

Structural and quantitative analysis of water association in ethylammonium nitrate mixtures using soft modeling resolution of NIR spectra and molecular dynamics simulations

M. Suliany Rodríguez-Barrios^b, Antonio Rodríguez-Fortea^{c*}, Luis M. Varela^d, Daniel Salavera^b,
M. Soledad Larrechi^{a*}, Alberto Coronas^b

Group of Research in Applied Thermal Engineering-CREVER. Mechanical Engineering Dept.

^aAnalytical and Organic Chemistry Dept., ^bMechanical Engineering Dept.

^cPhysical and Inorganic Chemistry Dept.,

Universitat Rovira i Virgili, Tarragona, Spain.

^dNanomaterials, Photonics and Soft Matter group. Department of Particle Physics, Universidade de Santiago de Compostela, Santiago de Compostela, Spain.

*Tel: +34 977 559 559, [e-mail: mariasoledad.larrechi@urv.cat](mailto:mariasoledad.larrechi@urv.cat); [e-mail: antonio.rodriguez@urv.cat](mailto:antonio.rodriguez@urv.cat)

Abstract

In this work we report on the structural and quantitative analysis of the water association in ethylammonium nitrate mixtures (EAN + H₂O) using multivariate curve resolution based on alternate least squares (MCR-ALS) of Near Infrared (NIR) spectra and Car-Parrinello Molecular Dynamics (MD) simulations.

MCR-ALS methodology was used to determine the concentration of the chemical species in the EAN+H₂O mixtures, as well as the molar ratio between the coordinated EAN-H₂O species. Measurements were performed over the entire range of IL mass fraction at three temperatures 298.15 K, 308.15 K and 318.15 K. The experimental results revealed the existence of three chemical environments, bulk water (H₂O), neat ionic liquid (EAN), and solvated ionic liquid (EAN-H₂O) in the mixtures. The hydration process of EAN was observed to be favorable for EAN mole fractions lower than 0.138.

Car-Parrinello MD simulations were used to perform the structural analysis of selected mixtures. Simulations showed an increase of the water/EAN molar ratio in EAN-water complexes when the percentage of water in the mixtures was increased. In addition, they confirmed the reliability of previous classical MD simulations to analyze the interactions in the hydrogen-bonded network that is solvating EAN anions and cations.

Keywords: Ionic liquid; Solvation; Near infrared spectroscopy; Multivariate curve resolution; Molecular dynamics simulation.

1. Introduction

Ionic liquids (ILs) have aroused great interest in many fields of application to replace traditional solvents. This is primarily due to their unique properties, such as negligible vapor pressure, and high solvent capacity of organic, inorganic, polymeric, polar and non-polar compounds [1]-[7]. In the literature it has

1 been reported that ILs properties are significantly affected by the presence of water traces [8–14]. Thus,
2 the investigation of the structural changes of ILs in the presence of water is crucial to predict their
3 physicochemical properties and evaluate their potential for a given application.

4 Aqueous mixtures of ethylammonium nitrate (EAN) are particularly interesting because this protic ionic
5 liquid has the capacity to enable H-bond networks, and thus to exhibit structural and solvent properties
6 similar to those of water [15–17]. In these mixtures, several authors have reported the existence of two
7 local chemical environments, where ions and molecules behave similarly as they do in pure liquids
8 [18–20]. Despite this, no phase separation has been observed. The non-separation of phases is explained
9 by the existence in the mixture of ion self-assembly in a similar way to surfactant solutions [21].

10 In particular, Greaves et al. [18] studied the nanostructures of the EAN using small -and wide-angle X-ray
11 scattering (SWAXS), as well as water molecular state by infrared spectroscopy, in (EAN+H₂O) mixtures.
12 They reported that in mixtures with IL mole fractions lower than 0.4-0.5, the water is predominately
13 present as bulk water. While at higher concentrations, water is perturbed by the ions of EAN. Hayes et al.
14 [19,20,22] reported similar conclusions from neutron diffraction data and EPSR calculations [20], [22].

15 Frequently, the changes in the structure of ionic liquids in the presence of water is addressed by the use
16 of computational strategies. For example, Varela and co-workers [20] used classical molecular dynamics
17 simulations to study aqueous EAN mixtures with water mole percentages between 0 and 98 %. The
18 authors concluded that at low concentrations of water, a water network is not formed. However, when
19 the mole percentage of water is higher than 50%, water molecules reach the first coordination layer of
20 the cation head and replace the anion.

21 From previous studies, it can be concluded that in EAN+H₂O mixtures, depending on the water
22 concentration, EAN interacting with water molecules coexist with bulk water and neat EAN. These studies
23 facilitate a better understanding of the structural changes of EAN in the presence of water and are
24 powerful tools to predict its physicochemical properties. However, to the best of our knowledge, the
25 amount of EAN that interacts with water in the mixtures has not been reported. This amount is a measure
26 of the real miscibility of the compounds in the mixture. Thus, this information is relevant in applications
27 where the EAN will be used as an absorber of water or to understand the behavior of the excess properties
28 of the mixture, which depend on the water-EAN interactions [9,23].

29 The main objective of the present work is to analyze quantitatively the association of water in EAN+ H₂O
30 mixture. For this, the soft modeling resolution curve method based on alternate least squares (MCR-ALS)
31 has been applied to the near-infrared (NIR) spectra measured for EAN + H₂O mixtures prepared over the
32 entire IL mass fraction. This well-known algorithm has been extensively used to resolve and elucidate the
33 composition of complex mixtures [24,25]. For example, Lendt [26] and Gowen [27] used infrared spectra
34 to elucidate the association of imidazolium-based ILs in water. More recently, the authors have used
35 infrared spectra to analyze the hydration of inorganic salts [28] and determine amount of free water in a

1 mixture of imidazolium ILs [29]. Our results support the reliability of this method to quantitatively
2 determine the concentration of the chemical compounds involved in the EAN+H₂O mixtures.

3 In addition, we use this methodology to estimate the H₂O/EAN ratio of the coordinated EAN-water
4 species, which can be compared with the results of computational strategies for structural analysis of the
5 mixtures, as for example molecular dynamics (MD) simulations.

6 Therefore, to analyze in more detail how these experimental H₂O/EAN ratios change with the amount of
7 water in the solutions and to get more insight about the interactions at a molecular level, we have done
8 Car-Parrinello MD simulations for different EAN-water mixtures as well as neat EAN (see **2.4**
9 **Computational details**). This type of simulations, within the group of so-called first-principles or *ab initio*
10 MD (AIMD), allow for a non-biased full-quantum description of the electrons in the system in contrast to
11 classical MD that rely on pre-built force fields. Thus, the electronic structure and the molecular
12 interactions are described at DFT level. The size of the simulated system and the simulation time,
13 compared to classical MD, are much smaller though, so the two types of MD simulations (first-principles
14 and classical) are in some way complementary. Unlike approaches based on classical molecular dynamics,
15 AIMD studies for the analysis of water / ionic liquid mixtures are less frequent in the literature. For
16 example, this approach has been used to study mixtures of water with mono-methyl ammonium nitrate
17 (MMAM) [30], which is a protic liquid similar to the ionic liquid analyzed in the present work (EAN). In
18 particular, these authors studied the influence of a small amount of water on the properties of the IL due
19 to this solvation solvation and found that water is depolarized in this protic IL. Here, we consider EAN +
20 water mixtures with a molar fraction of water greater than 0.445, which can be considered a
21 complementary condition regarding this previous work. Our simulations show, in good agreement with
22 our experiments and with previous classical MD simulations by Varela and co-workers [20], that the anion-
23 water and cation-water coordination numbers increase when the percentage of water in the mixtures is
24 increased.

25 To evaluate the effect of temperature in the EAN-water association, the study has been done at three
26 temperatures, 298.15 K, 308.15 K and 318.15 K.

28 **2. Experimental and computational section**

30 **2.1. Ethylammonium nitrate – water mixtures**

31 Ethylammonium nitrate (EAN), was supplied by Iolitec, with purity values greater than 98%. To eliminate
32 any traces of water, it was initially heated and stirred at 333.15 K under vacuum conditions (3x10⁻² mbar)
33 for at least 48 hours. Eleven aqueous mixtures of EAN were prepared gravimetrically using an analytical
34

balance (Mettler DeltaRange, mod. AE260). **Table 1** shows the weight of each compound in the prepared mixture and their EAN mole fraction.

Table 1. Amounts of H₂O and EAN used to prepare the mixtures and the corresponding EAN mole fraction (x_{EAN})

<i>Mixtures</i>	<i>mH₂O (g)</i>	<i>mEAN (g)</i>	<i>x_{EAN}</i>
1	6.897	0.000	0.000
2	6.446	0.703	0.018
3	5.800	1.446	0.039
4	5.277	2.189	0.065
5	4.633	2.992	0.097
6	3.983	3.838	0.138
7	3.297	4.695	0.192
8	2.573	5.618	0.267
9	1.811	6.583	0.377
10	1.024	7.580	0.552
11	0.000	8.823	1.000

$$u(m) = 0.002; u(x_{EAN}) = 0.002$$

2.2. Near-infrared (NIR) measurements

The near-infrared spectrum of each solution was acquired between 800 nm and 1070 nm using an Agilent 8453UV - Vis - NIR spectrophotometer. In this spectral region, the 2nd and 3rd overtone of stretching vibration of the -OH, -NH and -CH functional groups present in H₂O and in EAN are observed [31]. Standard quartz cuvette with an optical path of 1 cm was used for measurements according to the following procedure. The cuvette and the prepared mixtures were submerged in a thermostatic water bath at the suited temperature. A Sama mercury thermometer (Model: 6332N Taylor) was used to measure the temperature. The expanded uncertainty of the thermometer is equivalent to ± 1 °C. At each temperature, the 100% of the transmittance in the spectrophotometer was established with the empty cuvette. The cuvette, which was always kept in the bath, was filled with a portion of the individual prepared mixture using a Pasteur pipette. Then, the corresponding measurement was immediately performed on the spectrophotometer located next to the bath. After each measurement, the cuvette is cleaned with ethanol (98%) and once dried, the measurement procedure is repeated with each prepared mixture. A spectral data vector was obtained with 271 absorbance values. The measurements were obtained at three temperatures, 298.15 K, 308.15 K and 318.15 K.

2.3 Data analysis

The spectra obtained for the different mixtures at the same temperature were arranged in individual spectral data matrices M_{Ti} of dimensions (11 x 271) that were processed in MATLAB (The MathWorks Inc., Natick, MA, v 2018). In each matrix, the spectra were preprocessed using a weighted least-squared

baseline function of PLS-Toolbox v7 (The Eigen Vector Research, Manson, WA) to eliminate the shift of baseline. Each individual spectra matrix M_{Ti} ($T_i = 298.15\text{ K}, 308.15\text{ K}, 318.15$) was analyzed by Multivariate Curve Resolution-Alternating Least Squares (MCR-ALS) [31,32]. According to the following equation $M_{Ti} = C_{Ti}S_{Ti}^T + E_{Ti}$, this algorithm decomposes the data matrix M_{Ti} of dimension (11x271) into the product of two new matrices C_{Ti} of dimension (11 x n) and S_{Ti}^T of dimension ($n \times 271$). Here, n is the number of significant factors representative of the compounds (bulk water, water associated with EAN and neat EAN) in the solutions. C_{Ti} and S_{Ti}^T are the matrices that contain the concentration and spectra profiles of the compounds, respectively. E_{Ti} of dimension (11 x 271) contains information about the residuals not considered in the decomposition. This algorithm involves several stages. In a first stage, it requires the selection of the number of components in the solutions (n value). In the present work, this number was determined by examining the percentage of the variance of the singular values obtained in the singular value decomposition (SVD) of the data spectral matrix M_{Ti} [33]. Second, an initial estimate of C_{Ti} or S_{Ti}^T is needed to initialize the optimization step. In this work the matrix C_{Ti} was initially estimated by the analysis of evolving factors (EFA) [34]. Then, this estimate is optimized iteratively using a restricted alternate least square regression (ALS) procedure. In this step, the non-negativity of the spectra and the concentration profiles, the unimodality of the concentration profiles and the normalization of the spectra were used as restrictions for the solutions. The maximum number of iterations was limited to 50 and a convergence criterion of 0.1 was considered.

The implicit rotational ambiguity in the MCR solutions has been evaluated using the MCR-bands method [35–37]. This method is based on the calculation of the relative contribution “ f ” of every compound in a mixture. The difference between the values of the boundaries, $f^{\max}$ and $f^{\min}$, of the possible MCR-ALS solutions, gives a measure of their ambiguity. The closer to zero the values of the difference are, the lower the rotational ambiguity the solutions will present.

2.4 Computational details

Car-Parrinello molecular dynamics simulations were carried out using the CPMD code [38][39]. The description of the electronic structure was based on the expansion of the valence electronic wave functions into a plane wave basis set, which was limited by an energy cutoff of 70 Ry. The interaction between the valence electrons and the ionic cores was treated through the pseudopotential (PP) approximation (Martins–Troullier type) [40]. The PBE density functional was selected [41]. The simulations were carried out under periodic boundary conditions in a cubic cell with a side length that slightly depends on the system (see below), a fictitious electron mass of 800 a.u. and a time step of 0.144 fs. Car-Parrinello MD simulations were done for pure EAN (side length: 10.124 Å) and for two different EAN/water mixtures, (i) 1 EAN/ 28 H₂O and (ii) 3 EAN /20 H₂O (side length: 9.960 Å). The first one

corresponds to a very diluted EAN solution (molar fraction $x_{EAN} = 0.034$) and the second one to the molar fraction at which free EAN is observed in the experiments ($x_{EAN} = 0.130$). The production runs were 100 ps long and the simulated temperatures 300 K and 340 K. To analyze the spatial correlations of the different species in the mixtures we have calculated their radial distribution functions (rdfs) and their integrations, i.e. the coordination numbers [42]. The spatial distributions functions (sdfs) have been generated with TRAVIS [43,44].

3. Results and discussion

3.1. Infrared analysis and MCR-ALS resolution

Figure 1 shows the NIR spectra of the EAN-H₂O mixtures in the spectra data matrix $M_{T=298.15\text{ K}}$. The first spectrum was obtained for pure water ($x_{EAN} = 0.000$), and thus, it is representative of the bulk water (H₂O). Their wide absorption band around 973 nm, is characteristic of the 2nd overtones of the stretching vibration of the -OH group [45]. The last spectrum was obtained for the neat EAN solution ($x_{EAN} = 1.000$). The absorption band around 899 nm and 1008 nm are characteristic of the 3rd and 2nd overtones of the stretching vibration of the -NH groups present in the ethylammonium cation [45]. The weak intensity of these bands is indicative of the formation of aggregates in IL due to, among other causes, their capacity to form H-bonds between the ions [16].

As can be expected, in the spectrum of the EAN-H₂O mixtures as long as the mole fraction of EAN increases, the intensity of the absorption band representative of the -OH group decreases and the intensity of the absorption band of the -NH group increases. It is also observed that the peak of the OH-band moves towards longer wavelength, which suggests the formation of EAN-water associations through H-hydrogen bonds [8–14]. Similar behavior was observed at 308.15 and 318.15 K (**Figure 1s** in the **Supplementary Information**).

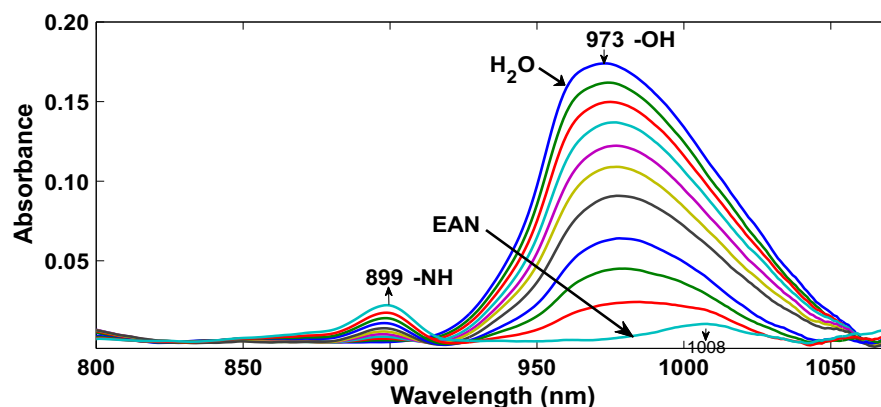


Figure 1. NIR spectra of data matrix $M_{Ti=298.15 K}$

The individual spectrum of each mixture reflects the chemical environment of the compounds, where bulk water molecules (H_2O) might coexist with different associations of water molecules interacting with the ionic liquid ($EAN-H_2O$) and molecules of neat ionic liquid (EAN) [18,19]. It is worth noting that using only NIR spectra information it is not possible to determine the different structural conformations representative of the water-ionic liquid interaction ($EAN-H_2O$). However, to quantitatively analyze the amount of water that interacts with the ionic liquid, it is only necessary to estimate the number of chemical environments that represent the total variability of the spectral data matrix. As indicated in **section 2.3**, this number was determined to analyze the rank of the spectral data matrix by SVD [33]. We verified that regardless of the temperature the first three factors retain percentages of variance higher than 99.98 %, and thus, three factors were considered to resolve the spectra data using MCR-ALS. The concentration profiles obtained by evolving factor analysis (EFA) [34] of the data matrix M_{Ti} with three factors were used to initialize the MCR-ALS algorithm. **Table 1s** in the **Supplementary Information** shows some quality parameters of the initial and final solutions. At the three temperatures, the explained variance is always higher than 99.95 % and the lack of fit lower than 2.29 %.

Figure 2 shows the MCR-ALS solutions of the M_{Ti} data matrices at 298.15 K (A, B), 308.15 K (C, D) and 318.15 K (E, F). In the spectral plots (A, C, E) the recovered spectrum with the maximum at 973 nm is representative of the bulk water molecules (H_2O). The recovered spectrum with maxima at 899 nm and 1007 nm, which are characteristic of the -NH group, is representative of the neat ionic liquid (EAN). The spectrum whose absorption band is characteristic of the -OH group but with the maximum shifted to higher wavelength (982 nm at 298.15 K and 978 nm at the higher temperatures 308.15 and 318.15 K) can be attributed to the water molecules associated with the ionic liquid ($EAN-H_2O$) through hydrogen-bonds [30]. Some differences can be observed in the ionic liquid spectrum at 298.15 K, plot A, with respect to the one recovered at 308.15 K and 318.15 K, plots C and E, respectively. At higher temperatures, the intensity of the absorption band around 1007 nm, characteristic of the 2nd overtone of the -NH group of the ionic liquid, is higher and the small peak does not appear around 958 nm. This can be attributed to

the intrinsic capacity of the protic liquid to enable hydrogen bonds that promote a higher aggregation state of the ionic liquid at low temperatures [16].

The extent of the rotational ambiguity of the solution assigned to H₂O, EAN-H₂O, and EAN in **Figure 2**, was assessed using as criteria the difference between the $f^{\max}$ and $f^{\min}$ values of the boundaries of the solutions obtained with the MCR-BANDS method [32,36]. The values for H₂O, EAN-H₂O and EAN were respectively (0.000, 0.001, 0.003) for the solutions of the $M_{Ti=298.15\text{ K}}$ matrix; (0.000, 0.003, 0.004) for the solutions of the $M_{Ti=308.15\text{ K}}$ matrix and (0.000, 0.003, 0.003) for the $M_{Ti=318.15\text{ K}}$ spectra matrix. In general, the values range between (0.000 and 0.004), which indicates that in all cases the profiles corresponding to the extreme values of $f^{\max}$ and $f^{\min}$ were practically equal to the initial ones shown in **Figure 2**. According to that, the analysis and calculations were done using the results shown in **Figure 2**. Detailed information of the solutions recovered from MCR-BANDS analysis of the spectral data matrices is included in **Table 2s** and **Figure 2s** of **Supplementary Information**.

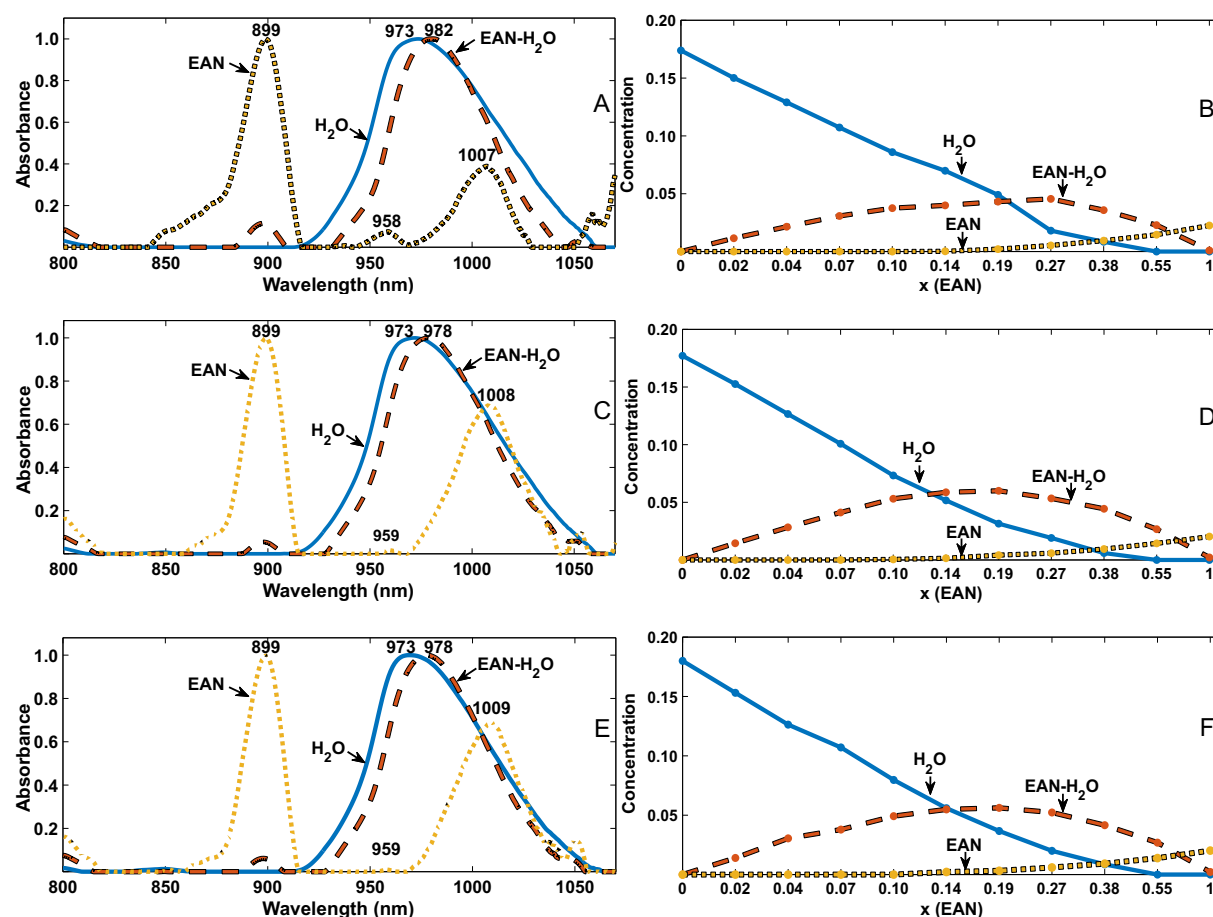


Figure 2. Spectral (A,C,D) and concentration (B, D, F) profiles recovered by MCR-ALS analysis of M_{Ti} data matrices at 298.15 K (A,B) at 308.15 K (C,D) and at 318.15 K (E,F). Color code for active chemical species: Neat ionic liquid (EAN) yellow dashed line; bulk water (H₂O) blue line and solvated ionic liquid (EAN-H₂O) orange dashed line.

The MCR-ALS spectral solutions obtained are in agreement with those described in the literature [18–20]. There is evidence of two chemical environments for the water molecules in the EAN+H₂O mixtures, as bulk water (H₂O) and as water solvating the ions of the ionic liquid (EAN-H₂O). Analogously, for the ionic liquid molecules in the mixtures, the presence of neat ionic liquid (EAN) and solvated ionic liquid (EAN-H₂O) can be claimed. Moreover, it is visible that pockets of pure water start forming at EAN molar fractions lower than 0.38.

According to the Lambert-Beer law, the MCR-ALS values reported in plots B, D and F of **Figure 2** are proportional to the values of the mole concentration of bulk water, neat EAN and solvated EAN (EAN-H₂O). From these plots we can observe that, regardless of the temperature, for EAN mole fractions lower than 0.138, the ionic liquid is only present in its solvated form (EAN-H₂O) with water molecules keeping their bulk structure. For larger EAN mole fractions, neat EAN molecules coexist with solvated EAN and bulk water.

3.2. Quantitative determination of (H₂O, EAN and EAN-H₂O) from MCR-ALS results

The following procedure to determine at each temperature the mole concentration values of H₂O, EAN or EAN-H₂O recovered by MCR-ALS in each mixture labeled as $C_{H_2O\ recovered}$, $C_{EAN\ recovered}$ and $C_{EAN-H_2O\ recovered}$ involves two steps. In the first step, the values of the concentration profiles obtained by MCR-ALS at each temperature were normalized. Normalization of the $C_{H_2O\ recovered}$ was carried out taking as a reference the value of the MCR-ALS matrix corresponding to pure water ($x_{EAN} = 0.000$). The normalization of the $C_{EAN\ recovered}$ was carried out using as a reference the value of the MCR-ALS matrix corresponding to the pure IL ($x_{EAN} = 1.000$). The normalized concentration values ranged from 0 to 1. Then, the $C_{H_2O\ recovered}$ and $C_{EAN\ recovered}$ are estimated by multiplying the normalized concentration values by the concentration of compounds in each of the prepared mixtures, C_{H_2O} and C_{EAN} . These two latter concentrations were calculated using the data shown in **Table 1** and the density values of the prepared mixtures. We used the density values measured by Zarrougui et al. [46] in mixtures of EAN+H₂O. **Table 3s** and **Figure 3s**, in the **Supplementary Information**, show the coefficients of the polynomial functions that correlate the EAN mole fraction of the mixture with the density (kg/m³). In the second step, the $C_{EAN-H_2O\ recovered}$ in each mixture was calculated from the difference between $C_{EAN} - C_{EAN\ recovered}$.

Table 2 reports the values of the EAN mole fraction, x_{EAN} , density and C_{H_2O} and C_{EAN} of the prepared mixtures at the three studied temperatures, as well as the mole concentration values recovered by MCR-ALS analysis, $C_{H_2O\ recovered}$ and $C_{EAN\ recovered}$.

- 1 **Table 2.** Density values calculated from Zarrougui data [38], EAN mole fraction (x_{EAN}) and the mole concentration of H₂O and EAN calculated from the
- 2 amount weighted of each compound and estimated from MCR-ALS at a) 298.15 K, b) 308.15 K and c) 318.15, in the prepared solutions.

	T = 298.15 K					T = 308.15 K					T = 318.15 K				
	Values in prepared mixtures			Values estimated from MCR-ALS		Values in prepared mixtures			Values estimated from MCR-ALS		Values in prepared mixtures			Values estimated from MCR-ALS	
x_{EAN}	Density (kg/m ³)	C_{H_2O} (M)	C_{EAN} (M)	C_{H_2O} recovered (M)	C_{EAN} recovered (M)	Density (kg/m ³)	C_{H_2O} (M)	C_{EAN} (M)	C_{H_2O} recovered (M)	C_{EAN} recovered (M)	Density (kg/m ³)	C_{H_2O} (M)	C_{EAN} (M)	C_{H_2O} recovered (M)	C_{EAN} recovered (M)
0.000	1000.40	55.5	0.00	55.5	0.00	997.40	55.35	0.00	55.35	0.00	994.4	55.18	0.00	55.18	0.00
0.018	1019.65	51.0	0.93	44.0	0.00	1015.81	50.82	0.92	43.79	0.00	1012.04	50.64	0.92	43.07	0.00
0.039	1037.62	46.2	1.90	34.3	0.00	1033.09	46.01	1.89	32.89	0.00	1028.61	45.81	1.88	32.14	0.00
0.065	1056.60	41.5	2.87	25.6	0.00	1051.37	41.24	2.85	23.47	0.00	1046.18	41.04	2.84	24.42	0.00
0.097	1077.98	36.4	3.91	17.9	0.00	1072.00	36.15	3.89	14.96	0.10	1066.07	35.95	3.87	15.92	0.00
0.138	1100.62	31.1	5.00	12.6	0.04	1093.94	30.92	4.97	9.03	0.37	1087.32	30.73	4.94	9.54	0.54
0.192	1123.68	25.7	6.11	7.3	0.57	1116.41	25.56	6.07	4.55	1.26	1109.25	25.40	6.03	5.18	0.95
0.267	1146.47	19.9	7.27	2.1	1.71	1138.90	19.85	7.23	2.14	2.10	1131.48	19.72	7.18	2.19	2.13
0.377	1165.92	13.9	8.46	0.7	3.53	1158.64	13.88	8.41	0.47	3.93	1151.53	13.79	8.35	0.66	3.80
0.552	1180.20	7.8	9.62	0.0	6.24	1174.01	7.75	9.57	0.00	6.79	1167.91	7.71	9.52	0.00	6.55
1.000	1206.00	0.0	11.16	0.0	11.16	1196.50	0.00	11.07	0.00	11.07	1188.80	0.00	11.00	0.00	11.00

3

Figure 3 shows the mole percentage of free water (% H₂O, calculated as $(C_{H_2O \text{ recovered}}/C_{H_2O}) * 100$) and the mole percentage of neat EAN (% EAN, calculated as $(C_{EAN \text{ recovered}}/C_{EAN}) * 100$) as a function of the ionic liquid mole fraction (x_{EAN}) in the mixture at three temperatures. At the top of the two plots, the water mole percentage (% C_{H₂O}) in each prepared mixture has been introduced to facilitate the comparative analysis with the results reported by Varela et al. [20] for EAN-H₂O mixtures. These values have been calculated as $(C_{H_2O}/(C_{H_2O} + C_{EAN})) * 100$ using the values included in **Table 1** for the prepared mixtures.

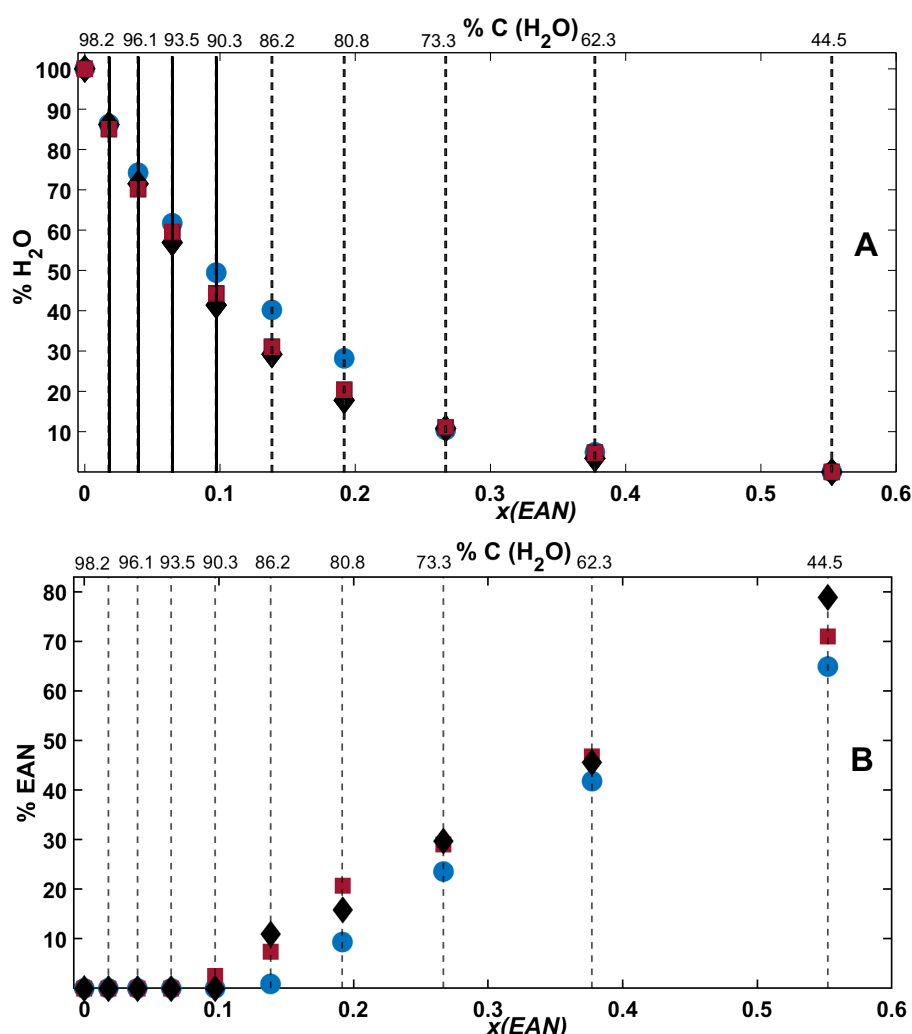


Figure 3. A) Mole percentage of free water (% H₂O) as a function of the mole fraction of EAN (x_{EAN}) at 298.15 K, filled blue circle; 308.15 K, filled red square and 318.15 K filled black diamond. **B)** Mole percentage of neat EAN (% EAN) as a function of the mole fraction of EAN (x_{EAN}) at 298.15 K, filled blue circle, 308.15 K filled red square and 318.15 K filled black diamond. At the top of two plots the water mole percentage values (% C_{H₂O}) in the prepared mixtures are included.

In agreement with Greaves et al. [16] and Hayes et al.[17], plot A shows that in mixtures with x_{EAN} values less than 0.4, bulk water is present in the mixture. For example, at 298.15 K in mixtures prepared with

$x_{EAN} = 0.097$, a 49.45 % of the mole concentration of the water used to prepare the mixture does not interact with the EAN. This percentage values decrease when the mole fraction of the EAN in the mixtures increases and cancels out for the mixture with $x_{EAN} = 0.552$ or water mole percentage % $C_{H_2O} = 44.8$ %, as previously seen. Moreover, this result is also in agreement with that reported by Varela and co-workers [20], who conclude that no water network is formed in mixtures with low water concentration, and only above 50% water concentration the number of molecules in the hydration shell of a water molecule exceeds that in the second coordination shell. In plot A, it can be observed that in mixture with water mole percentage (% $C_{H_2O} = 62.27$ %), the mole percentage of bulk water is 4.78 %. This indicates that practically all water molecules are interacting with the ions of the ionic liquid. These results support the results by Varela and co-workers [20], about the capacity of water molecules to reach the first coordination layer of the cation head and replace the nitrate anion when the water mole percentages in the mixture are higher than 50 %.

As far as the neat EAN mole percentage in the mixtures (% EAN) is concerned, plot B shows that in mixtures with high values of water concentration it exists an amount of EAN that is not interacting with water molecules. Regardless of the temperature, this occurs when in the mixture the water mole percentage is lower than 86.2 % ($x_{EAN} \geq 0.138$).

Comparing plots A and B in **Figure 3** we realize that neat EAN and free water behave differently when we change the water concentration in the mixtures. For example, at high water concentrations ($90.3\% \leq \% C_{H_2O} \leq 98.2\%$), there is almost no change in the % of neat EAN (essentially zero), but significant changes in the % of free water, from around 85% at $C_{H_2O} = 98.2$ % to 50% or even less, depending on the temperature, at $C_{H_2O} = 90.3$ %. This behavior suggests that the number of water molecules around an EAN molecule in solvated ionic liquid (EAN-H₂O) changes depending on the composition of the mixture. From plot A, we can also observe that the percentages-of free water (% H₂O) at the highest temperatures (308.15 K and 318.15 K) are lower than the values at 298.15 K, while plot B indicates that the percentages of neat EAN (% EAN) at this temperature are lower than at 308.15 K and 318.15 K. These results suggest that the number of water molecules solvating EAN species in the ionic liquid (EAN-H₂O) increases with temperature. To corroborate this, we have calculated the mole ratios [moles H₂O/moles EAN] in each EAN-H₂O mixture at three temperatures (**Table 3**) considering the moles of coordinated water as the difference between the total moles of water and the moles of recovered water, $C_{H_2O} - C_{H_2O \text{ recovered}}$, and, analogously, the moles of coordinated EAN as $C_{EAN} - C_{EAN \text{ recovered}}$. The trends shown in **Table 3** indicate that the H₂O/ EAN molar ratios are lower at 298.15 K than at higher temperatures. This is probably due to the increase in the disorder in the solvation shells associated to the weakening of hydrogen bonding with temperature [47]. Besides, for a given temperature, the H₂O/ EAN molar ratios increase

when the water mole percentage (% H₂O) increases, in line with the coordination numbers estimated by Varela and co-workers [20].

Table 3. Mole ratios (*moles H₂O*/*moles EAN*), estimated using the MCR-ALS solutions, as a function of EAN molar fraction in the different mixtures.

Mixture x_{EAN}	Ratio (moles H ₂ O)/ (moles of EAN)		
	298.15 K	308.15 K	318.15 K
0.018	7.4	7.6	8.2
0.039	6.1	6.7	7.3
0.065	5.4	6.2	5.9
0.097	4.5	5.6	5.2
0.138	3.6	4.8	4.8
0.192	3.2	4.4	4.0
0.267	3.0	3.5	3.5
0.377	2.5	3.0	2.9
0.552	1.9	2.8	2.6

The mole percentage of EAN interacting with water (% EAN-H₂O) in each of the prepared mixtures has been also analyzed at three different temperatures (**Figure 4**). At 298.15 K, for those mixtures with x_{EAN} lower than 0.097 ($0.018 \leq x_{EAN} \leq 0.097$) the mole percentages of EAN-H₂O are 100 % decreasing monotonically up to 35.1 % for the mixture with $x_{EAN} = 0.552$. At 318.15 K, the mole percentages of EAN-H₂O range between 100 % and 21.2 %. When the water mole percentage (% C_{H_2O}) is higher than 90.3 %, the mole percentage of EAN-H₂O is higher than 97 % regardless of the temperature.

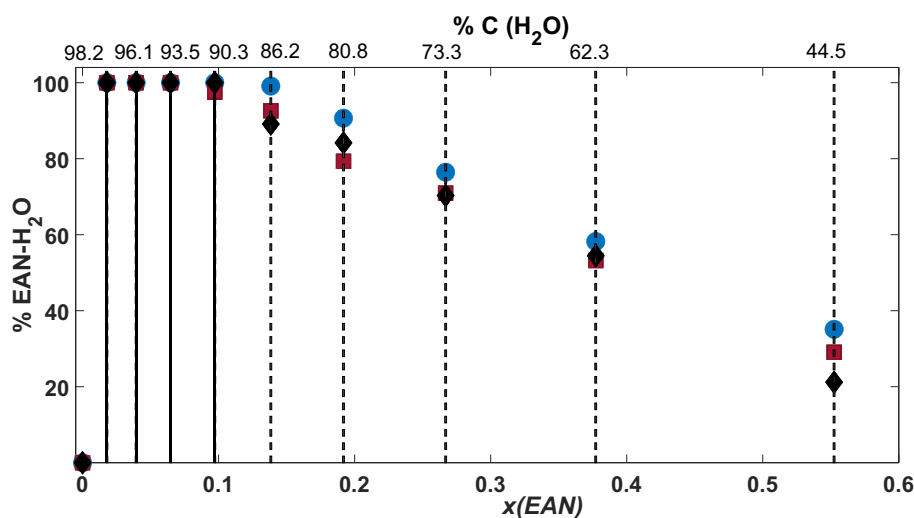


Figure 4. Mole percentage of EAN interacting with water (% EAN-H₂O) as a function of the ionic liquid mole fraction (x_{EAN}) at 298.15 K, filled blue circle; 308.15 K, filled red square and 318.15 K filled black diamond.

The discussed results are not only in agreement with the literature [18–20], but also allows to estimate quantitatively the proportion of water and EAN that are interacting in each solution.

3.3. Structural Analysis of EAN-water mixtures by Car-Parrinello MD simulations

To obtain a deeper insight into the molecular interactions between EAN ions and water molecules in these mixtures with different composition, Car-Parrinello MD simulations were done with the aim of complementing classical MD studies [20]. To analyze the spatial correlations of the ethylammonium cations, nitrate anions and water molecules we have calculated their radial distribution functions (rdfs). For neat EAN, the cation-anion rdf, measured as $g_{N_{\text{ammonium}}-N_{\text{nitrate}}}(r)$, shows a 1Å-wide peak at around 3.4-3.5 Å (see **Figure 5a**), which integrates (up to the first minimum) 3.5 ions. A hydrogen-bond network is formed between the nitrate anions and the EA⁺ cations, as shown in **Figure 5b**, where a snapshot of the simulation is represented. Each EA⁺ cation is interacting with three nitrate anions, as represented in the spatial distribution function of O atoms around an EA⁺ cation (**Figure 6a**), and each nitrate anion with three EA⁺ cations (see also **Figure 5s** in the **Supplementary Information**). In contrast to the results reported by Zhan et al. [30], who analyzed the influence of small amount of water in the structure of MMAM using Car-Parrinello MD simulations, we observe that when the amount of water incorporated to the mixtures increases, the height of this peak decreases significantly and a new shallower peak shifted to larger distances (> 5 Å) appears for very diluted mixtures, i.e. with 96.6% water. Therefore, the anion is expelled from the first coordination shell of the cation, which is preferentially interacting, i.e. solvated, with water molecules in these diluted mixtures, as pointed out by Varela and co-workers [20]. This result can be visualized from the spatial distribution function of O atoms of water molecules and nitrate anions with respect to the EA⁺ cation obtained from the simulations of the mixture at 87% water (**Figure 6b**). This is also in agreement with the fact that the strength of hydrogen bonding between water and ammonia molecules (6.44 kcal/mole [48]) is appreciably larger than those between water molecules (5.5 kcal/mole [49,50]), which explains that quite limited formation of free water pockets is registered until the number of water molecules is approximately half that in the mixture. Indeed, the N---H-O hydrogen bond between ammonia and water is known to be very strong single-well hydrogen bond [48,51], which contributes to explain the marked preference of water molecules for the EAN cation.

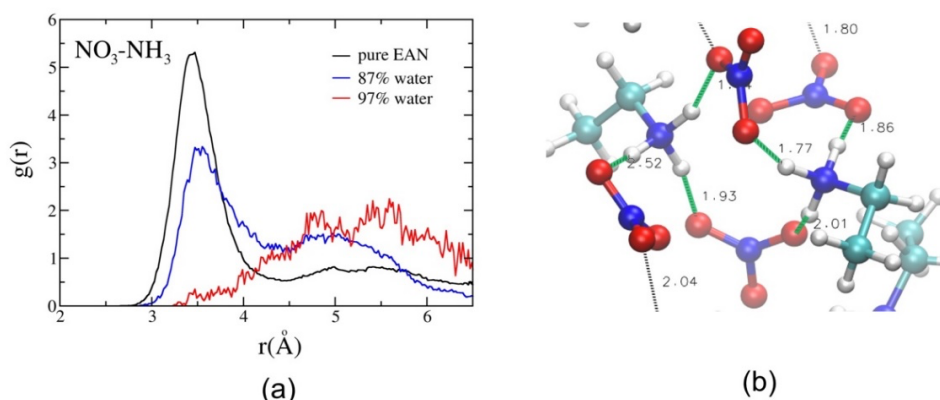


Figure 5. (a) Anion-cation radial distribution functions for pure EAN and for EAN-water mixtures at high water concentrations (87% and 97%); (b) Hydrogen-bond network between EA cations and nitrate anions in pure IL from a snapshot of the CPMD trajectory. Color code for the atoms: N dark blue, O red, C light blue and H white. H-bond distances (in Å) are also shown. The three hydrogen bonds that each EA⁺ cation makes with three nitrate anions are highlighted in green.

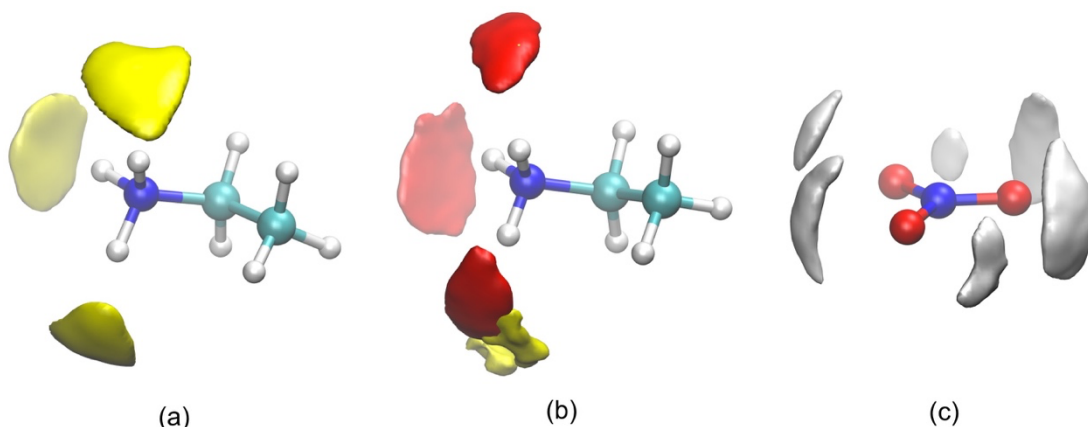


Figure 6. Spatial distribution function of (a) O atoms of nitrate (yellow surface) with respect to EA⁺ cation in pure EAN; (b) O atoms of water (red surface) and O atoms of nitrate (yellow surface) with respect to EA⁺ cation in the mixture at 87% water; and (c) H atoms of water (white surface) with respect to nitrate anion in the mixture at 87% water.

When analyzing the EAN-water interactions in mixtures with high water concentrations, our results are also in line with those of Varela and co-workers [20] confirming the suitability of the classical MD force field to describe hydrogen bonds between EAN ions and water molecules. In particular, for the interaction between the nitrate anion and water, a peak in the rdf at around 3.5 Å is observed with a minimum at around 4 Å (**Figure 7a**). For the more diluted mixture (97% water), a second peak appears at around 5 Å denoting a more-structured second solvation shell of the anion. The coordination number (CN) derived from the $N_{\text{ni-O}_w}$ rdf (see **section 2.4 Computational details**) as a function of the distance is also represented in **Figure 7a**. The CN at the position of the minimum (around 4 Å) is around 4 for the mixture with lower water content (87%) and increases to around 6 for the more diluted mixture (97%). The spatial

distribution function of H atoms of water molecules solvating the nitrate anion for the mixture with 87% water (**Figure 6c**) shows that each O atom of the nitrate interacts in average with more than one H atom of water. For the EA cation-water interaction, the N_{am-O_w} rdf in **Figure 7b** shows a peak below 3 Å (2.7-2.8 Å) and a second maximum at distances beyond 4.5 Å, which is more pronounced for the mixture with 97% water. The coordination numbers at the distance of the minimum (3.5 Å) show similar behavior as for the anion, with the cation somewhat more solvated at more diluted conditions (CN around 4 at 97% vs CN around 3 at 87%). Therefore, if we add the CN of the nitrate and that of EAN we could obtain an upper bound of the water/EAN molar ratio in solvated EAN-water complexes. For example, for the mixture with 87% water, i.e. $x_{EAN} = 0.13$, 4 (nitrate) + 3 (EA) = 7, to be compared with the experimental determination by the MCR-ALS analysis of the IR spectra, 3.6 at $x_{EAN} = 0.14$ and $T = 298.15$ K (see **Table 3**). For 96.6% water, i.e. $x_{EAN} = 0.034$, we obtain 6 (nitrate) + 4 (EA) = 10, to be compared to 6.1 at $x_{EAN} = 0.039$. The trends are correctly reproduced, but the differences with experiments seem significative. Such differences come from the fact that we are integrating the rdf up to a rather large distance (the minimum of the rdf). If we considered ion-water “complexation” distances, i.e. distances at which significant changes would appear in the NIR spectra, as for example the distances of the first peak or even slightly larger, for example, $N_{ni-O_w} = 3.7$ Å and $N_{am-O_w} = 3.0$ Å, then we would get CN more comparable to our experiment (at $x_{EAN} = 0.13$, $CN_{nitrate} = 3$ and $CN_{EA} = 2$; at $x_{EAN} = 0.034$, $CN_{nitrate} = 4$ and $CN_{EA} = 2.7$). These coordination numbers are completely compatible with those previously reported by Varela and coworkers [20].

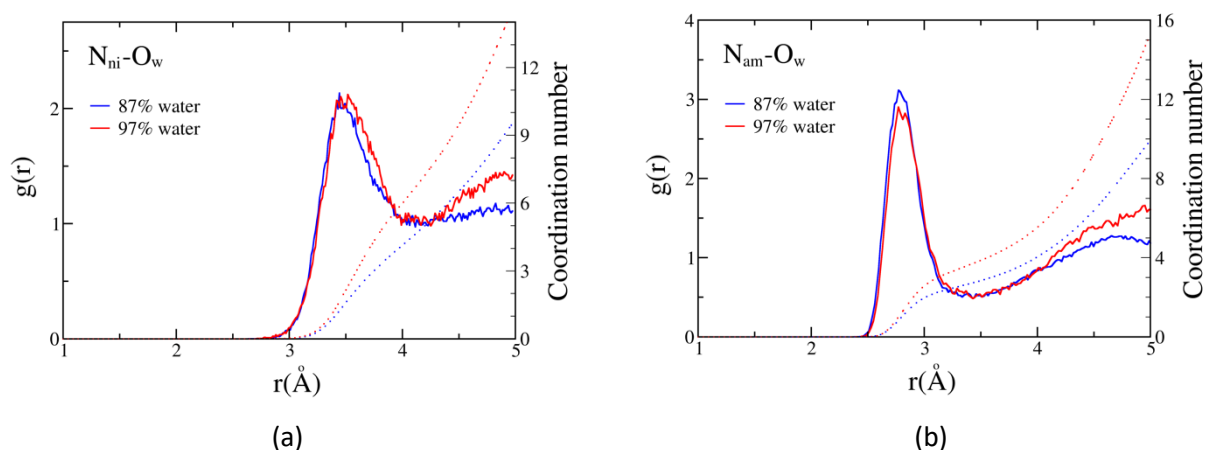


Figure 7. Radial distribution functions and coordination numbers for EAN-water mixtures at high water concentrations (87% and 97%). (a) Anion-water rdfs, measured as $N_{nitrate-O_{water}}$ distance, and (b) Cation-water rdfs, measured as $N_{ammonium-O_{water}}$ distance.

Finally, we have made simulations to analyze the effect of temperature on the EAN-water interactions and how the coordination numbers of the ions could be affected. We have chosen in our study a slightly higher temperature ($T = 340$ K) than in experiments ($T = 318.15$ K) to better identify the effects of this variable. In general, the peaks in the rdfs are, as expected, smaller at higher temperature, but the differences are not that important (see **Figure 6s** in the **Supplementary Information**). In particular, the

coordination numbers seem to be essentially unaffected at rather short distances. A different behavior is observed though when we compare the EA⁺ cations and the nitrate anions. For the cations, a tiny amount of water seems to be expelled from the first coordination shells, with lower CN at higher temperature. Contrarily, for the nitrate anions, some water appears to be approaching the anion at intermediate distance (N_{ni-O_w} around 4 Å), especially at the more diluted mixture. Therefore, from this preliminary analysis, we could think that solvation of the IL ions is somewhat different at higher temperatures. However, our simulations, at this point, are not able to confirm the moderate increase of the water/EAN molar ratio in experiments at higher temperatures.

4. Conclusions

In this work, EAN-water mixtures have been quantitatively and structurally analyzed using multivariate curve resolution of NIR spectra and Car-Parrinello MD simulations. The measurements of the NIR spectra were performed at three temperatures 298.15 K, 308.15 K, and 318.15 K, and over the entire range of EAN mass fraction. The measurements were complemented with Car-Parrinello MD simulations for selected compositions of EAN-water mixtures, and also for neat EAN.

The results revealed the existence of three chemical environments, bulk water (H₂O), neat ionic liquid (EAN), and solvated ionic liquid (EAN-H₂O) in the mixtures. We found that regardless of the temperature, for mixtures with EAN mole fractions lower than 0.138, the ionic liquid is only present in its solvated form (EAN-H₂O), with water molecules keeping their bulk structure. However, for EAN mole fractions greater 0.138, neat EAN molecules coexist with solvated EAN and bulk water.

The quantitative analysis of the amount of EAN interacting with water in the mixtures evidenced that the hydration process at EAN is favorable for EAN mole fractions lower than 0.138.

The quantitative resolution of the NIR spectra allowed us to calculate the molar ratio between the coordinated EAN-H₂O species and analyze the temperature effect in the molar ratio H₂O/EAN. The trend of the results could be related to the higher capacity of the EAN-H₂O mixtures to absorb water when increasing temperature.

Our Car-Parrinello MD simulations are in line with the experimental results that show an increase of the water/EAN molar ratio in EAN-water complexes when the percentage of water in the mixtures is increased. Moreover, the simulations confirmed the reliability of previous classical MD simulations to analyze the interactions in the hydrogen-bonded network that is solvating EAN anions and cations. The preliminary simulations at higher temperatures show a different behavior of the water solvating anions and cations, result that will be confirmed in future experiments.

Our results evidence the suitability of combining an experimental methodology with molecular simulations to get a deeper insight of the water association process in EAN Ionic Liquid.

5. Acknowledgment

The authors are grateful to the Spanish Ministry of Science, Innovation and Universities (Projects RED2018-102679-T and CTQ2017-87269-P) for its financial support.

6. References

- [1] J.P. Hallett, T. Welton, Room-temperature ionic liquids: Solvents for synthesis and catalysis. 2, *Chem. Rev.* 111 (2011) 3508–3576. <https://doi.org/10.1021/cr1003248>.
- [2] T.L. Greaves, C.J. Drummond, Protic Ionic Liquids: Evolving Structure-Property Relationships and Expanding Applications, *Chem. Rev.* 115 (2015) 11379–11448. <https://doi.org/10.1021/acs.chemrev.5b00158>.
- [3] S. Zhang, N. Sun, X. He, X. Lu, X. Zhang, Physical properties of ionic liquids: Database and evaluation, *J. Phys. Chem. Ref. Data.* 35 (2006) 1475–1517. <https://doi.org/10.1063/1.2204959>.
- [4] M. Freemantle, *An Introduction to Ionic Liquids*, The Royal Society of Chemistry, 2009.
- [5] T. Welton, P. Wasserscheid, *Ionic Liquids in Synthesis*, Second Edition, Wiley Online Library, 2008. <https://doi.org/10.1002/9783527621194>.
- [6] R. Rives, A. Mialdun, V. Yasnou, V. Shevtsova, A. Coronas, Experimental determination and predictive modelling of the mutual diffusion coefficients of water and ionic liquid 1-(2-hydroxyethyl)-3-methylimidazolium tetrafluoroborate, *J. Mol. Liq.* 296 (2019) 111931. <https://doi.org/10.1016/j.molliq.2019.111931>.
- [7] Z. S., X. Lu, Q. Zhou, X. Li, X. Zhang, *Ionic Liquids: Physicochemical Properties*, Elsevier Science Bv, Amsterdam, 2009.
- [8] L. Cammarata, S.G. Kazarian, P.A. Salter, T. Welton, Molecular states of water in room temperature ionic liquids, *Phys. Chem. Chem. Phys.* 3 (2001) 5192–5200. <https://doi.org/10.1039/b106900d>.
- [9] T. Köddermann, C. Wertz, A. Heintz, R. Ludwig, The association of water in ionic liquids: A reliable measure of polarity, *Angew. Chemie - Int. Ed.* 45 (2006) 3697–3702. <https://doi.org/10.1002/anie.200504471>.
- [10] A. Mele, C.D. Tran, S.H. De Paoli Lacerda, The structure of a room-temperature ionic liquid with and without trace amounts of water: The role of C-H...O and C-H...F interactions in 1-n-butyl-3-methylimidazolium tetrafluoroborate, *Angew. Chemie - Int. Ed.* 42 (2003) 4364–4366. <https://doi.org/10.1002/anie.200351783>.
- [11] K. Miki, P. Westh, K. Nishikawa, Y. Koga, Effect of an “ionic liquid” cation, 1-butyl-3-methylimidazolium, on the molecular organization of H₂O, *J. Phys. Chem. B.* 109 (2005) 9014–9019. <https://doi.org/10.1021/jp046309c>.
- [12] T. Méndez-Morales, J. Carrete, Ó. Cabeza, L.J. Gallego, L.M. Varela, Molecular dynamics simulation of the structure and dynamics of water-1-alkyl-3-methylimidazolium ionic liquid mixtures, *J. Phys.*

- Chem. B. 115 (2011) 6995–7008. <https://doi.org/10.1021/jp202692g>.
- [13] S.V.J. Yuvaraj, R.K. Zhdanov, R. V. Belosludov, V.R. Belosludov, O.S. Subbotin, K. Kanie, K. Funaki, A. Muramatsu, T. Nakamura, Y. Kawazoe, Solvation Mechanism of Task-Specific Ionic Liquids in Water: A Combined Investigation Using Classical Molecular Dynamics and Density Functional Theory, *J. Phys. Chem. B.* 119 (2015) 12894–12904. <https://doi.org/10.1021/acs.jpcc.5b05945>.
- [14] F. Endres, S. Zein El Abedin, Air and water stable ionic liquids in physical chemistry, *Phys. Chem. Chem. Phys.* 8 (2006) 2101–2116. <https://doi.org/10.1039/b600519p>.
- [15] P. Walden, “Molecular weights and electrical conductivity of several fused salts,” *Bulletin of the Imperial Academy of Sciences (Saint Petersburg)*, 1800 (1914) 405–422.
- [16] K. Fumino, A. Wulf, R. Ludwig, Hydrogen Bonding in Protic Ionic Liquids: Reminiscent of Water, *Angew. Chemie Int. Ed.* 48 (2009) 3184–3186. <https://doi.org/10.1002/anie.200806224>.
- [17] T.L. Greaves, C.J. Drummond, Protic Ionic Liquids: Properties and Applications, *Chem. Rev.* 108 (2008) 206–237. <https://doi.org/10.1021/cr068040u>.
- [18] T.L. Greaves, D.F. Kennedy, A. Weerawardena, N.M.K. Tse, N. Kirby, C.J. Drummond, Nanostructured protic ionic liquids retain nanoscale features in aqueous solution while precursor Brønsted acids and bases exhibit different behavior, *J. Phys. Chem. B.* 115 (2011) 2055–2066. <https://doi.org/10.1021/jp1112203>.
- [19] R. Hayes, S. Imberti, G.G. Warr, R. Atkin, How water dissolves in protic ionic liquids, *Angew. Chemie - Int. Ed.* 51 (2012) 7468–7471. <https://doi.org/10.1002/anie.201201973>.
- [20] B. Docampo-Álvarez, V. Gómez-González, T. Méndez-Morales, J. Carrete, J.R. Rodríguez, Ó. Cabeza, L.J. Gallego, L.M. Varela, Mixtures of protic ionic liquids and molecular cosolvents: A molecular dynamics simulation, *J. Chem. Phys.* 140 (2014). <https://doi.org/10.1063/1.4879660>.
- [21] R. Hayes, G.G. Warrb, R. Atkin, At the interface: solvation and designing ionic liquids, *Phys. Chem. Chem. Phys.* 12 (2010) 1648–1648. <https://doi.org/10.1039/b920393a>.
- [22] A.K. Soper, Partial structure factors from disordered materials diffraction data: An approach using empirical potential structure refinement, *Phys. Rev. B - Condens. Matter Mater. Phys.* 72 (2005) 1–12. <https://doi.org/10.1103/PhysRevB.72.104204>.
- [23] V. Govinda, P. Venkatesu, I. Bahadur, Molecular interactions between ammonium-based ionic liquids and molecular solvents: Current progress and challenges, *Royal Society of Chemistry*, 2016. <https://doi.org/10.1039/c6cp00199h>.
- [24] C. Ruckebusch, L. Blanchet, Multivariate curve resolution: A review of advanced and tailored applications and challenges, *Anal. Chim. Acta.* 765 (2013) 28–36. <https://doi.org/10.1016/j.aca.2012.12.028>.
- [25] A. De Juan, J. Jaumot, R. Tauler, Multivariate Curve Resolution (MCR). Solving the mixture analysis problem, *Anal. Methods.* 6 (2014) 4964–4976. <https://doi.org/10.1039/c4ay00571f>.
- [26] M. López-Pastor, M.J. Ayora-Cañada, M. Valcárcel, B. Lendl, Association of methanol and water in ionic liquids elucidated by infrared spectroscopy using two-dimensional correlation and multivariate curve resolution, *J. Phys. Chem. B.* 110 (2006) 10896–10902. <https://doi.org/10.1021/jp057398b>.
- [27] A.A. Gowen, J.M. Amigo, R. Tsenkova, Characterisation of hydrogen bond perturbations in aqueous systems using aquaphotomics and multivariate curve resolution-alternating least squares, *Anal. Chim. Acta.* 759 (2013) 8–20. <https://doi.org/10.1016/j.aca.2012.10.007>.

- [28] M.I. Barba, M.S. Larrechi, A. Coronas, Quantitative analysis of the hydration of lithium salts in water using multivariate curve resolution of near-infrared spectra, *Anal. Chim. Acta.* 919 (2016) 20–27. <https://doi.org/10.1016/j.aca.2016.03.022>.
- [29] M.I. Barba, M.S. Larrechi, A. Coronas, Quantitative analysis of free water in ionic liquid-water mixtures, *Talanta.* 199 (2019) 407–414. <https://doi.org/10.1016/j.talanta.2019.02.087>.
- [30] S. Zahn, K. Wendler, L. Delle Site, B. Kirchner, Depolarization of water in protic ionic liquids, *Phys. Chem. Chem. Phys.* 13 (2011) 15083–15093. <https://doi.org/10.1039/c1cp20288j>.
- [31] J. Jaumot, R. Gargallo, A. De Juan, R. Tauler, A graphical user-friendly interface for MCR-ALS: A new tool for multivariate curve resolution in MATLAB, *Chemom. Intell. Lab. Syst.* 76 (2005) 101–110. <https://doi.org/10.1016/j.chemolab.2004.12.007>.
- [32] J. Jaumot, A. de Juan, R. Tauler, MCR-ALS GUI 2.0: New features and applications, *Chemom. Intell. Lab. Syst.* 140 (2015) 1–12. <https://doi.org/10.1016/j.chemolab.2014.10.003>.
- [33] and J.S.-V. D. L. Massart, B. G. M. Vandeginste, L. M. C. Buydens, S. De Jong, P. J. Lewi, *Handbook of Chemometrics and Qualimetrics: Part A*, Elsevier, New York, 1998. <https://doi.org/10.1021/ci980427d>.
- [34] M.M. Andreas D. Zuberbuehler, The Resolution Of Overlapping Chromatographic Peaks By Evolving Factor Analysis, *Anal. Chim. Acta.* 181 (1986) 287–291.
- [35] P.J. Gemperline, Computation of the range of feasible solutions in self-modeling curve resolution algorithms, *Anal. Chem.* 71 (1999) 5398–5404. <https://doi.org/10.1021/ac990648y>.
- [36] R. Tauler, Calculation of maximum and minimum band boundaries of feasible solutions for species profiles obtained by multivariate curve resolution, *J. Chemom.* 15 (2001) 627–646. <https://doi.org/10.1002/cem.654>.
- [37] J. Jaumot, R. Tauler, MCR-BANDS: A user friendly MATLAB program for the evaluation of rotation ambiguities in Multivariate Curve Resolution, *Chemom. Intell. Lab. Syst.* 103 (2010) 96–107. <https://doi.org/10.1016/j.chemolab.2010.05.020>.
- [38] Copyright IBM Corp 1990-2019, Copyright MPI für Festkörperforschung Stuttgart 1997-2001, (n.d.). <http://www.cpmd.org/>.
- [39] R. Car, M. Parrinello, Unified Approach for Molecular Dynamics and Density-Functional Theory, *Phys. Rev. Lett.* 55 (1985) 2471–2474. <https://doi.org/10.1378/chest.93.6.1314a>.
- [40] N. Troullier, J.L. Martins, Efficient pseudopotentials for plane-wave calculations, *Phys. Rev. B.* 43 (1991) 1993–2006. <https://doi.org/10.1103/PhysRevB.43.1993>.
- [41] J.P. Perdew, K. Burke, M. Ernzerhof, Generalized gradient approximation made simple, *Phys. Rev. Lett.* 77 (1996) 3865.
- [42] M.P. Allen, D.J. Tildesley, *Computer Simulations of Liquids*, Oxford University Press, New York, 1987.
- [43] M. Brehm, M. Thomas, S. Gehrke, B. Kirchner, TRAVIS—A free analyzer for trajectories from molecular simulation, *J. Chem. Phys.* 152 (2020). <https://doi.org/10.1063/5.0005078>.
- [44] M. Brehm, B. Kirchner, TRAVIS - A free analyzer and visualizer for monte carlo and molecular dynamics trajectories, *J. Chem. Inf. Model.* 51 (2011) 2007–2023. <https://doi.org/10.1021/ci200217w>.
- [45] J.J. Workman, L. Weyer, *Practical Guide and Spectral Atlas for Interpretive Near-Infrared Spectroscopy*, CRC Press, 2012.

1 [46] R. Zarrougui, M. Dhahbi, D. Lemordant, Transport and thermodynamic properties of
2 ethylammonium nitrate-water binary mixtures: Effect of temperature and composition, *J. Solution*
3 *Chem.* 44 (2015) 686–702. <https://doi.org/10.1007/s10953-014-0283-z>.

4 [47] T.I. Mizan, P.E. Savage, R.M. Ziff, Temperature dependence of hydrogen bonding in supercritical
5 water, *J. Phys. Chem.* 100 (1996) 403–408. <https://doi.org/10.1021/jp951561t>.

6 [48] L. Piela, On the hydrogen bonding between water and ammonia molecules, *Chem. Phys. Lett.* 15
7 (1972) 199–202. [https://doi.org/10.1016/0009-2614\(72\)80148-9](https://doi.org/10.1016/0009-2614(72)80148-9).

8 [49] M.F. Chaplin, Water’s hydrogen bond strength, *Water Life Unique Prop. H₂O.* (2010) 69–86.

9 [50] A. Kananenka, J.L. Skinner, Unusually strong hydrogen bond cooperativity in particular (H₂O)₂₀
10 clusters, *Phys. Chem. Chem. Phys.* (2020).

11 [51] A.F. Perry, Low Barrier Hydrogen Bonds, *Encycl. Biol. Chem.* (2004).

12

13