

SUPPLEMENTARY MATERIAL FOR

How sensitive are physical properties of choline chloride - urea mixtures to composition changes: Molecular Dynamics simulations and Kirkwood Buff theory

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In this Supplementary Material, we present the Generalized Amber Force Field parameters and the partial charges for choline chloride and urea mixtures. In Sections S2 to S4, we provide a discussion on how to combine RDFs for pseudo-binary mixtures, how to compute KBIs for pseudo-binary mixtures, and how to compute collective diffusion coefficients for pseudo-binary mixtures, respectively. Raw data for the computed densities, RDFs, HBs, KBIs, thermodynamic factors, partial molar volumes, viscosities, self-diffusivities, ionic conductivities, MS and Fick diffusivities are presented as a function of the mole fractions of urea. This Supplementary Material also provides the results for RDFs of ChCl–ChCl, ChCl–Urea and Urea–Urea.

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I. FORCE FIELD PARAMETERS FOR CHOLINE CHLORIDE AND UREA

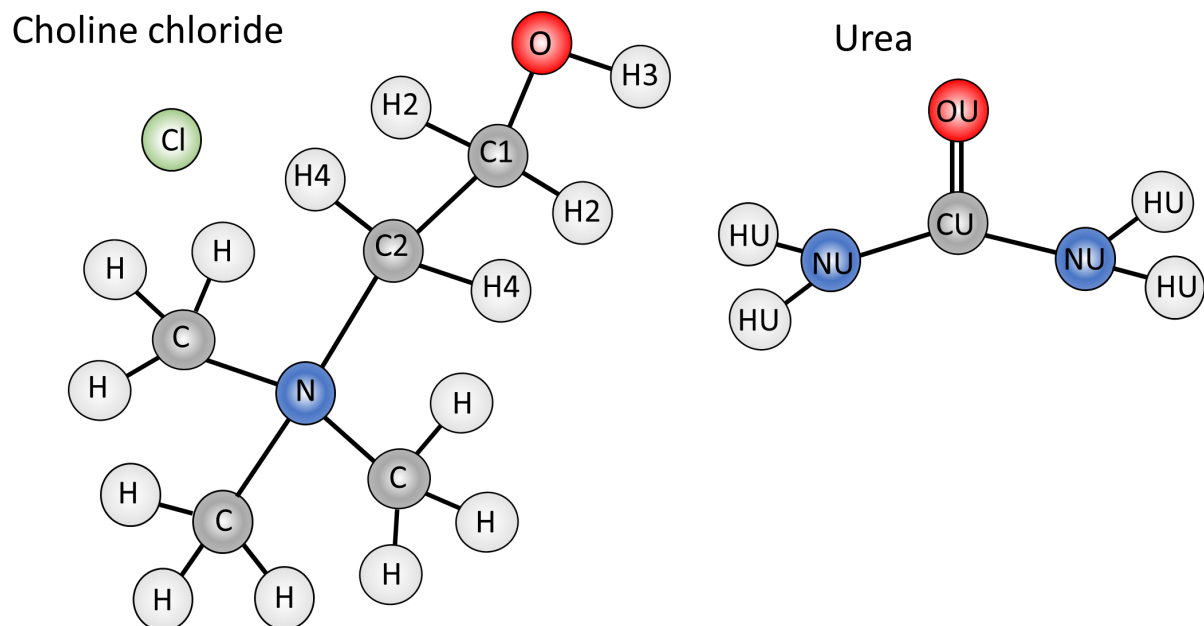


Figure S1: Molecular structure of choline chloride and urea, and atom labels.

Table SI: Partial charges, masses, and Lennard-Jones (12-6) parameters for all atomic species for choline chloride and urea. Choline chloride and urea molecules are modelled using GAFF.¹

Charges are taken from Perkins et al.² See Figure S1 for labeling of the atoms. The LJ potential is calculated as: $V_{LJ}(r)=4\epsilon[(\frac{\sigma}{r})^{12}-(\frac{\sigma}{r})^6]$.

No	Name	$q/[e]$	$m/[u]$	$\epsilon/k_B/[K]$	$\sigma/[\text{\AA}]$
1	C	-0.10736	12.0107	55.052	3.3996
2	C1	0.12008	12.0107	55.052	3.3996
3	C2	-0.02576	12.0107	55.052	3.3996
4	CU	1.0401	12.0107	43.277	3.3996
5	Cl	-0.8	35.453	50.322	4.401
6	H	0.09544	1.00794	7.901	1.9599
7	H2	0.0408	1.00794	7.901	2.4713
8	H3	0.3636	1.00794	0.503	0.1
9	H4	0.08928	1.00794	7.901	1.9599
10	HU	0.4167	1.00794	7.901	1.069
11	N	0.04016	14.0067	85.547	3.2499
12	NU	-1.0246	14.0067	85.547	3.25
13	O	-0.49512	15.9994	105.877	3.0664
14	OU	-0.6577	15.9994	105.676	2.96

Table SII: Bond-stretching parameters for choline chloride and urea molecules based on GAFF.¹

See Figure S1 for labeling of the atoms. The bond-stretching energy is calculated as:

$$E_{\text{Bond}}(r) = K_r(r - r_0)^2.$$

No	Name	$K_r/k_B/[K \text{ \AA}^{-2}]$	$r_0/[\text{\AA}]$
1	C-H	170440.5	1.09
2	C2-N	147745.3	1.5
3	C1-O	158061.3	1.43
4	C1-H2	169031.5	1.09
5	HU-NU	206420.7	1.01
6	C-N	147745.3	1.5
7	C1-C2	152525.9	1.54
8	C2-H4	170440.5	1.09
9	CU-NU	240639.7	1.35
10	H3-O	185990.0	0.97
11	CU-OU	326086.4	1.21

Table SIII: Angle-bending parameters for choline chloride and urea molecules based on GAFF.¹

See Figure S1 for labeling of the atoms. The angle-bending energy is calculated as:

$$E_{\text{Angle}}(\theta) = K_{\theta}(\theta - \theta_0)^2.$$

No	Name	K_{θ}/k_B /[K rad ⁻²]	θ_0
1	C-N-C2	31622.3	110.6
2	H2-C1-H2	19716.1	109.6
3	C2-C1-O	34078.0	109.4
4	H-C-N	24667.8	107.9
5	C2-C1-H2	23329.3	110.1
6	CU-NU-HU	24763.4	118.5
7	H2-C1-O	25649.1	109.9
8	C1-O-H3	23696.6	108.2
9	H4-C2-N	24667.8	107.9
10	C1-C2-N	32432.5	114.3
11	HU-NU-HU	19992.9	117.9
12	NU-CU-NU	37640.8	113.4
13	H-C-H	19645.7	110.7
14	NU-CU-OU	38159.1	122
15	C-N-C	31622.3	110.6
16	H4-C2-H4	19645.7	110.7
17	C1-C2-H4	23158.2	111.7

Table SIV: Dihedral torsion parameters for choline choride and urea molecules based on GAFF¹.

See Figure S1 for labeling of the atoms. The torsion energy for the Charmm style is calculated

as: $E_{\text{Dihedral}}(\phi) = \frac{V_n}{2} [1 + \cos(n\phi - \gamma)]$. The torsion energy for the OPLS style is calculated as:

$$E_{\text{Dihedral}}(\phi) = \frac{K_1}{2} [1 + \cos(\phi)] + \frac{K_2}{2} [1 - \cos(2\phi)] + \frac{K_3}{2} [1 + \cos(3\phi)].$$

No	Name	$V_n/2/k_B/[K]$	n	γ	Style
1	H4-C2-N-C	78.50	3	0	Charmm
2	C1-C2-N-C	78.50	3	0	Charmm
3	O-C1-C2-H4	78.50	3	0	Charmm
4	H-C-N-C2	78.50	3	0	Charmm
5	H2-C1-C2-H4	78.50	3	0	Charmm
6	NU-CU-NU-HU	1258.05	2	180	Charmm
7	H2-C1-O-H3	84.04	3	0	Charmm
8	H2-C1-C2-N	78.50	3	0	Charmm
9	H-C-N-C	78.50	3	0	Charmm
10	O-C1-C2-N	78.50	3	0	Charmm
No	Name	$K_1/k_B/[K]$	$K_2/k_B/[K]$	$K_3/k_B/[K]$	Style
11	OU-CU-NU-HU	2012.88	2516.10	0	OPLS
12	C2-C1-O-H3	251.61	0	161.03	OPLS

Table SV: Improper torsion parameters for choline chloride and urea molecules using GAFF¹.

See Figure S1 for labeling of the atoms. The torsion energy is calculated as:

$$E_{\text{Dihedral}}(\phi) = \frac{V_n}{2} [1 + \cos(n\phi - \gamma)].$$

No	Name	$V_n/2/k_B$ /[K]	n	γ
1	CU-HU-NU-HU	553.54	180	2
2	NU-NU-CU-OU	5283.81	180	2

II. RADIAL DISTRIBUTION FUNCTIONS OF PSEUDO-BINARY MIXTURES

In this section, we describe how to combine RDFs for components that should be treated as indistinguishable. We are specifically looking at the case where we merge the identity of two pair correlation functions, to create a new "virtual" component. First, we show the derivation for a ternary mixture α , θ and γ , where the identities of θ and γ are combined as β . Second, we will provide the expressions for the case of combining an arbitrary number of components. Finally, we show that the obtained RDFs converge to the correct answer in the case of an ideal gas.

The radial distribution function of molecules of the same type equals:³

$$g_{ii}(r) = \frac{n_{ii}(r)/V_{\text{shell}}(r)}{N_i/V_{\text{box}}} = \frac{n_{ii}(r)}{N_i}c(r) \quad (1)$$

where $n_{ii}(r)/V_{\text{shell}}$ is the local density of component i inside a small radial shell at distance r from a central molecule of type i , N_i/V_{box} is the overall number density of component i in the system and $c(r) = V_{\text{shell}}(r)/V_{\text{box}}$. In the case of molecules of two different types, RDFs are computed from

$$g_{ij}(r) = \frac{n_{ij}(r)}{N_j}c(r) \quad (2)$$

where $n_{ij}(r)$ is the number of atoms of type j in a radial shell formed around a central molecule of type i . Based on these general expressions, we can write the following RDFs for the ternary system composed of α , θ and γ :

$$g_{\alpha\alpha}(r) = \frac{n_{\alpha\alpha}(r)}{N_\alpha}c(r) \quad (3)$$

$$g_{\theta\theta}(r) = \frac{n_{\theta\theta}(r)}{N_\theta}c(r) \quad (4)$$

$$g_{\gamma\gamma}(r) = \frac{n_{\gamma\gamma}(r)}{N_\gamma}c(r) \quad (5)$$

$$g_{\alpha\theta}(r) = \frac{n_{\alpha\theta}(r)}{N_\theta}c(r) \quad (6)$$

$$g_{\alpha\gamma}(r) = \frac{n_{\alpha\gamma}(r)}{N_\gamma}c(r) \quad (7)$$

$$g_{\theta\alpha}(r) = \frac{n_{\theta\alpha}(r)}{N_\alpha}c(r) \quad (8)$$

$$g_{\gamma\alpha}(r) = \frac{n_{\gamma\alpha}(r)}{N_\alpha} c(r) \quad (9)$$

$$g_{\gamma\theta}(r) = \frac{n_{\gamma\theta}(r)}{N_\theta} c(r) \quad (10)$$

$$g_{\theta\gamma}(r) = \frac{n_{\theta\gamma}(r)}{N_\gamma} c(r) \quad (11)$$

Note that RDFs are symmetric, so $g_{ij}(r)$ equals $g_{ji}(r)$. For example, $g_{\alpha\theta}(r)$ equals $g_{\theta\alpha}(r)$ which means that $\frac{n_{\alpha\theta}(r)}{N_\theta}$ equals $\frac{n_{\theta\alpha}(r)}{N_\alpha}$. The expressions above are used to find RDFs of the pseudo binary mixture (α and β) resulting from combining the identity of θ and γ into β . For this new system, we need to find expressions for $g_{\beta\beta}(r)$ and $g_{\beta\alpha}(r)$. To find $g_{\beta\beta}(r)$, we start with the general RDF expression for similar molecules (Eq. (1))

$$g_{\beta\beta}(r) = \frac{n_{\beta\beta}(r)}{N_\beta} c(r) \quad (12)$$

The local number of molecules $n_{\beta\beta}(r)$ is composed of different contributions: $n_{\theta\theta}(r)$, $n_{\theta\gamma}(r)$, $n_{\gamma\theta}(r)$, and $n_{\gamma\gamma}(r)$. The probabilities that the central molecule is of type θ or of type γ are N_θ/N_β and N_γ/N_β , respectively. N_β is the total number of indistinguishable molecules, so $N_\beta = N_\theta + N_\gamma$. Including these contributions in Eq. (12) yields

$$\begin{aligned} g_{\beta\beta}(r) &= \frac{\left(\frac{N_\theta}{N_\beta} n_{\theta\theta}(r) + \frac{N_\gamma}{N_\beta} n_{\gamma\gamma}(r) + \frac{N_\gamma}{N_\beta} n_{\gamma\theta}(r) + \frac{N_\theta}{N_\beta} n_{\theta\gamma}(r) \right)}{N_\beta} c(r) \\ &= \frac{\left(N_\theta n_{\theta\theta}(r) + N_\gamma n_{\gamma\gamma}(r) + N_\gamma n_{\gamma\theta}(r) + N_\theta n_{\theta\gamma}(r) \right)}{N_\beta^2} c(r) \end{aligned} \quad (13)$$

Multiplying and dividing the nominator by $\frac{N_\theta N_\gamma}{N_\theta N_\gamma}$, yields

$$g_{\beta\beta}(r) = \frac{\left(\frac{N_\theta^2 N_\gamma}{N_\theta N_\gamma} n_{\theta\theta}(r) + \frac{N_\gamma^2 N_\theta}{N_\theta N_\gamma} n_{\gamma\gamma}(r) + \frac{N_\gamma^2 N_\theta}{N_\theta N_\gamma} n_{\gamma\theta}(r) + \frac{N_\theta^2 N_\gamma}{N_\theta N_\gamma} n_{\theta\gamma}(r) \right)}{N_\beta^2} c(r) \quad (14)$$

Using Eqs. (4), (5), (10) and (11) results in

$$g_{\beta\beta}(r) = \frac{\left(\frac{N_\theta^2 N_\gamma}{N_\gamma} g_{\theta\theta}(r) + \frac{N_\gamma^2 N_\theta}{N_\theta} g_{\gamma\gamma}(r) + \frac{N_\gamma^2 N_\theta}{N_\gamma} g_{\gamma\theta}(r) + \frac{N_\theta^2 N_\gamma}{N_\theta} g_{\theta\gamma}(r) \right)}{N_\beta^2} \quad (15)$$

The functions $g_{\theta\gamma}(r)$ and $g_{\gamma\theta}(r)$ are equal and Eq. (15) can be further simplified to

$$g_{\beta\beta}(r) = \frac{N_{\theta}^2 g_{\theta\theta}(r) + N_{\gamma}^2 g_{\gamma\gamma}(r) + 2N_{\theta}N_{\gamma}g_{\theta\gamma}(r)}{N_{\beta}^2} \quad (16)$$

Similarly, to find $g_{\beta\alpha}(r)$, we apply the general expression for RDFs of two different molecules (Eq. (2))

$$g_{\beta\alpha}(r) = \frac{n_{\beta\alpha}(r)}{N_{\alpha}} c(r) \quad (17)$$

where $n_{\beta\alpha}(r)$ accounts for two contributions: $n_{\theta\alpha}(r)$ and $n_{\gamma\alpha}(r)$. The probability that the central molecule is of type θ is N_{θ}/N_{β} . Similarly, the probability that the central molecule is of type γ is N_{γ}/N_{β} . As a result Eq. (17) can be rewritten as

$$\begin{aligned} g_{\beta\alpha}(r) &= \frac{\left(\frac{N_{\theta}}{N_{\beta}}n_{\theta\alpha}(r) + \frac{N_{\gamma}}{N_{\beta}}n_{\gamma\alpha}(r)\right)}{N_{\alpha}} c(r) \\ &= \frac{N_{\theta}}{N_{\beta}N_{\alpha}}n_{\theta\alpha}(r)c(r) + \frac{N_{\gamma}}{N_{\beta}N_{\alpha}}n_{\gamma\alpha}(r)c(r) \end{aligned} \quad (18)$$

Using Eqs. (8) and (9) results in

$$g_{\beta\alpha}(r) = \frac{N_{\theta}g_{\theta\alpha}(r) + N_{\gamma}g_{\gamma\alpha}(r)}{N_{\beta}} \quad (19)$$

In the same way, Eqs. (16) and (19) can be generalized for the case of a system of component α and n indistinguishable components 1, 2, 3, ... n denoted as β . The RDFs of the pseudo binary mixture composed of α and β ($N_{\beta} = N_1 + N_2 + \dots N_n$) can be written as:

$$g_{\beta\beta}(r) = \frac{\sum_{i=1}^n \sum_{j=1}^n N_i N_j g_{ij}(r)}{\left(\sum_{i=1}^n N_i\right)^2} \quad (20)$$

$$g_{\beta\alpha}(r) = \frac{\sum_{i=1}^n N_i g_{i\alpha}(r)}{\sum_{i=1}^n N_i} \quad (21)$$

In the case of an ideal gas, RDFs of the combined molecules $g_{\beta\beta}(r)$ and $g_{\beta\alpha}(r)$ should converge to $(N_{\beta} - 1)/N_{\beta}$ and 1, respectively.⁴ Considering an ideal gas mixture that consists of α and n indistinguishable components, we start with Eq. (20) and substitute the RDFs in the expressions with the ideal gas answer: $g_{ii}(r) = (N_i - 1)/N_i$ and $g_{ij}(r) = 1$ (where $i \neq j$). This results in:

$$\begin{aligned}
g_{\beta\beta}(r) &= \frac{\sum_{i=1}^n \sum_{j=1(j \neq i)}^n N_i N_j g_{ij}(r) + \sum_{i=1}^n N_i^2 g_{ii}(r)}{\left(\sum_{i=1}^n N_i\right)^2} \\
&= \frac{\sum_{i=1}^n \sum_{j=1(j \neq i)}^n N_i N_j + \sum_{i=1}^n N_i^2 \frac{N_i-1}{N_i}}{\left(\sum_{i=1}^n N_i\right)^2} \\
&= \frac{\sum_{i=1}^n \sum_{j=1}^n N_i N_j - \sum_{i=1}^n N_i^2 + \sum_{i=1}^n N_i(N_i-1)}{\left(\sum_{i=1}^n N_i\right)^2} \\
&= \frac{\sum_{i=1}^n N_i \sum_{j=1}^n N_j - \sum_{i=1}^n N_i^2 + \sum_{i=1}^n N_i^2 - \sum_{i=1}^n N_i}{\left(\sum_{i=1}^n N_i\right)^2} \\
&= \frac{\left(\sum_{i=1}^n N_i\right)^2 - \sum_{i=1}^n N_i}{\left(\sum_{i=1}^n N_i\right)^2} \\
&= \frac{\sum_{i=1}^n N_i - 1}{\sum_{i=1}^n N_i}
\end{aligned} \tag{22}$$

Similarly, for $g_{\beta\alpha}(r)$

$$g_{\beta\alpha}(r) = \frac{\sum_{i=1}^n N_i g_{i\alpha}(r)}{\sum_{i=1}^n N_i} = \frac{\sum_{i=1}^n N_i}{\sum_{i=1}^n N_i} = 1 \tag{23}$$

Hence, for an ideal gas, Eqs. (20) and (21) provide the correct answer.

III. KIRKWOOD–BUFF INTEGRALS FOR PSEUDO–BINARY MIXTURES

For fluid mixtures, KBIs are useful to investigate the affinity between different components. Various thermodynamic properties can be computed from KBIs.^{3,5} The KB theory was derived for infinitely large and open systems. However, recently a number of methods were developed to compute KBIs from molecular simulations of finite and closed systems. In this study, we implement the method of Krüger and co-workers^{6–8} where the values of KBIs in the thermodynamic limit $G_{\alpha\beta}^{\infty}$ are computed using KBIs of finite and open subvolumes embedded in a larger reservoir (e.g. simulation box). The expression of KBIs of finite subvolumes $G_{\alpha\beta}^V$ is⁶

$$G_{\alpha\beta}^V = \int_0^L [g_{\alpha\beta}(r) - 1] 4\pi r^2 w(x) dr \quad (24)$$

where L is the size of the subvolume, and $w(x)$ is a function that depends on the shape and dimensionality of the subvolume. For a 3D spherical subvolume with diameter L , $w(x) = 1 - 3x/2 + x^3/2$ where $x = r/L$ is the dimensionless distance. KBIs of finite subvolumes $G_{\alpha\beta}^V$ scale with the inverse size of the system,^{6,8–10}

$$G_{\alpha\beta}^V(L) = G_{\alpha\beta}^{\infty} + \frac{F_{\alpha\beta}^{\infty}}{L} \quad (25)$$

where $F_{\alpha\beta}^{\infty}$ is a term that relates to surface effects of computing KBIs of small subvolumes. This scaling can be used to obtain $G_{\alpha\beta}^{\infty}$. Various methods has been recently investigated to extrapolate KBIs to the thermodynamic limit.¹⁰ It was found that the easiest approach is to plot the product $LG_{\alpha\beta}^V$ as a function of L . The KBI in the thermodynamic limit is found from the slope of this line, and the surface term $F_{\alpha\beta}^{\infty}$ is found from the intercept. Furthermore, we address the finite-size effects related to RDFs by applying the Ganguly and van der Vegt correction¹¹.

To compute KBIs of a pseudo binary mixture, the steps below can be followed:

1. Using molecular simulations, compute RDFs of the ternary mixture: α , θ and γ (e.g. urea, choline and chloride).
2. Correct RDFs for finite-size effects (here, we are using the Ganguly and van der Vegt correction¹¹).
3. Use Eqs. (20) and (21) to compute RDFs of the pseudo binary mixture (α and β) from RDFs of the ternary mixture (α , θ and γ).

4. Numerically integrate RDFs up to half the box size ($L_{\text{box}}/2$) to compute $G_{\alpha\beta}^V$ (Eq. (24)).
5. Plot $LG_{\alpha\beta}^V$ as a function of the diameters of the spherical subvolumes L .
6. Fit the linear regime to obtain $G_{\alpha\beta}^\infty$ (Eq. (25)).

In this work, the values of KBIs in the thermodynamic limit $G_{\alpha\beta}^\infty$ are used to compute the thermodynamic factor Γ and partial molar volumes. For the computations of Γ , mole fractions are needed. For a pseudo binary mixture, mole fractions are calculated as:

$$x_\alpha = \frac{N_\alpha}{N_\alpha + N_\theta + N_\gamma} \quad (26)$$

$$x_\beta = 1 - x_\alpha \quad (27)$$

IV. MAXWELL–STEFAN AND FICK DIFFUSION COEFFICIENTS FOR PSEUDO–BINARY MIXTURES

Maxwell-Stefan diffusion (MS) coefficient in a three-dimensional system can be computed from the Onsager coefficients (Λ_{ij}). Onsager coefficients are defined as the cross-correlation of the displacement of the molecules of species i and j in a multicomponent mixture.^{12,13}

$$\Lambda_{ij} = \lim_{t \rightarrow \infty} \frac{1}{2t} \frac{1}{3N} \left\langle \left(\sum_{k=1}^{N_i} [\mathbf{r}_{k,i}(t) - \mathbf{r}_{k,i}(0)] \right) \cdot \left(\sum_{l=1}^{N_j} [\mathbf{r}_{l,j}(t) - \mathbf{r}_{l,j}(0)] \right) \right\rangle \quad (28)$$

where N , N_i and N_j are the total number of molecules, number of molecules of species i and j , respectively. The matrix of Onsager coefficients has a symmetric nature, and these coefficients are described in a reference frame in which center of mass velocity is zero.¹⁴ Thus, we can correlate the Onsager coefficients of a binary mixture in terms of the molar masses of the two components α and β (M_α and M_β):¹⁴

$$\Lambda_{\alpha\beta} = - \left[\frac{M_\alpha}{M_\beta} \right] \Lambda_{\alpha\alpha} = - \left[\frac{M_\beta}{M_\alpha} \right] \Lambda_{\beta\beta} \quad (29)$$

For binary mixtures, there is a single MS and Fick diffusion coefficient defined. The MS diffusion coefficient \mathcal{D} is related to the Onsager coefficients by:¹⁵

$$\mathcal{D} = \left[\frac{(M_\beta + x_\alpha(M_\alpha - M_\beta))^2}{x_\alpha x_\beta M_\beta^2} \right] \Lambda_{\alpha\alpha} \quad (30)$$

For a binary liquid mixture, the Fick diffusion coefficient D is related to the the MS diffusion coefficient by the matrix of thermodynamic factors, which describes the non-ideality of a mixture.¹⁶

$$D = \Gamma \mathcal{D} \quad (31)$$

In the above equation, the thermodynamic factor (Γ) can be computed from Kirkwood-Buff Integrals.¹⁴

A. Pseudo-binary mixture

In a conventional ternary system consisting of molecules of α , θ and γ , there are six Onsager coefficients as $\Lambda_{\alpha\alpha}$, $\Lambda_{\alpha\theta}$, $\Lambda_{\alpha\gamma}$, $\Lambda_{\theta\theta}$, $\Lambda_{\theta\gamma}$, and $\Lambda_{\gamma\gamma}$. In a pseudo-binary system, there are only three

onsager coefficients that are interdependent according to Eq. (29). A pseudo-binary system consist of an independent and an indistinguishable species, which could be described as molecules of α and $\beta=(\theta+\gamma)$, respectively. For this pseudo-binary system, three Onsager coefficients are $\Lambda_{\alpha\alpha}$, $\Lambda_{\alpha\beta}$, and $\Lambda_{\beta\beta}$.

To compute Onsager coefficients of the pseudo-binary system $\Lambda_{\alpha\alpha}$, $\Lambda_{\alpha\beta}$, and $\Lambda_{\beta\beta}$

1. Perform MD simulations of the ternary systems consisting of α , θ and γ molecules.
2. Compute Onsager coefficients for this ternary system. ($\Lambda_{\alpha\alpha}$, $\Lambda_{\alpha\theta}$, $\Lambda_{\alpha\gamma}$, $\Lambda_{\theta\theta}$, $\Lambda_{\theta\gamma}$, and $\Lambda_{\gamma\gamma}$) using MSDs obtained from the OCTP tool in LAMMPS.¹⁷ Eq. (28) requires information on the total number of molecules, which is $N = N_\alpha + N_\theta + N_\gamma$.
3. The value of $\Lambda_{\alpha\alpha}$ is identical in the ternary and pseudo-binary systems. Use $\Lambda_{\alpha\alpha}$ in Eq. (30) to compute MS diffusion coefficient of the pseudo-binary mixture.
4. In Eq. (30), molecular weights (M_α and M_β) of the pseudo-binary mixture are essential. M_β is the average molecular weight of the indistinguishable particle, computed from:

$$M_\beta = \frac{N_\theta M_\theta + N_\gamma M_\gamma}{N_\theta + N_\gamma} \quad (32)$$

in the case of a salt solution $N_\gamma = N_\theta$:

$$M_\beta = \frac{M_\theta + M_\gamma}{2} \quad (33)$$

5. For pseudo-binary mixtures, the mole fractions defined in Eqs. (26) and (27) can be used when applying Eq. (30).
6. Fick diffusion coefficients are computed using Eq. (31).

V. ADDITIONAL SIMULATION RESULTS

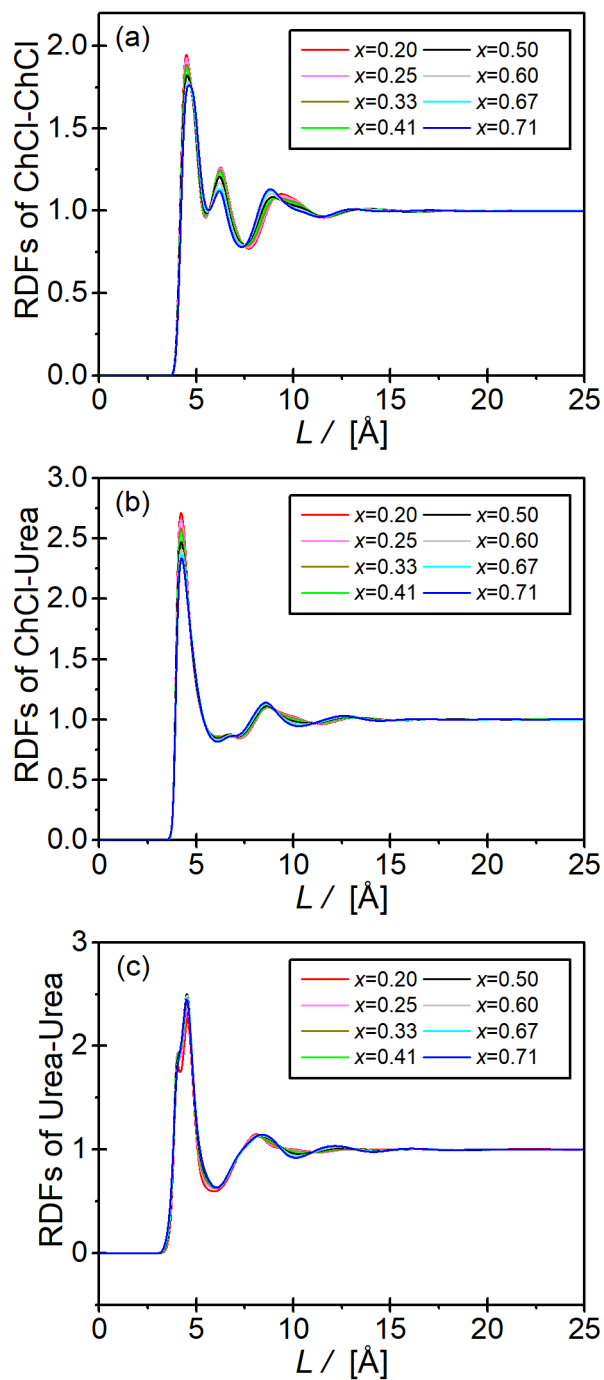


Figure S2: Radial Distribution Functions of choline chloride and urea at 343.15 K, 1 atm and various mole fractions of urea (as defined in Eq. (26)).

VI. RAW SIMULATION DATA

Table SVI: Computed densities of ChCl and urea mixtures at 343.15 K and 1 atm as a function of the mole fraction of urea (as defined in Eq. (26)). The experimental density at $x_{\text{Urea}}=0.5$ was measured as 1170.8 kg/m³ in the study by Yadav et al.¹⁸

x_{Urea}	$\rho/[\text{kg/m}^3]$
0.20	1077.8
0.25	1094.1
0.33	1123.3
0.41	1151.9
0.50	1188.0
0.60	1232.1
0.67	1263.4
0.71	1286.9

Table SVII: Computed viscosities of ChCl and urea mixtures at 343.15 K and 1 atm as a function of the mole fraction of urea (as defined in Eq. (26)). The experimental viscosity at $x_{\text{Urea}}=0.5$ was measured as 41.6 mPa.s in the study by Yadav et al.¹⁸

x_{Urea}	η /[mPa s]
0.20	71±4
0.25	64±5
0.33	57±5
0.41	46±4
0.50	38±3
0.60	31±3
0.67	27±3
0.71	24±2

Table SVIII: Finite-size effects corrected self-diffusion coefficients of Ch^+ , Cl^- , and Urea molecules at 343.15 K and 1 atm as a function of the mole fraction of urea (as defined in Eq. (26)).

x_{Urea}	$D_{\text{Self}}^{\infty}/[10^{-11} \text{ m}^2 \text{ s}^{-1}]$		
	Urea	Choline	Chloride
0.20	4.3±0.1	2.3±0.1	2.9±0.1
0.25	4.5±0.1	2.47±0.04	3.13±0.05
0.33	5.1±0.2	2.82±0.02	3.6±0.1
0.41	5.71±0.03	3.3±0.1	4.21±0.04
0.50	6.5±0.3	3.9±0.1	5.1±0.1
0.60	7.4±0.4	4.62±0.05	6.2±0.1
0.67	8.4±0.5	5.3±0.1	7.4±0.2
0.71	9.1±0.7	5.8±0.1	8.2±0.3

Table SIX: Computed ionic conductivities of ChCl and urea mixtures at 343.15 K and 1 atm as a function of the mole fraction of urea (as defined in Eq. (26)).

x_{Urea}	$\kappa/[\text{mPa s}^{-1}]$
0.20	0.70 ± 0.02
0.25	0.72 ± 0.01
0.33	0.75 ± 0.01
0.41	0.80 ± 0.01
0.50	0.85 ± 0.02
0.60	0.87 ± 0.01
0.67	0.88 ± 0.02
0.71	0.87 ± 0.02

Table SX: Kirkwood-Buff Integrals of ChCl and urea mixtures at 343.15 K and 1 atm as a function of the mole fraction of urea (as defined in Eq. (26)). The term G^f is computed from: $G_{11} + G_{22} + 2G_{12}$.

Kirkwood-Buff Integrals				
x_{Urea}	$G_{\text{Urea-Urea}}/[\text{\AA}^3]$	$G_{\text{ChCl-Urea}}/[\text{\AA}^3]$	$G_{\text{ChCl-ChCl}}/[\text{\AA}^3]$	$G^f/[\text{\AA}^3]$
0.20	-147±15	-51±2	-120±1	-164±18
0.25	-130±12	-45±2	-120±2	-156±17
0.33	-100±1	-56±1	-129±1	-120±2
0.41	-73±5	-63±2	-133±2	-76±12
0.50	-63±5	-69±3	-137±2	-69±8
0.60	-66±2	-70±2	-150±5	-77±2
0.67	-64±1	-72±4	-155±1	-73±5
0.71	-64±3	-76±4	-164±7	-70±9

Table SXI: Thermodynamic factors, finite-size corrected Maxwell-Stefan diffusion coefficients, and finite-size corrected Fick diffusion coefficients of ChCl and urea mixtures at 343.15 K and 1 atm as a function of the mole fraction of urea (as defined in Eq. (26)).

x_{Urea}	Γ	$D^\infty/[10^{-11} \text{ m}^2 \text{ s}^{-1}]$	$D^\infty/[10^{-11} \text{ m}^2 \text{ s}^{-1}]$
0.20	1.33±0.04	3.9±0.2	5.2±0.2
0.25	1.38±0.06	4.0±0.2	5.5±0.2
0.33	1.35±0.01	4.2±0.2	5.7±0.1
0.41	1.26±0.05	4.4±0.3	5.5±0.3
0.50	1.21±0.05	4.8±0.2	5.8±0.2
0.60	1.27±0.04	5.1±0.2	6.5±0.2
0.67	1.25±0.04	5.4±0.2	6.8±0.2
0.71	1.24±0.06	5.7±0.3	7.1±0.3

Table SXII: Partial molar volumes of ChCl and urea mixtures at 343.15 K and 1 atm as a function of the mole fraction of urea (as defined in Eq. (26)).

Partial Molar Volumes		
x_{Urea}	$v_{\text{ChCl}}/[\text{\AA}^3 \text{ molecule}^{-1}]$	$v_{\text{Urea}}/[\text{\AA}^3 \text{ molecule}^{-1}]$
0	113.1	NA
0.20	113.8	66.9
0.25	114.4	65.6
0.33	113.7	66.9
0.41	113.6	67.3
0.50	112.7	68.2
0.60	112.2	68.4
0.67	110.4	69.2
0.71	111.1	69.2
1	NA	68.7

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