Why Do Liquids Mix? The Mixing of Protic Ionic Liquids Sharing the Same Cation is Apparently Driven by Enthalpy, not Entropy

Benjamin Golub,[1] Daniel Ondo,[2] Ralf Ludwig,[1,3] and Dietmar Paschek[1,*]
[1]*Physikalische und Theoretische Chemie, Institut für Chemie,*
Universität Rostock, Albert-Einstein-Straße 27, D-18059 Rostock, Germany
[2]*Deparment of Physical Chemistry, University of Chemistry and Technology, Technická 5., 166 28 Prague 6, Czech Republic*
[3]*Leibniz-Institut für Katalyse, Albert-Einstein-Straße 29a, D-18059 Rostock, Germany*

(Dated: 2022/02/28 at 09:43:43)

We study hydrogen bond (HB) redistribution in mixtures of two protic ionic liquids (PILs) sharing the same cation: triethylammonium-methanesulfonate ([TEA][OMs]) and triethylammonium-trifluoromethanesulfonate ([TEA][OTf]). The mixture is exhibiting large negative energies of mixing. Based on results obtained from atomic detail molecular dynamics (MD) simulations, we derive a lattice model, discriminating between HB and *nonspecific* intermolecular interactions. We demonstrate that due to the ordered structure of the PILs, only the HB interactions contribute to the mixing energy. This allows to us to connect the equilibrium of HBs to each of the two anion species with the corresponding excess energies and entropies. The entropy associated with HB redistribution is shown to be negative, and even overcompensating the positive entropy associated with a statistical distribution of the ions in the mixture. This is strongly suggesting that the mixing process is driven by enthalpy, not entropy.

Protic ionic liquids (PILs) [1] have attracted considerable interest since they possess qualities such as biocompatibility [2] and low toxicity.[3] Mixtures of ionic liquids (ILs) have gained increasing attention in recent years.[4–19] Mixtures of ILs are often characterised by their general mixing behaviour, analysing to what degree they are deviating from Raoult's law (i.e. *ideal* mixing behaviour).[20] As a rule of thumb, ILs often mix well.[20] However, whether we find a *nonideal* mixing behaviour is, of course, depending on the interaction forces between the ions. Combinations of strong dispersion forces [21], but also hydrogen bonding [22, 23], can lead to a significant *nonideal* mixing. A direct way to investigate the formation or change of interactions due to mixing is to determine the enthalpy or energy of mixing.[20–29] If the enthalpy of mixing is close to zero, the interactions scale exactly proportional to the mixture composition. Positive or negative enthalpies of mixing, however, imply the “making or breaking” [30] of interactions and are therefore related with changes of the structure of the liquid.[31] Extensive reviews of mixtures of ionic liquids are available in refs [20, 26, 30].

In this study we would like to focus on a specific mixture of PILs, which has the potential to disentangle the contribution from hydrogen bonding and other *nonspecific* forms of intermolecular interactions: the mixture of two protic ionic liquids sharing the same cation. The two PILs are triethylammonium-methanesulfonate ([TEA][OMs]) and triethylammonium-trifluoromethanesulfonate ([TEA][OTf]). In the PIL, a [TEA] cation acts as a hydrogen bond (HB) donor, being able to donate a single HB. Both, the [OMs] and the [OTf] anions can act as HB acceptors, which can accept multiple HBs via their respective SO_3-groups. In previous publications [11, 12, 32] we could demonstrate that a mixture of those PILs experiences a redistribution of HBs between the cation and the anions in the mixture apparently due to stronger HBs between [TEA] and [OMs] ions [12, 33, 34]. This is leading to *nonideal* mixing behaviour, almost completely stripping the [OTf] anion of HB partners in the [OMs]-rich region.[11] Note that the local environment of each of the anions is formed by a solvation shell composed predominantly of cations. Hence the environment of each anion is very similar in the mixture compared to the respective pure PILs, such that the *nonideal* mixing behaviour is most likely only due to HB redistribution effects.

To study the pure PILs and mixtures, we performed isobaric isothermal (NPT) molecular dynamics (MD) simulations investigating eleven compositions between $x_{\mathrm{OMs}} = 0.0$ and $x_{\mathrm{OMs}} = 1.0$ for five temperatures between $T = 320\,\mathrm{K}$ and $T = 400\,\mathrm{K}$ at a pressure of $1\,\mathrm{bar}$. All studied systems were composed of 500 ion pairs. More details about the performed MD simulations are provided in the SI.

In a previous contribution we have shown that MD simulations of pure [TEA][OMs] and [TEA][OTf] as well as their mixtures exhibit a well defined intermolecular anion-cation order.[11] Here each ion was found to be surrounded by a solvation shell predominantly consisting of counter ions. The average coordination number, defined by a center of mass distance of $0.8\,\mathrm{nm}$ between ions of opposite charge (corresponding to the location of the first minimum of anion-cation pair correlation functions) was found to vary only slightly between 6.8 and 6.9 as a function of the mixture composition. The corresponding distribution functions (see Figure 6 of ref [11]), are characterised by maximum at seven neighbours with a half width of about two neighbours. A representative snapshot of the solvation of a [TEA] cation in [TEA][OMs]/[TEA][OTf] mixture is shown in Figure 1.

HBs are characterised here by means of geometric criteria. Based on the analysis discussed in ref [11], we use a distance criterion of $r_{\mathrm{HN}\ldots\mathrm{O}} \leq 0.24\,\mathrm{nm}$ to define a HB for both, the [OMs] and the [OTf] ions. We obtain the standard enthalpy associated with switching a HB between the two anion species from a van 't Hoff plot of the logarithm of the equilibrium constant $K = y_{\mathrm{OMs}}/y_{\mathrm{OTf}}$ versus the inverse temperature shown in

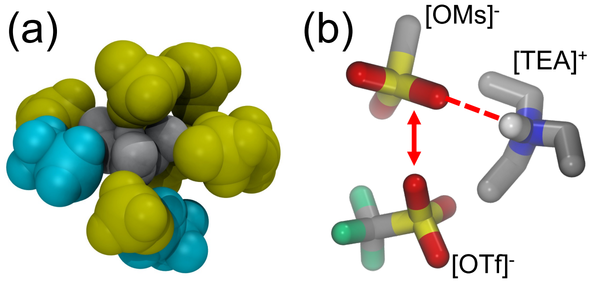

FIG. 1. a) Snapshot of the solvation of a central [TEA] cation, shown in grey, in a [TEA][OMs]/[TEA][OTf] mixture engaged in a HB to an adjacent [OMs] anion. The [OMs] anions are shown in yellow and the [OTf] anions are depicted in cyan. b) Illustrated equilibrium of the HBs donated by a [TEA] cation and accepted by the SO_3 groups of the [OMs] and [OTf] anions.

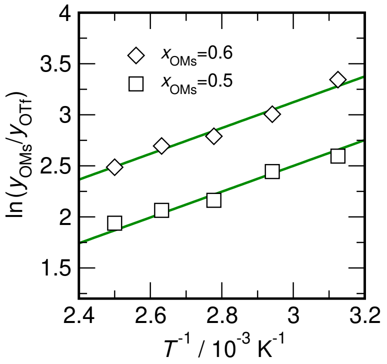

FIG. 2. Van 't Hoff plot of the logarithm of the equilibrium constant $K = y_{\text{OMs}}/y_{\text{OTf}}$ vs. the inverse temperature for compositions with $x_{\text{OMs}} = 0.5$, and $x_{\text{OMs}} = 0.6$. The slope of the green solid lines correspond to a ΔH° of $-10.5\,\text{kJ}\,\text{mol}^{-1}$.

Figure 2. Here y_{OMs} and y_{OTf} represent the fraction of HBs donated by the [TEA] cation to either of the two anion species. Depicted are data for compositions of $x_{\text{OMs}} = \{0.5, 0.6\}$, indicating a value of about $\Delta H^\circ = -10.5\,\text{kJ}\,\text{mol}^{-1}$ for the enthalpy associated with breaking a [TEA][OTf] HB and forming a new [TEA][OMs] HB.

From the MD simulations we can directly determine the energies of mixing according to

$$\begin{aligned}\Delta U_{\text{mix}} &= U(x_{\text{OMs}}) - x_{\text{OMs}} \cdot U_{\text{[TEA][OMs]}} \\ &\quad -(1-x_{\text{OMs}}) \cdot U_{\text{[TEA][OTf]}} \,,\end{aligned} \qquad (1)$$

where $U(x_{\text{OMs}})$ represents the total energy of the mixture [TEA][OTf]/[TEA][OMs] with a given composition x_{OMs}, while $U_{\text{[TEA][OTf]}}$ and $U_{\text{[TEA][OMs]}}$ are the energies of the pure PILs. A strong *nonideal* mixing behaviour is observed. The negative mixing energies of the equimolar mixture are found to be $(-4.02 \pm 0.18)\,\text{kJ}\,\text{mol}^{-1}$. In addition, we observe that the minima are shifted to a x_{OMs} value of about $x_{\text{OMs}} = 0.4$.

The regular local structure of the PILs is characterised by a well defined anion-cation order as discussed in ref [11]. This has motivated us to describe the mixture in terms of a lattice model based solely on local nearest neighbour interactions. In the model we discriminate between HBs and *nonspecific* interactions (i.e. van der Waals and non-localised polar interactions). Here each of the ions in the PILs is placed on a regular lattice with a coordination number c. As illustrated in Figure 3 the anions and cations are arranged in an alternating fashion on the lattice. Hence there exist $(N_{\text{TEA}} \cdot c)$ *nonspecific* nearest neighbour interactions and (N_{TEA}) HBs. The total energy of the pure PILs follows as

$$\begin{aligned}U_{\text{[TEA][OMs]}} &= N_{\text{TEA}} \cdot c \cdot \epsilon_{\text{TEA-OMs}} + \\ &\quad N_{\text{TEA}} \cdot \epsilon_{\text{HB:TEA-OMs}}\end{aligned} \qquad (2)$$

and

$$\begin{aligned}U_{\text{[TEA][OTf]}} &= N_{\text{TEA}} \cdot c \cdot \epsilon_{\text{TEA-OTf}} + \\ &\quad N_{\text{TEA}} \cdot \epsilon_{\text{HB:TEA-OTf}} \,,\end{aligned} \qquad (3)$$

where N_{TEA} is the number of [TEA] cations, c is the coordination number, and $\epsilon_{\text{TEA-OMs}}$, $\epsilon_{\text{TEA-OTf}}$, $\epsilon_{\text{HB:TEA-OMs}}$, and $\epsilon_{\text{HB:TEA-OTf}}$ are the parameters characterising the respective *nonspecific* and HB interactions of the cation with either of the two anions. Assuming that in a mixture the sites of the anion sublattice are statistically occupied by one of the two anion species in accordance with the mixture composition, the energy of the mixture with a composition x_{OMs} is given by

$$\begin{aligned}U(x_{\text{OMs}}) &= N_{\text{TEA}} \cdot c \cdot x_{\text{OMs}} \cdot \epsilon_{\text{TEA-OMs}} + \\ &\quad N_{\text{TEA}} \cdot y_{\text{OMs}} \cdot \epsilon_{\text{HB:TEA-OMs}} + \\ &\quad N_{\text{TEA}} \cdot c \cdot (1 - x_{\text{OMs}}) \cdot \epsilon_{\text{TEA-OTf}} + \\ &\quad N_{\text{TEA}} \cdot (1 - y_{\text{OMs}}) \cdot \epsilon_{\text{HB:TEA-OTf}} \,,\end{aligned} \qquad (4)$$

where y_{OMs} represents the fraction of cations forming a HB to the neighbouring [OMs] anions. Note that in the present case the condition $y_{\text{OMs}} + y_{\text{OTf}} = 1$ is well fulfilled. From Equations 1, 2, 3, and 4 follows directly that

$$\Delta U_{\text{mix}} = N_{\text{TEA}} \cdot (y_{\text{OMs}} - x_{\text{OMs}}) \cdot \Delta\epsilon_{\text{HB}} \qquad (5)$$

with

$$\Delta\epsilon_{\text{HB}} = \epsilon_{\text{HB:TEA-OMs}} - \epsilon_{\text{HB:TEA-OTf}} \,. \qquad (6)$$

Note that $\Delta\epsilon_{\text{HB}} < 0$ for the case of $\epsilon_{\text{HB:TEA-OMs}} < \epsilon_{\text{HB:TEA-OTf}}$ and is leading to negative mixing energies if the condition $y_{\text{OMs}} > x_{\text{OMs}}$ is fulfilled. It is evident from Equation 5 that the difference of the hydrogen bonding strengths of HBs donated by the [TEA] cation to each of the two anion species can thus be obtained from the knowledge of $\Delta_{\text{mix}}U$, y_{OMs} and x_{OMs}.

The lattice model outlined in Figure 3 also allows us to derive the entropic contributions due to HB redistribution. First, let us assume that the anions in the mixture occupy the anion positions on the anion sublattice randomly according to their mixture composition. Since none of the nonbonded interactions change during the mixing process, the corresponding energy of mixing is $\Delta U_{\text{mix-id.}} = 0$, and

$$\Delta A_{\text{mix-id.}} = N k_B T \left[x \ln(x) + (1-x)\ln(1-x)\right] \qquad (7)$$

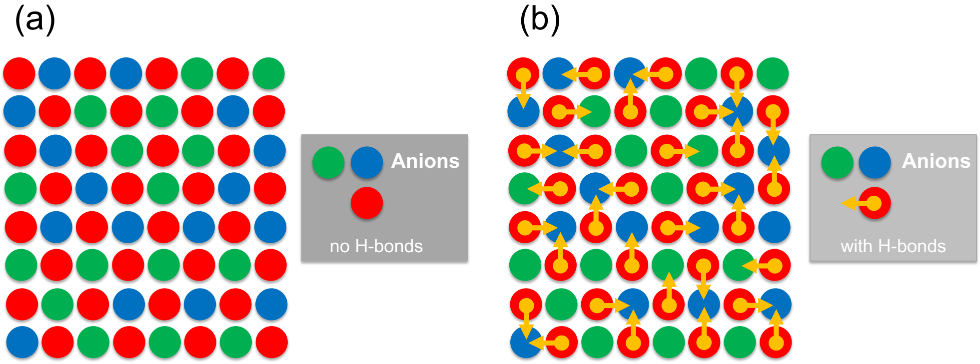

FIG. 3. 2D lattice representation (with coordination number $c = 4$) of an equimolar mixture of [TEA][OMs] and [TEA][OTf]. The color coding is: red = [TEA]$^+$, blue = [OMs]$^-$, and green = [OTf]$^-$. a) Lattice sites are occupied by cations and anions in an alternate fashion, leading to a number of *nonspecific* cation-anion contacts of $N_{\text{[TEA]}} \cdot c$. The anions are randomly distributed on the lattice-sites of the anion-sublattice according to their mixture composition. b) The arrows indicate HBs between the cations and one of the adjacent anions, therefore representing one additional HB interaction per cation. Note that the majority of HBs is found between [TEA] cations and [OMs] anions.

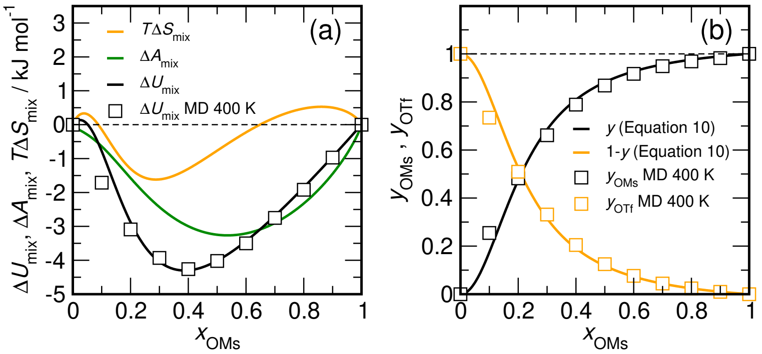

FIG. 4. Theoretical predictions of the thermodynamic mixing properties for mixtures at $T = 400\,\text{K}$ using $\Delta\epsilon_{\text{HB}} = -10.5\,\text{kJ mol}^{-1}$ and $\alpha == 2.05$. a) Open squares indicate the energies of mixing as function of x_{OMs} obtained from MD simulations. The heavy solid lines represent the ΔA_{mix}, ΔU_{mix} and $T\Delta S_{\text{mix}}$ according to Equations 13, 11, and 14, respectively. b) Shown are the fraction y_{OMs} and y_{OTf} of [TEA] cations involved in a HB with [OMs] and [OTf] anions. Open circles represent data obtained from MD simulations. The heavy solid line represents data according to Equation 10.

with $x = x_{\text{OMs}}$ and k_B being the Boltzmann constant and N representing the total number of anions in the mixture. Hence

$$\Delta S_{\text{mix-id.}} = -Nk_B\left[x\ln(x) + (1-x)\ln(1-x)\right] \qquad (8)$$

is the ideal mixing entropy contribution due to the statistical distribution of the anions on the anion sublattice.

The *nonideal* behaviour is solely based on HB redistribution, which is expressed by a partition function of the HB states for the cations, which are grouped into two distinct energy states with $\epsilon_{\text{HB,OMs}} = \Delta\epsilon_{\text{HB}}$ and $\epsilon_{\text{HB,OTf}} = 0$, populating the c surrounding HB acceptence-sites according to the mixture composition with

$$q_{\text{HB}}^N = \left[cx^\alpha\, e^{-\beta\Delta\,\epsilon_{\text{HB}}} + c\,(1-x^\alpha)\right]^N , \qquad (9)$$

where $\beta = (k_BT)^{-1}$, $N = N_{\text{[TEA]}}$, and $x = x_{\text{OMs}}$. The parameter α is introduced to account for a potential non-stoichiometric availability of [OMs] and [OTf] HB acceptor sites within the mixture. Here $cx^\alpha\, e^{-\beta\Delta\,\epsilon_{\text{HB}}}$ describe the HBs to the [OMs] anions and $c\,(1-x^\alpha)$ the corresponding HBs to the [OTf] anions. Hence the fraction of HB to the [OMs] anions is according to

$$y = \frac{x^\alpha\, e^{-\beta\Delta\,\epsilon_{\text{HB}}}}{x^\alpha\, e^{-\beta\Delta\,\epsilon_{\text{HB}}} + 1 - x^\alpha} \qquad (10)$$

with $y = y_{\text{OMs}}$, and $(1-y) = y_{\text{OTf}}$. A statistical mechanical treatment of the partition function [35] given by Equation 9 directly leads to

$$\begin{aligned} U_E &= N\Delta\epsilon_{\text{HB}} \cdot \frac{x^\alpha\, e^{-\beta\Delta\,\epsilon_{\text{HB}}}}{x^\alpha\, e^{-\beta\Delta\,\epsilon_{\text{HB}}} + 1 - x^\alpha} \qquad (11)\\ &\quad - Nx\Delta\epsilon_{\text{HB}} \\ &= N\Delta\epsilon_{\text{HB}} \cdot (y - x)\ . \qquad (12) \end{aligned}$$

Note that Equation 12 is identical to Equation 5. The excess

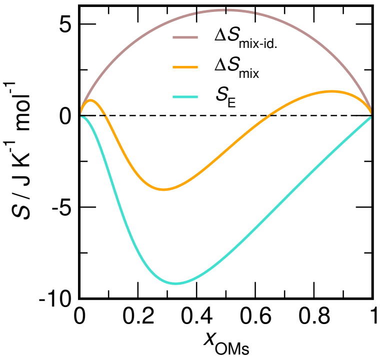

FIG. 5. Different contributions to the entropy of mixing ΔS_{mix} of the PIL mixture at $T = 400$ K. The excess entropy S_E due to HB redistribution according to Equation 14 is negative, even overcompensating the positive *ideal* contribution $\Delta S_{\text{mix-id.}}$ due to the statistictical distribution of the anions in the mixture in the range $0.1 \leq x_{\text{OMs}} \leq 0.65$.

Helmholtz energy is accordingly

$$\begin{aligned} A_E &= -xN\Delta\epsilon_{\text{HB}} \\ &\quad -Nk_BT\ln\left[x^\alpha e^{-\beta\Delta\epsilon_{\text{HB}}} + 1 - x^\alpha\right] . \end{aligned} \tag{13}$$

From Equation 13 and Equation 11 follows the excess entropy as

$$\begin{aligned} S_E &= Nk_B\ln\left[x^\alpha e^{-\beta\Delta\epsilon_{\text{HB}}} + 1 - x^\alpha\right] \\ &\quad + Nk_B\, y\, \frac{\Delta\epsilon_{\text{HB}}}{k_BT} . \end{aligned} \tag{14}$$

The equilibrium of HBs between the two anion species can be expressed by employing Equation 10 with

$$K = \frac{y_{\text{OMs}}}{y_{\text{OTf}}} = \frac{y}{1-y} = \frac{x^\alpha}{1-x^\alpha}\, e^{-\beta\Delta\epsilon_{\text{HB}}} . \tag{15}$$

Since

$$K = \frac{x}{1-x}\, f \tag{16}$$

with being f the ratio of the individual HB acceptance capabilities $f = p_{\text{OMs}}/p_{\text{OTf}}$ discussed in ref [11]. The parameter f can be expressed according to Equation 15 as

$$\frac{x^{\alpha-1}(1-x)}{1-x^\alpha} e^{-\beta\Delta\epsilon_{\text{HB}}} = f . \tag{17}$$

Figure 4 shows a comparison of the thermodynamic mixing properties obtained from MD simulations at $T = 400$ K with theoretical predictions employing $\Delta\epsilon_{\text{HB}} = -10.5\,\text{kJ mol}^{-1}$ and $\alpha = 2.05$. Obviously, the model is describing the simulation data very well using the energy difference obtained independently from the van 't Hoff analysis discussed in Figure 2. In addition, the corresponding fractions of HBs to both anion species are described similarly well. This is strongly suggesting that HB redistribution is indeed *the* dominating contribution to the energy of mixing. In addition, however, the model is also predicting the entropic contribution to free energy of mixing. In particular, we would like to point out the curious negative mixing entropies ΔS_{mix} observed in the range $0.1 \leq x_{\text{OMs}} \leq 0.65$ in Figure 4a. As illustrated in Figure 5, this feature is observed because the excess entropy due to HB redistribution effects according to Equation 14 is throughout negative and overcompensating the positive ideal contribution to the entropy of mixing. The fact that $S_E < 0$ can be understood as follows: the interaction $\Delta\epsilon_{\text{HB}}$ is steering the HBs donated by the [TEA] cations towards [TEA]-[OMs] accepting sites and is therefore imposing a constraint on the configuration space available to the cations in the mixture. This is contrasted by the situation in the pure liquid, where all HB-interactions with surrounding HB-acceptors have the same energy. The cation can hence explore the HB-accepting sites of all the surrounding anions freely. The negative excess energy is correlated with an excess entropy of the same sign, exhibiting an "enthalpy-entropy compensation" behaviour.[36] The resulting Helmholtz energy of mixing, however, is still negative, leading to the formation of thermodynamically stable mixtures. In a forthcoming publication we demonstrate that both, experimental and simulated mixtures behave qualitatively similar with respect to the enthalpic effect of hydrogen bond redistribution.[37] In conclusion, this particular mixture of PILs system seems to be one of few examples with a negative mixing entropy [38] and where where the mixing process is driven by enthalpy, not entropy.

We thank the Leibniz Association, the State of Mecklenburg-Vorpommern, and the University of Rostock for financial support within the ComBioCat programme. This work has been supported by the DFG Research Grant LU-506/14-2 (No. 286149019).

---

* dietmar.paschek@uni-rostock.de

[1] J.-P. Belieres and C. A. Angell. Protic ionic liquids: Preparation, characterization, and proton free energy level representation. *J. Phys. Chem. B*, 111:4926–4937, 2007.
[2] R. Caparica, A. Júlio, A. R. Baby, E. U. A. M. Araújo, A. S. Fernandes, J. G. Costa, and T. Santos de Almeida. Choline-amino acid ionic liquids as green functional excipients to enhance drug solubility. *Pharmaceutics*, 10:288, 2018.
[3] B. Peric, S. Sierra, E. Martí, R. Cruanas, M. A. Garau, J. Arning, U. Bottin-Weber, and S. Stolte. (eco)toxicity and biodegradability of selected protic and aprotic ionic liquids. *J. Hazard Mater.*, 261:99–105, 2013.
[4] H. Every, A. G. Bishop, M. Forsyth, and D. R. MacFarlane. Ion diffusion in molten salt mixtures. *Electrochimica Acta*, 45:1279–1284, 2000.
[5] K. A. Fletcher, S. N. Baker, G. A. Baker, and S. Pandey. Probing solute and solvent interactions within binary ionic liquid mixtures. *New J. Chem.*, 27:1706–1712, 2003.
[6] J. N. Canongia Lopes, T. C. Cordeiro, J. M. S. S. Esperanca, H. J. R. Guedes, S. Huq, L. P. N. Rebelo, and K. R. Seddon. Deviations from ideality in mixtures of two ionic liquids containing a common ion. *J. Phys. Chem. B*, 109:3519–3525, 2005.
[7] P. Navia, J. Troncoso, and L. Romaní. Viscosities fir ionic liquid binary mixtures with a common ion. *J. Solution Chem.*, 37:677–688, 2008.

[8] Gary Annat, M. Forsyth, and D. R. MacFarlane. Ionic liquid mixtures - variations in physical properties and their origins in molecular structure. *J. Phys. Chem. B.*, 116:8251–8258, 2012.

[9] M. B. Oliveira, M. Domínguez-Pérez, O. Cabeza, J. A. Lopes da Silva, M. G. Freire, and J. A. P. Coutinho. Surface tensions of binary mixtures of ionic liquids with bis(trifluoromethylsulfonyl)imide as the common anion. *J. Chem. Thermodynamics*, 64:22–27, 2013.

[10] R. S. Payal and S. Balasubramanian. Homogenous mixing of ionix liquids: Molecular dynamics simulations. *Phys. Chem. Chem. Phys.*, 15:21077–21083, 2013.

[11] D. Paschek, B. Golub, and R. Ludwig. Hydrogen bonding in a mixture of protic ionic liquids: A molecular dynamics simulation study. *Phys. Chem. Chem. Phys.*, 17:8431–8440, 2015.

[12] K. Fumino, A.-M. Bonsa, B. Golub, D. Paschek, and R. Ludwig. Non-ideal mixing behaviour of hydrogen bonding in mixtures of protic ionic liquids. *ChemPhysChem*, 16:299–304, 2015.

[13] R. P. Matthews, I. J. Villar-Garcia, C. C. Weber, J. Griffith, F. Cameron, J. P. Hallett, P. A. Hunt, and T. Welton. A structural investigation of ionic liquid mixtures. *Phys. Chem. Chem. Phys.*, 18:8608–8624, 2016.

[14] D. W. Bruce, C. P. Cabry, J. N. Canongia Lopes, M. L. Costen, L. D'Andrea, I. Grillo, B. C. Marshall, K. G. McKendrick, T. K. Minton, S. M. Purcell, S. Rogers, J. M. Slattery, K. Shimizu, E. Smoll, and M. A. Tesa-Serrate. Nanosegregation and strcturing in the bulk and at the surface of ionic-liquid mixtures. *J. Phys. Chem. B*, 121:6002–6020, 2017.

[15] T. Vogl, S. Passerini, and A. Balducci. The impact of mixtures of protic ionic liquids on the operative temerature range of use of battery systems. *Electrochem commun*, 78:47–50, 2017.

[16] C. P. Cabry, L. D'Andrea, K. Shimizu, I. Grillo, P. Li, S. Rogers, D. W. Bruce, J. N. Canongia Lopes, and J. M. Slattery. Exploring the bulk-phase structure of ionic liquid mixtures using small-angle neutron scattering. *Faraday Discuss.*, 206:265–289, 2018.

[17] S. Thawarkar, N. D. Khupse, and A. Kumar. Binary mixtures of aprotic and protic ionic liquids demonstrate synergistic polarity effect: An unusual observation. *J. Sol. Chem.*, 49:210–221, 2020.

[18] E. P. Yambou, B. Gorska, and F. Béguin. Binary mixtures of ionic liquids based on emim cation and fluorinated anions: Physico-chemical characterization in view of their application as low-temperature electrolytes. *J. Mol. Liq.*, 298:111959–, 2020.

[19] M. Chakraborty, S. Barik, A. Mahapatra, and M. Sarkar. Binary mixtures of ionic liquids: Ideal, non-ideal, or quasi-ideal? *J. Chem. Phys.*, 154:224507, 2021.

[20] H. Niedermeyer, J. P. Hallett, I. J. Villar-Garcia, P. A. Hunt, and T. Welton. Mixtures of ionic liquids. *Chem. Soc. Rev.*, 41:7780–7802, 2012.

[21] A. Podgorsek, A. S. Pensado, C. C. Santini, M. F. Costa Gomes, and A. A. H. Pádua. Interaction energies of ionic liquids with metallic nanoparticles: Solvation and stabilization effects. *J. Phys. Chem. C*, 117:3537–3547, 2013.

[22] L. F. Lepre, J. Szala-Bilnik, A. A. H. Padua, M. Traikia, R. A. Ando, and M. F. Costa Gomes. Tailoring the properties of acetate-based ionic liquids using the tricyanomethanide anion. *Phys. Chem. Chem. Phys.*, 18:23285–23295, 2016.

[23] C. Herrera, M. Atilhan, and S. Aparicio. A theoretical study on mixtures of amino acid-based ionic liquids. *Phys. Chem. Chem. Phys.*, 20:10213–10223, 2018.

[24] P. Navia, J. Troncoso, and L. Romaní. Excess magnitudes for ionic liquid binary mixtures with a common ion. *J. Chem. Eng. Data*, 52:1369–1374, 2007.

[25] H. J. Castejón and R. J. Lashock. Mixtures of ionic liquids with similar molar volumes form regular solutions and obey the cross-square rules for eectrolyte mixtures. *J. Mol. Liq.*, 167:1–4, 2012.

[26] A.Podgorsek, J. Jacquemin, A. A. H. Pádua, and M. F. Costa Gomes. Mixing enthalpy for binary mixtures containing ionic liquids. *Chem. Rev.*, 116:6075–6106, 2016.

[27] I. Otero, L. F. Lepre, A. Dequidt, P. Husson, and M. F. Costa Gomes. How does the addition of a third ion affect the molecular interations and the thermodynamic properties to acetate-based ionic liquids? *J. Phys. Chem. B*, 121:9725–9736, 2017.

[28] B. Docampo-Álvarez, V. Gómez-González, T. Méndez-Morales, J. R. Rodríguez, , O. Cabeza, M. Turmine, L. J. Gallego, and L. M. Varela. The effect of alkyl chain length on the structure and thermodynamics of protic-aprotic ionic liquid mixtures: A molecular dynamics study. *Phys. Chem. Chem. Phys.*, 20:9938–9949, 2018.

[29] L. F. Lepre, M. F. Costa Gomes, A. A. H. Pádua, R. A. Ando, and M. C. C. Ribeiro. On the regular behavior of a binary mixture of ionic liquids. *J. Phys. Chem. B*, 123:6579–6587, 2019.

[30] G. Chatel, F. F. B. Pereira, V. Debbeti, H. Wang, and R. D. Rogers. Mixing ionic liquids - simple mixture or double salts? *Green Chem.*, 16:2051–2083, 2014.

[31] R. Caminiti and L. Gontrani, editors. *The Structure of Ionic Liquids*. Springer, 2014.

[32] B. Golub, K. Fumino, P. Stange, V. Fossog, R. Hempelmann, D. Ondo, D. Paschek, and R. Ludwig. Balance between contact and solvent separated ion pairs in mixtures of the protic ionic liquid [Et_3NH][$MeSO_3$] with water controlled by water content and temperature. *J. Phys. Chem. B*, 125:4476–4488, 2021.

[33] K. Fumino, V. Fossog, K. Wittler, R. Hempelmann, and R. Ludwig. Dissecting anion-cation interation energies in protic ionic liquids. *Angew. Chem. Int. Ed.*, 52:2368–2372, 2013.

[34] E. Bodo, M. Bonomo, and A. Mariani. Assessing the structure of protic ionic liquids based on triethylammonium and organic acid anions. *J. Phys. Chem. B*, 125:2781–2792, 2021.

[35] T. L. Hill. *An Introduction to Statistical Thermodynamics*. Dover, 1960.

[36] H. Qian and J. J. Hopfield. Entropy-enthalpy compensation: Perturbation and relaxation in thermodynamic systems. *J. Chem. Phys.*, 105:9292–9298, 1996.

[37] B. Golub, D. Ondo, V. Overbeck, R. Ludwig, and D. Paschek. Hydrogen bond redistribution effects in mixtures of protic ionic liquids sharing the same cation: Nonideal mixing with large negative mixing enthalpies. Preprint, 2022.

[38] O. Delaire, T. S. Swan-Wood, and B. Fultz. Negative entropy of mixing for vanadium-platinum solutions. *Phys. Rev. Lett.*, 93:185704, 2004.