\text{SI30})$$

Table S1. UNIQUAC Parameters  $r_i$  and  $q_i$  for the ILs and water

<i>Component</i>	$r_i$	$q_i$
[emim][EtSO <sub>4</sub> ]	6.00	5.00
[emim][OTf]	11.11	6.44
[emim][TFA]	5.85	5.53
water	0.92	1.4

## Supplementary References

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