Supplementary Materials
The Melting Properties of Choline Chloride in the Representation of Deep Eutectic Systems Phase Diagrams

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Modeling Details

Ion pairs and dissociated ions modeling approaches

In the assumption of fully dissociated ions, the cholinium cation and chloride anion are considered separate species in the liquid phase of the choline chloride (ChCl)+water system. The mole fraction of any ion species (k) was calculated as follows:

$$x_k^{ternary} = \frac{x_i^{binary}}{1 + x_{ChCl}^{binary}} \quad (1)$$

where $x_k^{ternary}$ is the mole fraction of ion k in the ternary cholinium + chloride + water solution and x_i^{binary} is the corresponding mole fraction of ChCl or water in the binary ChCl + water solution. The activity coefficient of component i (γ_i) was calculated as the sum of the short-range (γ_i^{SR}) and long-range (γ_i^{LR}) contributions

$$\ln \gamma_i = \ln \gamma_i^{SR} + \ln \gamma_i^{LR} \quad (2)$$

The short-range contribution was calculated using the NRTL model:[1]

$$\ln \gamma_i^{SR} = \frac{\sum_{j=1}^{m} \tau_{ji} G_{ji} x_j}{\sum_{l=1}^{m} G_{li} x_l} + \sum_{j=1}^{m} \frac{x_j G_{ij}}{\sum_{l=1}^{m} G_{lj} x_l} \left(\tau_{ij} - \frac{\sum_{r=1}^{m} \tau_{rj} G_{rj} x_r}{\sum_{l=1}^{m} G_{lj} x_l} \right) \quad (3)$$

$$G_{ij} = \exp\left(-\alpha_{ij}\tau_{ij}\right) \text{ with } \alpha_{ij} = \alpha_{ji} \quad (4)$$

$$\tau_{ij} = \frac{A_{ij}}{R} + \frac{B_{ij}}{RT} \quad (5)$$

where A_{ij}, A_{ji}, B_{ij}, and B_{ji} are the binary interaction parameters between species i and j, and α_{ij} is the nonrandomness parameter.

Considering dissociation, the activity coefficients of the ions are initially calculated, while the corresponding activity coefficient of ChCl is calculated as the mean ionic activity coefficient by:

$$\ln \gamma_{\pm}^{SR} = \frac{1}{2}\left(\ln \gamma_{+}^{SR} + \ln \gamma_{-}^{SR}\right) \tag{6}$$

where subscripts (±), (+), and (−) represent the salt, cation, and anion, respectively. According to the symmetric convention, the reference state is the pure liquid at the system pressure and temperature. When considering ion dissociation, ChCl is an equimolar mixture of cholinium and chloride. Thus, the short-range contribution for salt activity coefficient at mole fraction x and temperature T is calculated as follows:

$$\ln \gamma_{\pm}^{SR}(x,T) = \frac{1}{2}\left(\ln \gamma_{+}^{SR}(x,T) + \ln \gamma_{-}^{SR}(x,T)\right) - \frac{1}{2}\left(\ln \gamma_{+}^{SR}(0.5,T) + \ln \gamma_{-}^{SR}(0.5,T)\right) \tag{7}$$

The long-range contribution to the mean rational activity coefficient of ChCl ($\gamma_{\pm}^{LR}$) was calculated using the Pitzer-Debye-Hückel (PDH) term as follows:[2]

$$\ln \gamma_{\pm}^{LR} = -\left(\frac{500}{M}\right)^{1/2} A_{\phi}\left\{\left(2^{3/2}/b\right)\ln\left(\frac{1 + 2^{-1/2} b\, x_2^{1/2}}{1 + 2^{-1/2} b}\right) + \frac{\left(x_2^{1/2} - x_2^{3/2}\right)}{\left(1 + 2^{-1/2} b\, x_2^{1/2}\right)}\right\} \tag{8}$$

where x_2 is the summation of cation and anion mole fractions; M is the molecular weight of water; A_{ϕ} is the Debye-Hückel parameter; b is the closest approach parameter, generally a fixed value of 14.9.[2] The long-range contribution to the activity coefficients of water was calculated as follows:

$$\ln \gamma_{water}^{LR} = \left(\frac{1000}{M}\right)^{1/2} A_{\phi}\left\{\frac{\left(\frac{1}{2}x_2\right)^{3/2}}{\left(1 + b\left(\frac{1}{2}x_2\right)^{1/2}\right)}\right\} \tag{9}$$

The Debye-Hückel parameter (A_{ϕ}) at different temperatures was taken from Clarke and Glew[3] and fitted to the following linear function ($R^2 = 0.98$)

$$A_{\phi} = 0.0730\, T + 0.73020 \tag{10}$$

The unsymmetric activity coefficients (i.e., $\gamma_{\pm,unsymm} \to 1$ as $x_{ion} \to 0$) of ChCl were calculated from the symmetric mean activity coefficients as follows:

$$\ln \gamma_{\pm,unsymm} = \ln \gamma_{\pm} - \ln \gamma_{\pm}^{\infty} \tag{11}$$

The partial molar excess enthalpy of water ($\bar{h}_{water}^{E}$) was calculated as follows

$$\left(\frac{\partial \ln \gamma_{water}}{\partial T}\right)_{x,P} = - \frac{\bar{h}_{water}^{E}}{RT^2} \tag{12}$$

When ChCl is regarded as ion pairs, the NRTL model (Equations (3) to (5)) was used to calculate both ChCl and water activity coefficients without considering the long-range interaction term.

Phase equilibria calculations

The bubble-point of the binary ChCl + water mixture was calculated assuming the ideality of the vapor phase and ChCl as non-volatile compound:

$$P = x_{water}\gamma_{water}P_{water}^{sat} \tag{13}$$

where P is the total pressure and P_{water}^{sat} is the saturation pressure of water at the bubble-point temperature. The saturation pressure of water was calculated using the correlation from Matsunaga and Nagashima.[4]

Model parameters estimation

The NRTL model binary parameters for ChCl + water were estimated by simultaneously fitting experimental VLE [5-7] and SLE data for the water liquidus line, water activity,[8, 9] the partial molar excess enthalpy of water,[10] and the mean ionic activity coefficients of ChCl obtained from isopiestic measurements.[11-13] The following objective function was minimized:

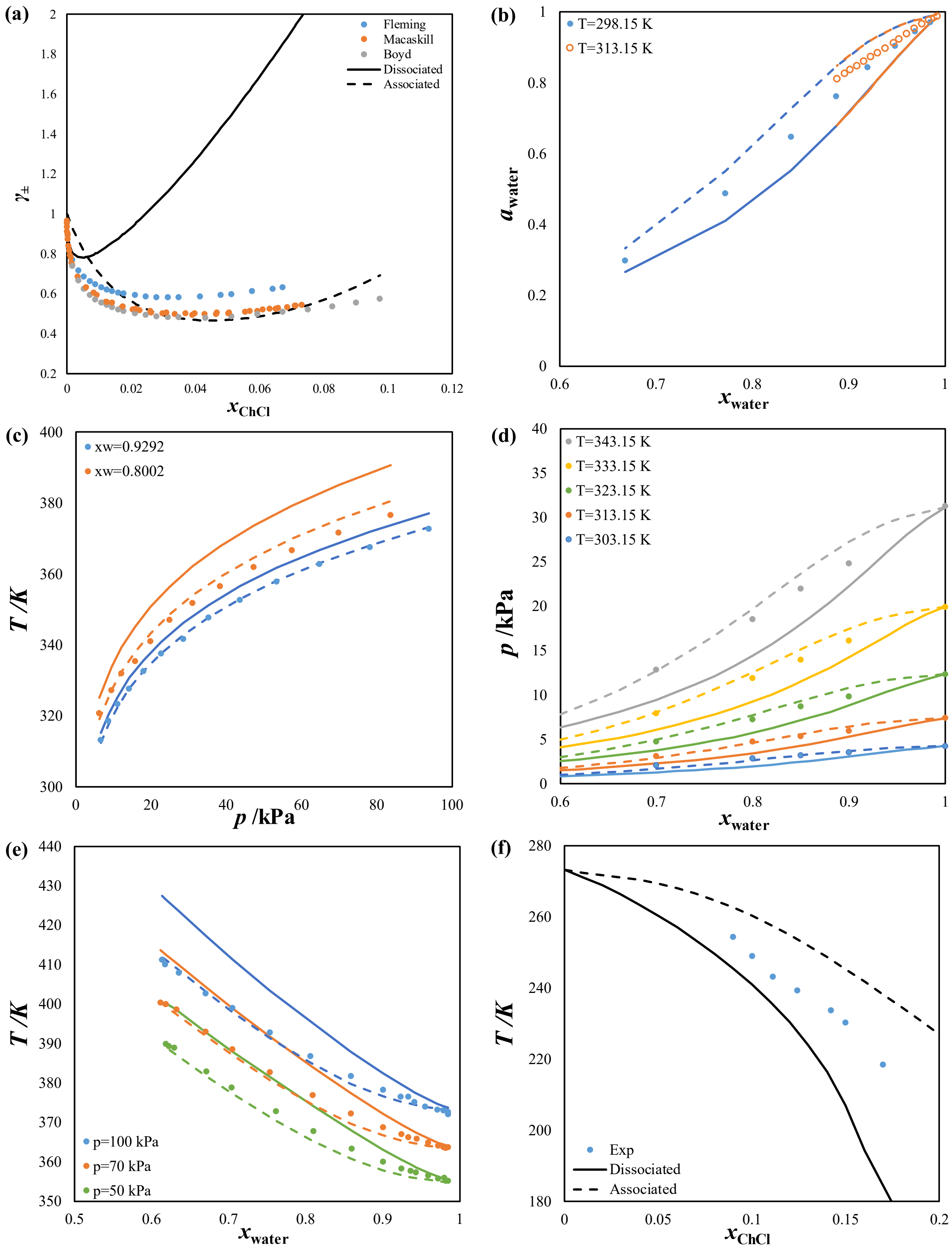
$$OF1 = \sum \left(\frac{M^{cal} - M^{exp}}{M^{exp}}\right)^2 \times 100 \tag{14}$$

where M^{cal} and M^{exp} are the calculated and experimental properties, respectively. The properties used in Equation (14) are the activity coefficients of ChCl and water in the case of VLE, SLE, water activity, and ChCl activity coefficients, or the partial molar excess enthalpy of water.

Table S1 shows the NRTL binary parameters obtained for the ChCl + water system assuming different ChCl molecular representations, and Figure S1 shows the phase equilibria data for ChCl + water modeled in this work, compared with experimental data.

Table S1. Binary interaction parameters for choline chloride + water mixture.

	$A_{12}/kJ\ mol^{-1}K^{-1}$	$A_{21}/kJ\ mol^{-1}K^{-1}$	$B_{12}/kJ\ mol^{-1}$	$B_{21}/kJ\ mol^{-1}$	α
ChCl (1)/water (2)	−1.3672	7.6289	−0.0251	0.0309	0.3
$[Ch]^{+}$(1)/$[Cl]^{-}$(2)	−14.5177	−12.0	0.0078	0.0312	0.3
$[Ch]^{+}$ (1)/water (2)	0	1.0012	−0.0145	0	0.3
$[Cl]^{-}$ (1)/water (2)	−8.0	18.1408	0	−0.0625	0.3


(a)
$\gamma_{\pm}$
x_{ChCl}
Fleming
Macaskill
Boyd
Dissociated
Associated
(b)
a_{water}
x_{water}
T=298.15 K
T=313.15 K
(c)
T /K
p /kPa
xw=0.9292
xw=0.8002
(d)
p /kPa
x_{water}
T=343.15 K
T=333.15 K
T=323.15 K
T=313.15 K
T=303.15 K
(e)
T /K
x_{water}
p=100 kPa
p=70 kPa
p=50 kPa
(f)
T /K
x_{ChCl}
Exp
Dissociated
Associated

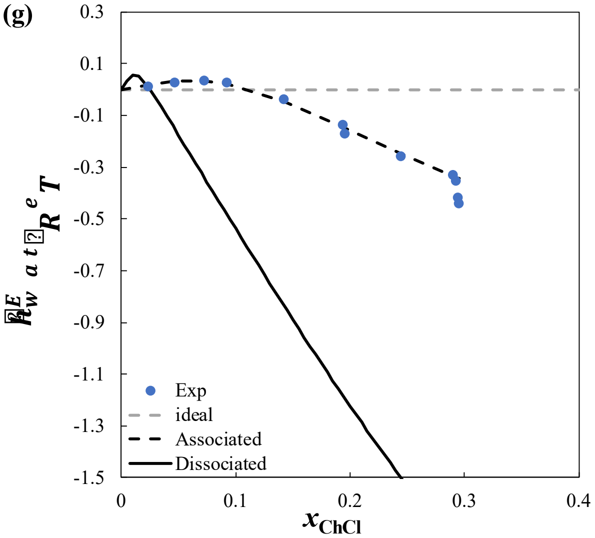


Figure S1. Phase equilibria data used to obtain the NRTL model binary parameters, assuming different representations of choline chloride (ChCl). Solid lines represent data calculated when considering ChCl as dissociated ions, and dashed lines represent data calculated when considering ChCl as ion pairs. (a) ChCl mean activity coefficients in ChCl + water at 298.15 K. Experimental data were taken from Fleming, [11] Macaskill et al., [12] and Boyd et al.[13] (b) Water activity in the ChCl+water system at 298.15 and 313.15 K. Experimental data were taken from Khan et al.[8] and Velho et al.[9] (c) Bubble-point of the ChCl+water system at different mole fractions of water. Experimental data were taken from Francisco et al. [5] (d) Isothermal bubble-point pressure of the ChCl+water system. Experimental data were taken from Gholami and Roosta.[6] (e) Isobaric bubble-point temperature of the ChCl+water system. Experimental data were taken from Carvalho et al.[7] (f) Solid-liquid phased diagram of the ChCl+water system. Experimental data were taken from Lobo Ferreira et al.[14] (g) Partial molar excess enthalpy of water in ChCl/water. Experimental data were taken from van den Bruinhorst et al.[10]

Table S2. NRTL binary parameters for choline chloride (ChCl) (1) + urea (2). A_{ij} was set to zero for ChCl + urea.

	Ion pairs			Dissociated ions		
	$B_{12}/kJ\ mol^{-1}$	$B_{21}/kJ\ mol^{-1}$	α	$B_{12}/kJ\ mol^{-1}$	$B_{21}/kJ\ mol^{-1}$	α
	$T_m = 597K$					
$\Delta C_{p,m} = 0$	−9.5358	5.8191	0.3	−9.5367	5.6252	0.3
$\Delta C_{p,m} = 15\ J\ mol^{-1}K^{-1}$	−9.4976	5.6653	0.3	−9.4922	5.5249	0.3
$\Delta C_{p,m} = 30\ J\ mol^{-1}K^{-1}$	−9.4173	5.3501	0.3	−9.4047	5.1923	0.3
	$T_m = 627K$					
$\Delta C_{p,m} = 0$	−9.5197	5.7644	0.3	−9.6840	5.8294	0.3
$\Delta C_{p,m} = 15\ J\ mol^{-1}K^{-1}$	−9.4580	5.5271	0.3	−9.4490	5.3740	0.3
$\Delta C_{p,m} = 30\ J\ mol^{-1}K^{-1}$	−9.3433	5.1017	0.3	−9.3138	4.8016	0.3
	$T_m = 687K$					
$\Delta C_{p,m} = 0$	−9.4762	5.6330	0.3	−9.4765	5.4986	0.3
$\Delta C_{p,m} = 15\ J\ mol^{-1}K^{-1}$	−9.3667	5.2188	0.3	−9.3511	5.0159	0.3
$\Delta C_{p,m} = 30\ J\ mol^{-1}K^{-1}$	−9.1858	4.5995	0.3	−9.0918	3.8159	0.3

Table S3. Estimated melting enthalpy of choline chloride (ChCl) in kJ mol^{-1}, assuming different melting temperatures and heat capacity change of ChCl.

$\Delta C_{p,m}/J\ mol^{-1}K^{-1}$	$T_m = 597K$		$T_m = 627K$		$T_m = 687K$	
	Ion pairs	Dissociated	Ion pairs	Dissociated	Ion pairs	Dissociated
0	5.55	5.96	5.16	5.31	4.5	4.68
15	7.90	8.07	7.73	7.87	7.61	7.72
30	10.17	10.29	10.23	10.39	10.62	10.85

Table S4. Root-mean-square deviation between experimental and calculated liquidus temperature in ChCl+urea ($RMSD_{urea)}$ and ChCl+water ($RMSD_{water}$).

	Ion pairs		Dissociated ions	
	$RMSD_{urea}$	$RMSD_{water}$	$RMSD_{urea}$	$RMSD_{water}$
	$T_m = 597K$			
$\Delta C_{p,m} = 0$	10.2	21.0	7.7	19.9
$\Delta C_{p,m} = 15\,J\ mol^{-1}K^{-1}$	10.9	21.5	10.36	17.8
$\Delta C_{p,m} = 30\,J\ mol^{-1}K^{-1}$	15.6	23.3	15.5	15.7
	$T_m = 627K$			
$\Delta C_{p,m} = 0$	11.3	21.4	10.7	19.0
$\Delta C_{p,m} = 15\,J\ mol^{-1}K^{-1}$	15.7	22.6	15.5	17.0
$\Delta C_{p,m} = 30\,J\ mol^{-1}K^{-1}$	22.7	26.0	22.7	15.1
	$T_m = 687K$			
$\Delta C_{p,m} = 0$	17.3	22.7	17.0	18.3
$\Delta C_{p,m} = 15\,J\ mol^{-1}K^{-1}$	27.5	25.5	27.5	16.2
$\Delta C_{p,m} = 30\,J\ mol^{-1}K^{-1}$	38.8	32.3	39.0	15.7

Table S5. Estimated choline chloride melting enthalpy (ΔH_m) and heat capacity difference ($\Delta C_{p,m}$) at different melting temperatures.

	Ion pairs		Dissociated	
$T_m\,/K$	$\Delta C_{p,m}/J\ mol^{-1}K^{-1}$	$\Delta H_m\,/kJ\ mol^{-1}$	$\Delta C_{p,m}/J\ mol^{-1}K^{-1}$	$\Delta H_m\,/kJ\ mol^{-1}$
597	15.7	8.0	10.22	7.39
627	6.05	6.21	0	5.46
687	0	4.50	0	4.68

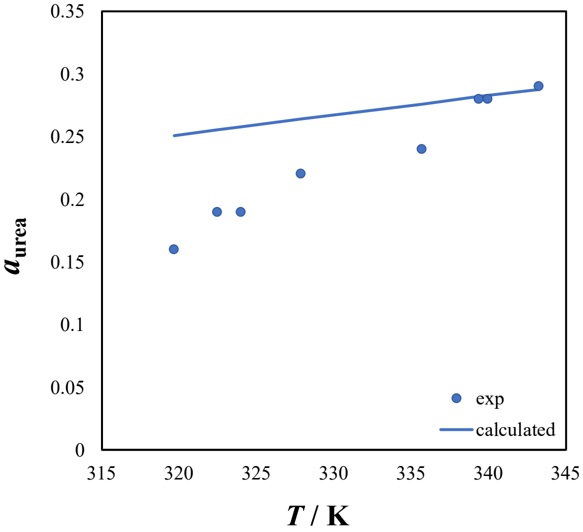


Figure S2. Urea activity with respect to pure liquid urea obtained from vapor pressure data of ChCl/urea at a urea mole fraction of 0.67. Data are taken from Travaglini et al.[15]

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