Transitioning from Ionic Liquids to Deep Eutectic Solvents

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ABSTRACT: Ionic liquids (ILs) and deep eutectic solvents (DESs) have been lately the solvents of choice in a number of processes because they offer a valid alternative to conventional solvents. Despite main interactions in ILs differ from those in DESs (e.g., electrostatic-type in the former and H-bond-type in the latter), these two neoteric solvents are more closely related that appeared and can be seen as the two sides, the face and the cross, of the same coin. Herein, we hypothesized about a way for transitioning from one to the other. In particular, we promoted the transition from 1-ethyl-3-methylimidazolium chloride (EMIMCl) to EMIMCl-nAcOH-based DESs by the simple addition of stoichiometric amounts of acetic acid (AcOH) to EMIMCl. 1H NMR spectroscopy and DSC studies confirmed the occurrence of such a transition. Molecular dynamics (MD) simulations revealed the capability of the Cl anion to fully accommodate up to 4 AcOH molecules (e.g., EMIMCl·AcOH, EMIMCl·2AcOH, EMIMCl·3AcOH, and EMIMCl·4AcOH) without signs of H-bond self-interactions between AcOH molecules. These DESs exhibited quite different solvent properties, with α and β Kamlet-and-Taft parameters that differed from those of EMIMCl and 1-ethyl-3-methylimidazolium acetate (EMIMOAc). Interestingly, excess molar volume and excess viscosity measurements as well as Brillouin spectroscopic experiments indicated that aqueous dilutions of EMIMCl·AcOH-based DESs deviated from ideality as a consequence of the formation of HBs between water molecules and the anion, as observed by 1H NMR spectroscopy.

KEYWORDS: Ionic liquids, Deep eutectic solvents, Transition, Hydrogen bonds, NMR, MD simulations, Excess properties

INTRODUCTION

Despite the first description of a room temperature molten salt dates back to 1914, it was in the 1980s when all the scattered works published since then were definitively grouped and became a topic of research for many different research works. Nowadays ILs are widely used not only as solvents for synthesis, extraction, or dissolution of recalcitrant substances but also as electrolytes and catalysts. ILs were originally conceived as molten salts combining a single organic cation and a single organic or inorganic anion so that the charges are neutralized. More recently, certain mixtures of ILs have resulted in the formation of “new solutions” with properties that were somehow different from those of the original ILs. In these cases, one should not look to the individual ILs as an identity but as a combination of ions interacting alternatively with all the possible counterions. For instance, compositions containing more than one cation or anion (e.g., [C1][A1][A2][1−x] with one cation and two anions or [C1][C2][1−x][A] with two cations and one anion) have been defined as “double salt ionic liquids” (DSILs) and can be simply obtained upon the mixing of [C1][A] and [C2][A] in the former case or [C1][A] and [C2][A] in the latter one. Thus, mixing of the two IL parents in different ratios may provide a full range of DSILs, this being particularly interesting for those ratios corresponding to eutectic compositions and hence showing unique melting points and glass transition temperatures. These sorts of compositions have recently received great attention because such property changes opened the path to either improve the performance of existing ILs in a particular application or even to explore new ones.

Besides ILs, deep eutectic solvents (DESs) have also received great attention. DESs were first described by Abbott and co-workers in 2003 as supramolecular complexes formed between one hydrogen bond donor (HBD) and one hydrogen bond acceptor (HBA, typically an ammonium or phosphonium salt). The charge delocalization that occurs between the HBD and the HBA is responsible for the decrease of the melting point of the mixture as compared to those of the individual components. More recently, DESs have been described as mixtures of two or more pure compounds for which the eutectic point temperature is below that of an ideal liquid mixture, presenting significant negative deviations from...
ideality. Additionally, the temperature depression should be such that the mixture is liquid at the operating temperature for a certain composition range. Otherwise, a simpler term “eutectic solvent” could be used to describe mixtures that do not fulfill these criteria. As compared to ILs, DESs cover a broader range of mixtures, including charged and neutral species in either equimolar or unbalanced ratios.

The many properties shared by DESs and ILs (e.g., nonreactive with water, nonvolatile, and eventually biodegradable) make them members of the group of the so-called neoteric solvents. Few attempts have been made to correlate DESs and ILs, and they could actually be seen as the two independent sides of a coin, the face and the cross, with ionic interactions in ILs and hydrogen bonds (HBs) in DESs mainly governing their most characteristic features. This view could be revisited according to recent works describing certain features such as the presence of HBs in ILs and aqueous dilutions of ILs with the anion (chloride in most of cases, but other ones may be too) playing a critical role, similarly to what happens in DESs and HBs dilutions. Actually, this was also the case of aqueous dilutions of hydrated salts, recently described as DESs at a certain range of dilution.

If DESs and ILs are more closely related than appeared, there should be an easy way for transitioning from one to the other. In chloride-salts-type ILs, such a link would indeed be the chloride ion as can also play the role of HBA in DESs. This approach has actually been explored for the preparation of 1-ethyl-3-methylimidazolium chloride (EMIMCl)-based DESs with HBDS, such as succinonitrile, several amides, and glycol derivatives and different azole and pyridinium bases. Most of these DESs as well as some others based on different imidazolium salts like 1-butyl-3-methylimidazolium chloride (BMIMCl) or 1-hexyl-3-methylimidazolium chloride (HMIMCl) were used for gas absorption (mainly SO2, but also CO2 or NH3) using acetic acid (AcOH) as the HBD. EMIMCl was the IL of the 13C NMR chemical shifts of carbons 2 and 3, respectively, with AcOH addition was achieved to obtain EMIMCl-AcOH mixtures right after AcOH addition.

Transitioning from EMIMCl to EMIMCl:nAcOH upon the addition of AcOH. EMIMCl:nAcOH mixtures were obtained by simple addition of AcOH (e.g., 0.5, 0.66, 1, 2, 3, or 4 equiv of AcOH to obtain DESs with n_{nAcOH} = 0.5, 0.66, 1, 2, 3, or 4, respectively) to EMIMCl under gentle stirring at 20 °C. EMIMCl:nAcOH mixtures were obtained right after AcOH addition.

Materials and Methods. 1-ethyl-3-methylimidazolium chloride (EMIMCl, 65039-09-9, 99.9%) was purchased from Merck. 1-Ethyl-3-methylimidazolium acetate (EMIMOA, 143314-17-4, 98.9%), acetic acid (AcOH, 64-19-7, 100%), pyridine-N-oxide (694-59-7, 98.9%), and 4-nitroaniline (100-01-6, >99.9%) were purchased from Sigma-Aldrich. N,N-Diethyl-4-nitroaniline was purchased from Flurochem (2216-15-1, >97%). Ultra pure water with 18.2 M Ω of resistivity was obtained from an ELGA Maxima Ultra Pure Water system (ELGA Berkfeld LabWater). All chemicals were used as received without further purification.

The characteristic interactions between the DES species and the ILs with the anion (chloride in most of cases, but other ones may be too) playing a critical role, similarly to what happens in DESs and HBs dilutions. Actually, this was also the case of aqueous dilutions of hydrated salts, recently described as DESs at a certain range of dilution.

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Samples Characterization. Water content of the samples was determined by Karl Fischer titration using a Titrando 888 (Metrohm). Densities and viscosities of samples and their water dilutions were measured in a DSA 5000 M coupled with a LOVIS 2000 ME module from Anton Paar at different temperatures. This is a rolling-ball viscometer, which measures the rolling time of a ball through transparent and opaque liquids based on Hoopepler’s falling-ball principle. The equipment allows testing shear-dependent flow using variable inclination angles (from 15° to 80°). Lovis 2000 M/ME measures viscosities from 0.3 to 10000 mPa s. Therefore, the viscosity of every sample was measured by combining the ball with a capillary of the appropriate diameter (1.59, 1.8, and 2.5 mm) and calibrated with the standard liquid (N7.5, N26, and N100 viscosity oils). Deviation of the experimental measurements of density (ρ) and viscosity (η) were calculated in terms of excess molar volumes (V^E) and logarithmic excess viscosities (lnη^E) as included below. DSC scans were performed in a TA Instruments Discovery Q2000 system, under a nitrogen atmosphere. Samples were placed onto an aluminum pan in a sealed furnace. A cooling rate of 5 °C min^{-1} was applied to decrease the temperature from room temperature to −150 °C, and two full heating and cooling cycles at the same scan rate of 5 °C min^{-1} were performed. We used the peaks at the DSC scans to assign the melting points (T_m). 1H and 13C NMR spectra were recorded using a Bruker Avance DRX500 spectrometer operating at 500 and 125.77 MHz, respectively, with a 30° pulse, acquisition time of 3.1719 or 1.0912 s, relaxation delay of 1 or 2 s, and 16 or 128 scans, respectively. The temperature was set to 25 or 85 °C in every experiment using a Bruker Variable Temperature BVT 3000. The samples were placed in capillary tubes, using deuterated DMSO (DMSO-d6) as the external reference. The peaks were identified, and spectra were processed using the software MestReNova. 13C NMR spectra of samples containing 0.25 mol mL^{-1} of pyridine-N-oxide were also measured, and a solution of tetramethylsilane (TMS) in pure deuterated water (99.96% D) was used as the external standard. The α parameters (α_{24} and α_{4}) were calculated from the differences, d_{24} and d_{4} (in ppm) of the 13C NMR chemical shifts of carbons 2 and 4, respectively, with respect to that of carbon 4 of pyridine-N-oxide according to the following equations:
\[ \alpha_{34} = 2.32 - 0.15d_{2.32} \quad (1) \]

and

\[ \alpha_{34} = 0.40 - 0.16d_{0.40} \quad (2) \]

Stock solutions of the solvatochromic probes with concentrations of 4 mg mL\(^{-1}\) for \(N,N\)-diethyl-4-nitroaniline (DENA) and 3 mg mL\(^{-1}\) for 4-nitroaniline (NA) were prepared by their dissolution in acetone in precleaned glass vials in absence of the light. For the determination of the \(\beta\) parameters, an appropriate amount of the probe solution (5 \(\mu\)L) was transferred from the stock solution to the vials and the acetone was evaporated using a gentle stream of high purity nitrogen gas. Then, a precalculated amount of every sample (1 mL) was directly added to the vial and the solution thoroughly mixed in absence of light. The samples were transferred into a 10 mm light path quartz cuvette and a Cary Varian 4000 double beam spectrophotometer was used for acquisition of the UV–vis molecular absorbance data. The \(\beta\) parameters were calculated using eq 3:

\[ \beta = \frac{1.035n_{\text{max}}(\text{DENA}) + 2.064 - n_{\text{max}}(\text{NA})}{2.8} \quad (3) \]

Brillouin spectra were recorded using a Sandercock 3 + 3 Pass Tandem Fabry-Pérot interferometer as Brillouin spectrometer and the light source was a DPPS laser working at a wavelength \((\lambda_0)\) of 532 nm. In this case, the liquid samples were placed in optical cuvettes (Starna) with 1 mm in optical path length. Experiments were performed using 90 A scattering geometry. The Brillouin peaks were fitted using a Lorentzian function with an adequate background function. The constraints associated with this experimental setup made impossible the application of a typical damped harmonic oscillator model. The 90 A scattering geometry is independent of the refractive index \((n)\), and its acoustic wave vector is

\[ q^{90A} = \frac{4\pi\sin(\pi/4)}{\lambda_0} \quad (4) \]

where \(\lambda_0\) is the wavelength used excitation. The hypersonic sound propagation velocity \((V_{90A})\) can be obtained from the relation between the Brillouin frequency shift \((f)\) and \(q^{90A}\) and expressed as

\[ V_{90A} = \lambda(2nf)/q^{90A} \quad (5) \]

Thus, the hypersonic velocity could also be written as

\[ V_{90A} = \lambda f^{90A} / \sqrt{2} \quad (6) \]

**Simulations.** We used a combination of classical MD simulations and quantum semi-empirical calculations to reveal the interactions of the components of the EMIMCl-nAcOH mixtures at the molecular level. The MD simulations were carried out using the GROMACS simulation software.\(^{50-53}\) The molecular models for the IL (e.g., EMIMCl) and the solvent (e.g., AcOH) were reported in the literature by Wang et al. and Jedlovszky et al., respectively.\(^{54,55}\) We created the systems by randomly placing the IL and organic molecules in an initial cubic box of 40 Å side length, close to their density. This included 215 EMIMCl ion pairs and 215 AcOH molecules for \(n_{\text{AcOH}} = 1\). We decrease the number of IL ion pairs and increase the number of organic molecules to obtain stoichiometric amounts of AcOH until \(n_{\text{AcOH}} = 8\), including 65 EMIMCl ion pairs and 520 AcOH molecules, respectively. We carried out energy minimization, followed by MD simulations in the NPT and NVT ensemble to equilibrate and obtain the structural properties of the EMIMCl-nAcOH mixtures. We employed the same MD settings than in our previous work.\(^{56}\)

We also performed quantum semiempirical calculations at the density functional tight binding (DFTB) level of theory to complement the MD simulations. We used the extended tight binding GFN1-xTB method developed by Grimme et al.\(^{57,58}\) This method contains a parametrization for almost all the elements of the periodic table (up to \(Z \approx 86\)), and it has been particularly tested for describing the potential energy curve for the dissociation of ionic liquids\(^{59}\) and to compute a variety of properties of ionic crystals such as halide perovskites.\(^{59}\) To obtain the optimized structures of the
In non-ideal solvent mixtures with HB capabilities, deviation from ideality (Figure 1d) revealing a compression of the mixture as compared to how an ideal mixture would result in significant changes in some specific physicochemical features of the mixture as compared to those of the original components. Thus, the melting point of EMIMCl was at 89.5 °C in the DSC scan depicted in Figure 1a. Neither a Tm nor a crystallization temperature (Tc) was found in the DSC scans of EMIMCl-nAcOH mixtures with nAcOH = 0.5, 0.66, 1, and 2 (Figure 1a). Both transitions were observed for the mixtures with nAcOH = 3 and 4 (Figure 1a). The mixture with nAcOH = 3 exhibited both the Tm and the Tc at the lowest temperatures of whole whole set of samples (e.g., ca. −23 and −105 °C, respectively) (Figure 1a,c), but only the mixtures with nAcOH = 0.5, 0.66, 1, and 2 stayed in their liquid form at −78 °C (Figures 1b and S1). Given the uncertainty in the determination of the eutectic composition of these mixtures, we also measured densities of liquid binary mixtures of EMIMCl and AcOH at 85 °C to calculate excess molar volumes (V e). Excess molar volumes exhibited a negative deviation from ideality (Figure 1d) revealing a compression of the mixture as compared to how an ideal mixture would behave. In non-ideal solvent mixtures with HB capabilities, negative excess molar volumes have been ascribed to the accommodation of the molecules of one of the components within the original HB network of the second one resulting in a new hybrid HB network that includes both components forming stronger and/or more numerous HBs than in the original pristine state. For instance, the maximum deviation of excess molar volumes in mixtures of H2O and DMSO is indeed at the molar fraction (XH2O ≈ 0.6),65 that is, the mixture with the lowest Tm among all the mixtures with different H2O:DMSO molar ratios.63,64

In our case, this maximum deviation from ideality occurred at XEMIMCl ≈ 0.23 (Figure 1d), that is, the EMIMCl-nAcOH mixtures with nAcOH = 3 so this mixture could eventually be considered as the eutectic one.

Viscosity (measured at 85 °C) also experienced a significant decrease from ca. 30 cP for EMIMCl (water content was 2 wt % as determined by titration) to ca. 7.6, 4.0, 3.3, and 2.4 cP for EMIMCl-nAcOH mixtures with nAcOH = 1, 2, 3, or 4, respectively. It is worth noting that our viscosity data for EMIMCl and EMIMOAc agreed with those found in the bibliography (e.g., 65 cP for EMIMCl at 80 °C65 and 17–18 cP EMIMOAc at 70–80 °C65,66) considering slight fluctuations in viscosity can be ascribed to small differences in water content given the hygroscopicity of both ILs. Interestingly, the liquid nature of EMIMCl-nAcOH mixtures allowed the measurement of viscosities at 25 °C (e.g., 47.7, 17.2, 11.7, and 8.4 cP for nAcOH = 1, 2, 3, and 4, respectively).

Moreover, 1H and 13C NMR spectroscopy of EMIMCl, EMIMOAc, and EMIMCl-nAcOH-based mixtures with nAcOH = 1, 2, and 3 revealed some differences between ILs and DESs. It is worth noting how the 1H and 13C NMR spectra of EMIMCl and EMIMOAc performed in this work agreed with spectra reported in previous works.67,68 Thus, the stoichiometric integration of the peak at around 10 ppm (e.g., 1 for EMIMCl-1AcOH, 2 for EMIMCl-2AcOH, etc.) was the clearest evidence toward the negligible acid dissociation of AcOH in EMIMCl-nAcOH-based mixtures. This negligible dissociation can only be explained on the basis of the participation of this acidic proton in HBs with the chloride anion.

The formation of these new HBs should have some influences on the original HBs formed between the chloride

![Figure 2](https://doi.org/10.1021/acssuschemeng.1c06999)
and the aromatic protons of the EMIM cation (note aliphatic protons do not participate in HBs).[^69] In particular, all the peaks assigned to the H at the imidazolium ring of the EMIM cation (e.g., HC2I, HC4I, and HC5I at positions 2, 4, and 5, respectively; see Figure 2a) were upfield shifted in the $^1$H NMR spectra depicted in Figure 2 when transitioning from EMIMCl to EMIMCl–nAcOH mixtures. The shift of the $^1$H peaks to higher frequencies (e.g., upfield shift) is associated with a shortening of the HB so the shorter the HB, the larger the proton deshielding. The opposite also applies to the shift of the $^1$H signal to lower frequencies (e.g., downfield shift), so the larger the HB, the larger the proton shielding.[^70] Thus, the shielding effect experienced by HC2I, HC4I, and HC5I upon AcOH addition to EMIMCl (Figure 2 and Table S1) revealed the elongation of their respective HBs with the chloride anion. This weakening of the ionic interaction between the imidazolium ring and the chloride anion was ascribed to the elongation of their respective HBs with the chloride anion. Thus, neat AcOH forms intermolecular HB structures, and different dimer structures have also been recently described in the liquid phase. Moreover, the formation of HBs in EMIMCl–AcOH between the carbonyl group of the acetate anion and the aromatic protons of the EMIM cation has been reported (i.e., stronger for HC2I than for HC4I and HC5I).[^77] In EMIMCl–nAcOH mixtures, the COA peak appeared at chemical shifts that corresponded to neither the carbamate nor the carboxylic form (see, respectively, EMIMOA and AcOH in Figure 3). It has been reported that HB causes a shielding of the carbonyl group and, hence, the upfield shift of its chemical shift in the $^{13}$C NMR spectrum. As compared to AcOH, this was actually the case observed for the peak assigned to COA in EMIMCl–nAcOH mixtures. This behavior agreed with the presence of stronger and/or more numerous HBs in EMIMCl–nAcOH mixtures than in AcOH, according to the negative excess molar volume depicted in Figure 1d. This participation of COA in HBs was also corroborated by MD simulations (see below). Moreover, downfield shifts of COA groups in EMIMCl–nAcOH mixtures along with the increase of the medium. The opposite trend observed in the chemical shifts of the aliphatic and aromatic protons of the EMIM cation could only be explained ascribing the shifting of the former to bulk medium effects and the shifting of the latter to more specific interactions (e.g., HBs).[^73]

$^{13}$C NMR spectroscopy was also quite useful to discern the formation of HBs in EMIMCl–nAcOH mixtures (Figure 3, Table S2). In this case, carbon atoms in the EMIM cation were less sensitive to shielding/deshielding effects and the chemical shifts of EMIM peaks were basically the same for EMIMCl and EMIMCl–nAcOH mixtures. However, some interesting information could be obtained from the peak assigned to the carbonyl group of AcOH (e.g., COA). It is worth noting that carbonyl groups can act as both HBD (through the acidic proton of the OH group) and HBA (through the carbonyl group). Thus, neat AcOH forms intermolecular HB structures, either cyclic ones in gas phase[^78] or linear ones in solid phase,[^74] and different dimer structures have also been recently described in the liquid phase.[^76] Moreover, the formation of HBs in EMIMOA between the carbonyl group of the acetate anion and the aromatic protons of the EMIM cation has been reported (i.e., stronger for HC2I than for HC4I and HC5I).[^77] In EMIMCl–nAcOH mixtures, the COA peak appeared at chemical shifts that corresponded to neither the carbamate nor the carboxylic form (see, respectively, EMIMOA and AcOH in Figure 3). It has been reported that HB causes a shielding of the carbonyl group and, hence, the upfield shift of its chemical shift in the $^{13}$C NMR spectrum. As compared to AcOH, this was actually the case observed for the peak assigned to COA in EMIMCl–nAcOH mixtures. This behavior agreed with the presence of stronger and/or more numerous HBs in EMIMCl–nAcOH mixtures than in AcOH, according to the negative excess molar volume depicted in Figure 1d. This participation of COA in HBs was also corroborated by MD simulations (see below). Moreover, downfield shifts of COA groups in EMIMCl–nAcOH mixtures along with the increase of

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**Figure 3.** $^{13}$C NMR spectra of EMIMCl (a) and EMIMCl–nAcOH mixtures with $n_{AcOH} = 1$ (b), 2 (c), and 3 (d). The $^{13}$C NMR spectra of EMIMOA (e) and AcOH (f) are also included for comparison. Atoms in EMIM cation were labeled as in Figure 2 for the assignment of peaks in all these $^{13}$C NMR spectra. For comparison purposes, all $^{13}$C NMR spectra were performed at 85 °C (note in Figure 1a that EMIMCl was solid below this temperature).
$n_{\text{AcOH}}$ revealed some weakening of the HB formed between Cl and every single carbonyl group. That is, there were more HBs, but they were individually weaker because of the presence of more COA groups.

As mentioned in the Introduction, a DFTB method (e.g., GFN1-xTB) combined with MD simulations was used to obtain further insights about the molecular structure of the HB complexes formed by addition of different stoichiometric amounts of AcOH to EMIMCl. Thus, the most stable configurations were obtained for EMIMCl:1AcOH, EMIMCl:2AcOH, EMIMCl:3AcOH, and EMIMCl:4AcOH mixtures (Figure 4 and Movies S1 and S2). The results revealed that, for $n_{\text{AcOH}} = 1$, the carboxyl group of AcOH formed a molecular bridge via interaction between the carbonyl group with the imidazolium cation and the acid proton of the OH group with the chloride anion. The increase of more COA groups resulted in more AcOH molecules binding to EMIMCl until, at a certain stage, the number of AcOH molecules exceeded the EMIMCl:AcOH molecules binding to EMIMCl.

This was actually observed in Figure 5a showing the short-range RDFs of the bond formed between the chloride ion and the acidic proton of AcOH (e.g., Cl−HA) for EMIMCl:nAcOH mixtures with $n_{\text{AcOH}}$ ranging from 1 to 8. The distance of the maximum value of the peak of the RDF for low $n_{\text{AcOH}}$ values matched with the value of 1.82 Å (Cl−HA equilibrium distance) obtained from the DFTB calculations. Bond distances of ca. 1.82 Å revealed the HB nature of the Cl−HA interaction (Cl−HA angles were basically linear, within the 172−178° range). Coordination numbers and the number of HBs formed (e.g., cn(r) and $n_{\text{HA}}$ for $r = 2.5$ Å) are also shown in Figure 5b,c as a function of $n_{\text{AcOH}}$. Interestingly, Figure 5b,c reveals the stoichiometric participation of AcOH in HB complexes for up to 4 AcOH molecules by the perfect matching between $n_{\text{AcOH}}$ and $n_{\text{HA}}$. For $n_{\text{AcOH}} = 5$ and above, this correlation no longer existed and extra AcOH molecules did not fully participate in HB complexes with the chloride ion (i.e., $n_{\text{HB}}$ reached a plateau of ca. 5 for $n_{\text{AcOH}} = 7−8$). The distances of Cl−HA bonds depicted in Figures 5a for $n_{\text{AcOH}} > 5$ also revealed a deviation of the peak to longer distances revealing some loosening of the Cl−HA interaction.

This behavior should be ascribed to the capability of COA to act as an HBA. As mentioned above, neat AcOH can form intermolecular HB structures so AcOH addition also resulted in the formation of HBs with HC2I, HC4I, and HCSI. Figures 6 and 7 show RDFs, $cn(r)$, and number of HBs for COA−HA and HC2I−COA interactions, respectively. The most illustrative was again the plot of $n_{\text{HB}}$ versus $n_{\text{AcOH}}$ with a clear change of tendency for $n_{\text{AcOH}}$ values below and above 4. Thus, $n_{\text{HB}}$ increased linearly for $n_{\text{AcOH}} < 4$ and tended to reach a plateau for $n_{\text{AcOH}} > 4$ (Figure 7c), while $n_{\text{HB}}$ was negligible for $n_{\text{AcOH}} = 1−4$ and increased linearly for $n_{\text{AcOH}} > 4$ (Figure 6c). In this latter case, it is also worth noting the 1, 2, and 3 distances marked in the RDF plots depicted in Figure 6a by dark gray, gray and light gray lines and corresponding to intermolecular COA−HA HBs, intramolecular COA−HA HBs, and intermolecular COA−Cl−HA interactions, respectively. The occurrence of intermolecular COA−HA HBs was negligible for $n_{\text{AcOH}} = 1−4$ and was only for $n_{\text{AcOH}} > 4$ that the HB complex formed with Cl cannot accommodate all the AcOH molecules as reflected by the progressive recovery of the main interaction occurring in neat AcOH (Figure 6a). Based on this, EMIMCl:nAcOH mixtures were able to fully accommodate up to 4 AcOH molecules via the formation of Cl−HA and HC2I−COA interactions.

This accommodation occurred at the expenses of weakening the original interaction between the EMIM cation and the Cl−HA bonds via interaction between the carbonyl group with the imidazolium cation and the acid proton of the OH group with the chloride anion.
corresponded to the respective cn(r) values at a distance of 2.24 Å. Thus, the interactions between single ion pairs in which the carbonyl group was interacting with the HC2I proton at the same position that the chloride anion in the “in plane” configuration. Interestingly, transitioning from monomer to dimer interactions in EMIMCl ion pairs led to significant structural changes via π···π arrangement between imidazolium cations (see the antiparallel and parallel structures in Figures S2d and S2e). Thus, it has been reported that HC2I−Cl distances are larger in dimers than in monomers71 while the angle formed between the imidazolium ring and the chloride ion (e.g., C2−H···Cl) shifted from ca. 180° in the "in plane" monomer configuration to ca. 129° and 145° in the most stable dimers.71 In our case, the HC2I−Cl distances obtained from DFTB were below 2 Å in the monomers and of ca. 2.4 Å in the dimers (Figure S2d,e). Meanwhile, the angles obtained from DFTB in the dimers were ca. 117° and 138° (Figure S2d,e). These configurations indicated the occurrence of HB between the chloride anion and the HC2I proton.

However, the characterization of this sort of HBs is not trivial given the absence of an established criterion and the long H−Cl distances (i.e., longer than in standard HBs). Thus, MD simulations were performed with the aim of gaining further insights. Figure 8a,b shows, respectively, the HC2I−Cl distances and angles of EMIMCl and EMIMCl–nAcOH mixtures. Interestingly, the maximum of the first peak of RDFs for HC2I−Cl in EMIMCl was at ca. 2.6−2.7 Å, and the distribution of angles corresponding to the HBs showed a maximum at ca. 120−140° (see n = 0 in Figure 8a,b, respectively) to a large extent in accordance with data described above from DFTB. MD simulations also revealed that the intensity of this first peak decreased smoothly up to distances of ca. 4 Å. While the peak at ca. 2.4 Å can be assigned to HB interactions, the extended intensity revealed the occurrence of interactions different than regular HBs. Based on the van der Waals radii of H and Cl atoms, Hunt et al. suggested a maximum distance of 2.95 Å for HBs.71 Using this value as a cutoff, the first coordination shell of chloride ions around the HC2I protons was divided in two contributions; HBs and weak bonds (i.e., this latter resulting from the Coulombic interaction of the anion and the C2H plane). Interestingly, transition−configuration to ca. 129° and 145° in Figure 8a,b, the first coordination shell of chloride ions in EMIMCl was at ca. 2.6 Å, and the distribution of angles corresponding to the HBs showed a maximum at ca. 120−140° (see n = 0 in Figure 8a,b, respectively) to a large extent in accordance with data described above from DFTB. MD simulations also revealed that the intensity of this first peak decreased smoothly up to distances of ca. 4 Å. While the peak at ca. 2.4 Å can be assigned to HB interactions, the extended intensity revealed the occurrence of interactions different than regular HBs. Based on the van der Waals radii of H and Cl atoms, Hunt et al. suggested a maximum distance of 2.95 Å for HBs.71 Using this value as a cutoff, the first coordination shell of chloride ions around the HC2I protons was divided in two contributions; HBs and weak bonds (i.e., this latter resulting from the Coulombic interaction of the anion and the C2H bond of EMIM). In EMIMCl–nAcOH mixtures, the number of both HBs and weak bonds decreased along with the increase of nAcOH (Figures 8c). However, the loosening of HBs is more significant than that of weak bonds, showing a cross point at nAcOH = 3 (Figure 8c). In addition to the weakening of HC2I−Cl bonds, the accommodation of AcOH molecules modified the angle distribution. Both HBs and weak bonds were shifted to larger values along with the increase of nAcOH, the shifting of weak bonds being larger than that of HBs so both values became more similar for nAcOH = 8 than they were for nAcOH = 0.

HC2I−Cl interactions were significant but not the only ones between EMIM and Cl ions. The RDFs, cn(r), and the number of Cl ions around the imidazolium ring showed how the AcOH molecules weakened the EMIMCl network (Figure S3). Interestingly, there was a significant reduction (ca. 70%) in the number of Cl ions in the first coordination shell of the EMIM rings from nAcOH = 0 to 4, the pace of this reduction being slowed down for nAcOH = 5 and above (Figure S3c). In
summary, AcOH molecules were integrated within the EMIMCl arrangements by forming numerous HBs with both EMIM and Cl ions until \( n_{\text{AcOH}} = 4 \) that resulted in the weakening of the EMIM-Cl self-interactions. For \( n_{\text{AcOH}} > 4 \), the capability of the EMIMCl network to accommodate additional AcOH molecules was far less than for \( n_{\text{AcOH}} < 4 \) so AcOH molecules started creating their own HB network.

This new HB arrangement formed among the original IL components and the added AcOH in EMIMCl-\( n \)AcOH mixtures must be reflected in their respective solvent properties. Insights about this matter were obtained by the determination of Kamlet-and-Taft parameters. In particular, the \( \alpha \) and \( \beta \) parameters related to, respectively, hydrogen bonding acidity and basicity were obtained. As described in detail in the experimental part, the \( \alpha \) parameters (\( \alpha_{24} \) and \( \alpha_{34} \)) were determined by \(^{13}\)C NMR spectroscopy using the probe pyridine-N-oxide \(^{9,80}\) from the difference between the chemical shifts of carbons 2 and 3, respectively, with respect to that of carbon 4 of the probe. Meanwhile, the \( \beta \) parameter was determined by UV–vis spectroscopy using the probes N,N-diethyl-4-nitroaniline (DENA) and 4-nitroaniline (NA) \(^{81}\) Given that the presence of water may modify these (and others) physicochemical properties, the water content was determined (measured by titration, see experimental part). This was around 0.3% in every EMIMCl-\( n \)AcOH mixture before the determination of \( \alpha \) and \( \beta \) parameters. For comparison, \( \alpha \) and \( \beta \) parameters were also determined for EMIMCl and EMIMOAc.

The \( \alpha_{24} \) and \( \alpha_{34} \) parameters obtained for EMIMCl-\( n \)AcOH mixtures are shown in Table 1. The linear correlation found between our \( \alpha_{24} \) and \( \alpha_{34} \) parameters agreed with that previously obtained for different ILs and solvents (Figure S4) where a correlation between \( \alpha_{24} \) and data obtained with the Reichardt’s dye (\( \alpha_{BD} \)) was also established (e.g., \( \alpha_{24} = 0.88 \alpha_{BD} \)) \(^{80} \). In our case, \( \alpha_{24} \) parameters ranged from 0.80 to 1.34 at 25 °C and from 0.67 to 1.26 at 85 °C for \( n_{\text{AcOH}} \) increasing from 1 to 4 (Table 1). This tendency revealed a larger efficiency for proton donating along with \( n_{\text{AcOH}} \) in agreement with previous \( \alpha \) parameters found for a carboxylic-acid-based DES with increased molar ratios of acid. \(^{82}\) Moreover, all the \( \alpha \) parameters in EMIMCl-\( n \)AcOH mixtures were higher than those measured at the same conditions of EMIMOAc (e.g., 0.27 at 25 °C and 0.24 at 85 °C) and EMIMCl (e.g., 0.33 at 85 °C) in agreement with previous works comparing \( \alpha \) parameters of different DESs and ILs.\(^{81,82}\) It is worth mentioning that, after the application of the above-mentioned correlation between \( \alpha_{24} \) and \( \alpha_{BD} \), the resulting \( \alpha_{BD} \) parameter of EMIMOAc (e.g., 0.31) was below some other ones measured previously (e.g., 0.40\(^{83}\) and 0.49\(^{84}\)). Nonetheless, dispersion among these previous data was already high. Meanwhile, the \( \beta \) parameter in EMIMCl-\( n \)AcOH mixtures ranged from 0.85 to 0.69 at 25 °C for \( n_{\text{AcOH}} = 1 \) and 4, following an opposite trend to that of \( \alpha \) parameters (Table 1).\(^{79}\) These \( \beta \) parameters were all below that we measured for EMIMCl also at 25 °C (e.g., 1.36) similarly to the trend described in previous works for aqueous dilutions of EMIMOAc.\(^{84}\)

These differences in the specific solvent properties described above for EMIMCl or EMIMOAc and EMIMCl-\( n \)AcOH mixtures were indeed reflected in their respective solvent capabilities. For instance, it is well-known that EMIMCl and EMIMOAc are excellent solvents for cellulose.\(^{85,86}\) The goodness of a particular solvent for cellulose dissolution has been ascribed to its \( \beta \) parameter (e.g., \( \beta > 0.8 \))\(^{80}\) or some other more elaborate criteria (e.g., 0.35 < \( \beta − \alpha < 0.9 \) and 0.8 < \( \beta < 1.2 \)).\(^{87}\) Moreover, recent works using MD simulations revealed the critical role played by chloride anion that penetrates between cellulose molecular chains and form HBs with them.\(^{88}\) These new HBs replace the original HBs between chains thus promoting chains cleavage and cellulose dissolution. In our case, neither the \( \alpha−\beta \)-based criteria nor the HB formation between the chloride anion and AcOH molecules anticipated the suitability of EMIMCl-\( n \)AcOH mixtures for cellulose dissolution. Actually, it was experimentally found that cellulose dissolution.
solubility in EMIMCl·nAcOH mixtures is negligible. Interestingly, one could take advantage of the different cellulose solubility in EMIMCl and EMIMCl·AcOH and the easy transition from one to another to design a more efficient and energy-saving method for cellulose regeneration and EMIMCl recovery (e.g., after cellulose dissolution in EMIMCl, transition from EMIMCl to EMIMCl·nAcOH mixtures upon addition of AcOH would result in cellulose precipitation and separation from the EMIMCl liquid phase). Further details of this process will be described in a forthcoming paper, but we can tell in advance that the high viscosity of the EMIMCl·nAcOH mixtures made necessary the use of H2O as an additional antisolvent.

Within the context of adding H2O to DESs, the determination of the dilution range where the characteristic HB network still prevails (i.e., the so-called water-in-DES regime) is currently receiving great attention as a strategy to overcome some drawbacks of neat DESs (e.g., high viscosity) that ultimately limit their applications. Many recent works have described the nonideal behavior of liquid binary mixtures of DESs with different solvents. As a general rule for any liquid binary mixture, nonideality is reflected in the discrepancy between experimental data found for extensive macroscopic quantities (e.g., volume, enthalpy or internal energy) and data obtained from the sum of the corresponding quantities of the individual components.

In this work, volumetric properties were calculated in terms of excess molar volume

\[ V^E = \left( \chi_{DES} M_{DES} + \chi_{H2O} M_{H2O} \right) / \rho - \left( \chi_{DES} M_{DES} / \rho_{DES} + \chi_{H2O} M_{H2O} / \rho_{H2O} \right) \]

where \( \chi_{DES}, M_{DES} \) and \( \rho_{DES} \) are the molar fraction, the molecular weight, and the density of DES; \( \chi_{H2O}, M_{H2O} \) and \( \rho_{H2O} \) are the molar fraction, the molecular weight, and the density of H2O; and \( \rho \) is the density of the mixture. The excess of viscosity is

\[ \ln \eta^E = \ln \eta - \left( \chi_{DES} \ln \eta_{DES} + \chi_{H2O} \ln \eta_{H2O} \right) \]

where \( \eta_{DES}, \eta_{H2O}, \) and \( \eta \) are the respective viscosities of DES, H2O, and the mixture. Densities and viscosities were measured at different temperatures (Figure S5). EMIMCl·nAcOH mixtures could be considered as either a binary mixture, and then, its molecular weight would be calculated as

\[ M_{DES}^B = \chi_{EMIMCl} M_{EMIMCl} + \chi_{AcOH} M_{AcOH} \]

or a single component, in this case, its molecular weight would be calculated as

\[ M_{DES}^S = M_{EMIMCl} + n_{AcOH} M_{AcOH} \]

Figure 9. Plot of excess molar volume (\( V^E \), top row, a, c, and e) and excess viscosity (\( \ln \eta^E \), bottom row, b, d, and f) versus DES molar fraction for EMIMCl·nAcOH mixtures with \( n_{AcOH} = 1 \) (a,b), 3 (c,d), and 4 (e,f) at 298.15 (black squares), 313.15 (red circles), 323.15 (blue triangles), and 333.15 K (inverted green triangles) and considering EMIMCl·nAcOH as binary mixtures.
recovery of intramolecular HB interactions (DES–DES and water–water).

Brillouin and NMR spectroscopies can also provide useful insights about the nonideality of aqueous DES solutions. The study of DES dilutions by Brillouin spectroscopy has been described elsewhere. Briefly, Brillouin spectroscopy focuses on the analysis of light inelastically scattered on the thermally induced sound waves (phonons) that propagate through a medium at a sound propagation velocity that depends on the sample density and rigidity and is expressed in terms of the storage longitudinal modulus. This technique has been widely used with aqueous binary mixtures where cosolvents (e.g., alcohols or even poly(ethylene-alcohol), among others) interact primarily via HBs and exhibit nonideal mixing. In all these mixtures, the plot of the hypersonic propagation velocity ($v_h$) obtained from Brillouin spectroscopy versus the molar fraction of cosolvent ($\chi_{\text{cosolvent}}$) revealed the existence of a deviation from the ideal behavior. This deviation is reflected in the shape plot depending on the cosolvent nature, displaying a maximum or a minimum when the cosolvent is a small molecule, or reaching a plateau after an initial logarithmic growth when the cosolvent is a polymer. In the current case, Brillouin spectroscopy was used to see whether aqueous dilutions of ILs differentiated from aqueous dilutions of DESs. It is worth noting that aqueous dilutions of DESs have been defined as HB complexes with water participating as a secondary HBA and/or HBD whereas aqueous dilutions of ILs as “solvent-separated ion pairs” with transient water-rich sequestered domains solvophobically accommodated around ions. Thus, in EMIMCl, the representation of $v_h$ versus $\chi_{\text{EMIMCl}}$ (that is, an IL aqueous dilution) only exhibited logarithmic growth without reaching any plateau (Figure 10). Meanwhile, in EMIMCl-nAcOH, the representation of $v_h$ versus $\chi_{\text{EMIMCl-nAcOH}}$ indeed reached a plateau right after the logarithmic growth in EMIMCl-nAcOH (Figure 10), thus revealing the occurrence of H-bonding similarly to the behavior observed for PEG aqueous dilutions. Interestingly, this plateau appearing right after the logarithmic growth became a maximum both in EMIMCl-2AcOH and (mainly) in EMIMCl-3AcOH, resembling the transition from a high-viscosity liquid binary mixtures to a low-viscosity one. Finally, EMIMCl-nAcOH mixtures with $n_{\text{AcOH}} = 1–4$ and aqueous dilutions thereof were studied by $^1$H NMR spectroscopy (Figures S7–S10), with special focus on the evolution of the chemical shift of the HDO peak along with dilution (Figure 11). It is worth noting that downfield shifts in HDO signals have been ascribed to the favored formation of H-bond structures in water. On the contrary, in aqueous dilutions of EMIMOAc, the upfield shift in the HDO peak indicates the formation of HBs between water molecules and the anion, stronger than those between water molecules themselves. This is the behavior also observed in EMIMCl-nAcOH mixtures with upfield shifts along with dilution increasing from $n_{\text{AcOH}} = 1$ to $n_{\text{AcOH}} = 4$ and thus corroborating the deviations from ideality observed in the plots of excess molar volume and viscosity, as well as in the representation of Brillouin spectroscopic data.

**CONCLUSIONS**

This manuscript describes how transitioning from EMIMCl to EMIMCl-nAcOH mixtures can be achieved by simple addition of stoichiometric amounts (e.g., up to $n_{\text{AcOH}} = 4$) of AcOH. Interestingly, transition from EMIM-based ILs to EMIMCl-based DESs could also be achieved using either different acids (even hydrophobic ones) or different ILs. For instance, Figures S11–S13 show, respectively, the mixtures resulting from addition of formic acid and octanoic acid to EMIMCl and of AcOH to EMIMTFSI, thus revealing certain universality in the strategy herein described for transitioning from ILs to DESs. In EMIMCl-nAcOH mixtures, the occurrence of this transition was confirmed by the clear differences existing in both the NMR spectra and the DSC scans as compared to those of EMIMCl. For instance, the appearance of the peak ascribed to the acidic proton of AcOH in the $^1$H NMR spectra of EMIMCl-1AcOH, EMIMCl-2AcOH, or EMIMCl-3AcOH (and how it is upfield shifted along with the increase of the AcOH molar ratio) confirmed the occurrence of H-bonding and, hence, of DES formation. Moreover, the $T_m$ experienced a significant decrease from ca. 90 °C for EMIMCl to below −20 °C for EMIMCl-3AcOH, as revealed by the DSC scans. MD simulations confirmed the formation of HB complex structures between EMIMCl and AcOH where the chloride anion acted as a molecular bridge thanks to its HBA capability with both the acidic proton of AcOH and the aromatic protons (mainly that at C2) of the imidazolium ring. In particular, the new HB complex was capable to fully accommodate up to 4 AcOH molecules (with no sign of AcOH HB self-interactions) to...
form EMIMCl·1AcOH, EMIMCl·2AcOH, EMIMCl·3AcOH, and EMIMCl·4AcOH DESs. These DESs also exhibited quite different solvent properties, with α and β Kamlet-and-Taft parameters that differed from those of EMIMCl and EMIMOAc. Aqueous dilutions of EMIMCl·nAcOH mixtures were also studied. Plots representing excess molar volume and viscosity revealed the nonideality of aqueous dilutions of EMIMCl·nAcOH mixtures coming from the strong formation of HBs between water molecules and the anion, more so than those between water molecules themselves. The deviation from ideality and the formation of strong HBs between water molecules and the anion was further confirmed by Brillouin and 1H NMR spectroscopies, respectively.

### ASSOCIATED CONTENT

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/10.1021/acssuschemeng.1c06999.

1H and 13C NMR chemical data and spectra, pictures of some EMIMCl·AcOH-based mixtures, RDFs obtained from MD simulations for EMIMCl·nAcOH mixtures, linear correlation between α23 and α45 for EMIMCl·nAcOH mixtures, DSC scans and pictures of EMIMCl-based mixtures with either HOOCH or HOOC-(CH2)nCH3, and EMIMTFSAcOH mixtures with n= 1 and 2, and densities, viscosities, excess molar volumes, and excess viscosities of and aqueous dilutions thereof. (PDF)

Movies of the evolution to and snapshots of the stable configurations obtained from DFTB calculations for EMIMCl·AcOH-based mixtures (MP4s)

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**Notes**

The authors declare no competing financial interest.

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