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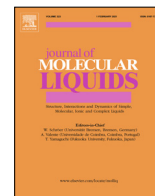
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Enhancement of the solubility of organic dyes in aqueous ionic solvents doped with surfactants



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ABSTRACT

Natural dyes can be poorly water-soluble, and improving their solubility with accurately designed solvents can benefit their application in most domains. Ionic liquids and deep eutectic solvents, systems with complex and diverse intermolecular interactions, are capable of dissolving compounds of different nature and polarity. A remarkable solubility increase of three natural dyes, indigo, alizarin and curcumin, is observed in the ionic liquid 1-ethyl-3-methylimidazolium ethyl sulfate and in the eutectic solvent formed by tetrabutylammonium acetate with lactic acid. Further addition of water and surfactants to these ionic media can make them more suitable and cost-effective for industrial use. By means of molecular dynamics, we exposed striking differences in the solvation of dyes in the ionic liquid and the deep eutectic solvent, with important structural changes upon addition of water. The experimental solubility of the dyes, measured at different compositions and compared with water as solvent, point at the favourable impact of small additions of water and surfactants on the dissolution process.

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1. Introduction

Dyes and pigments have been used for dyeing materials, textiles and paper, in applied arts, in cosmetics and in food production, for many thousands of years [1,2]. Natural dyes are obtained from plants, animals or minerals but their usage is often limited by their low water solubility. Rational solvent design aiming at increasing their solubility can contribute to the improvement of dyeing processes and broaden their usage [3].

Ionic liquids (ILs) and deep eutectic solvents (DES) are among the most promising solvents for natural dye solubilization. Both kinds of solvent media are liquid at room temperature, ILs being salts formed by large asymmetric ions with a delocalized electrostatic charge and conformational flexibility [4–6], and DES being eutectic mixtures of organic salts with hydrogen-bond donors [7,8]. The complexity and variety of interactions presented in these

systems, namely hydrogen bonding, electrostatic and dispersion forces [9,10], allow for the reasoned choice of the most appropriate combinations in view of their applications [4–6,11–13].

We have previously made an *in silico* screening study [14], based on the COSMO approach [15–17], of the best ionic solvents to dissolve three natural dyes, indigo, alizarin and curcumin, whose structures are depicted in Fig. 1. These dyes were selected due to their different colors, blue, red and yellow [18], and wide use: indigo [19–21] in the textile industry, especially for denim production, alizarin [22,18,23] and curcumin [11,24,23,18,25,26] in the pharmaceuticals and technology domains. The calculations performed were validated by comparisons with experimental measurements of the solubility of the selected dyes. The 1-ethyl-3-methylimidazolium ethylsulfate IL and the tetrabutylammonium acetate plus lactic acid DES surpassed other candidates showing a significant improvement in dye solubility when compared with water.

However, industrial application of pure ionic liquids and deep eutectic solvents can be limited due to their high cost and relatively large viscosity, the addition of water being one of the possible ways to overcome these drawbacks [27]. Further improvement of solubility of hydrophobic dyes in aqueous-ionic media could be achieved by adding surfactants, the amphiphilic structure of which

Abbreviations: IL, ionic liquid; DES, deep eutectic solvent; MD, molecular dynamics; SLES, sodium laureth sulfate; SLG, sodium lauroyl glutamate; RDF, radial distribution function; SDF, spatial distribution function; CMC, critical micelle concentration.

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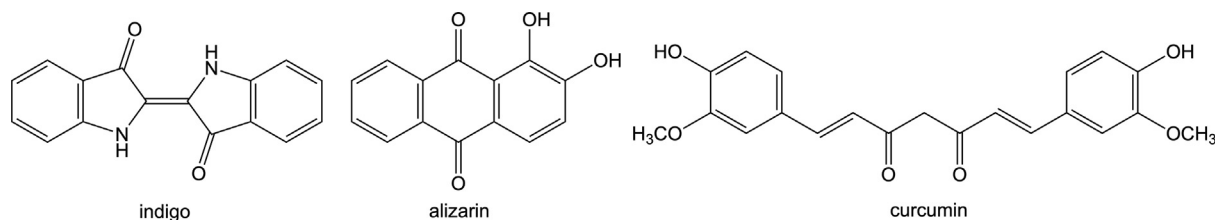


Fig. 1. Structural formulæ of indigo, alizarin and curcumin dyes.

lowers the free energy of oil/water interfaces. If the surfactant concentration exceeds the critical micelle concentration, molecules of the surfactant form micelles that are capable of stabilizing in aqueous solution substances that are *a priori* water insoluble [28,29]. We chose two anionic surfactants, sodium laureth sulfate and sodium lauroyl glutamate, that are safe and widely used in household chemicals and cosmetics [30,31] to examine their effect on dye solubility in aqueous-ionic phases.

In order to complement the experimental studies and to provide insights into the local structure of solutions, we used molecular dynamics (MD) simulations. The main advantage of this method is the possibility of modelling systems consisting of tens of thousands atoms for several tens of nanoseconds (which are unreachable with quantum mechanics) without losing details of specific site-site interactions, such as hydrogen bonds, which are sacrificed in coarse-grained simulations. For the MD study, indigo was chosen as a probe to study the solvation patterns in the ionic liquid and the deep eutectic solvent because of its simplicity, of the presence of moieties of different polarity and the absence of acid-base equilibria. The other dyes, alizarin and curcumin, can undergo deprotonation and thus require an accurate description of the effect of the ionic medium on acidity constants (two pK_a for alizarin, three for curcumin). Curcumin is also subject to keto-enol tautomerism [32], a chemical behaviour difficult to represent in classical molecular dynamics. Although *ab initio* MD can deal with chemical reactions (such as dissociation or proton transfer), it cannot be used for modelling systems with large enough size to reproduce actual solubility, due to the high computational demands. Thus, the theoretical study of indigo solutions using classical MD is the adequate strategy to obtain structural information.

The aim of the present work is thus to study the effect of water and surfactants on the solubility of natural dyes in IL and DES phases, by means of experimental and theoretical approaches. Combination of the two methodologies will provide valuable and more complete information on the solvation process and a better understanding of these phenomena at a molecular level.

2. Methods

2.1. Materials and solvent preparation

The ionic liquid 1-ethyl-3-methylimidazolium ethylsulfate ($[\text{C}_2\text{C}_1\text{Im}][\text{C}_2\text{SO}_4]$ 98%) was purchased from Iolitec and the components of the deep eutectic solvents, L-(+)-lactic acid (HLA > 98%) and tetrabutylammonium acetate ($[\text{N}_{4444}][\text{OAc}]$ >90%), were obtained from Merck and TCI Europe, respectively. The dyes were indigo (95%, Sigma-Aldrich), curcumin (>98%, Acros Organics) and alizarin (97%, Acros Organics). The surfactants (Fig. 2) were sodium laureth sulfate (SLES) and sodium lauroyl glutamate (SLG) supplied by L'Oréal Research and Innovation Laboratories. We used the chemicals as received without additional purification.

We prepared the eutectic solvent, $[\text{N}_{4444}][\text{OAc}] + \text{HLA}$ (1:3), following the protocol described in the literature [33,34]. After mixing the components, the system was heated at 100 °C under

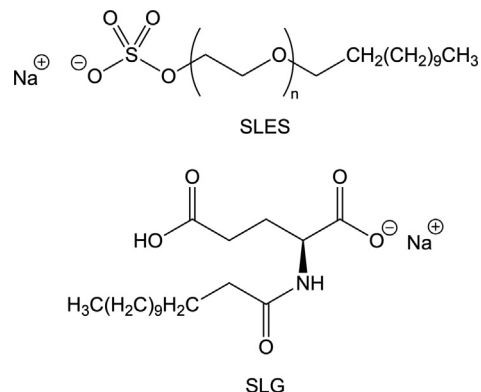


Fig. 2. Structural formulæ of sodium laureth sulfate (SLES) and sodium lauroyl glutamate (SLG) surfactants.

450 rpm stirring for one hour and then left at room temperature for 24 h to insure it remained a liquid.

To study the effect of water on the solubility of the dyes in the IL and in the DES, 36 solutions with 5%, 10%, 20%, 30%, 40% and 50% of water by mass were prepared gravimetrically.

Having prepared aqueous solutions with different SLES concentrations, solutions with mass fraction of surfactant of 0.05%, 0.2% and 0.5% were obtained by mixing with the DES. The solutions of SLG surfactant (DES + 40% H_2O + 0.05% SLG) were prepared by adding the surfactant, a fine powder at room temperature, to the DES + 40% H_2O solutions. In total, the solubility of the dyes in the presence of surfactants was studied in 12 solutions.

2.2. Solubility measurements

The solubility of the dyes in ionic solvents and their mixtures with water and surfactants was measured using a Perkin-Elmer Lambda 750 UV-vis-NIR spectrophotometer at room temperature (298 K). The following procedure was applied: 1) the dye was dissolved in the studied solvent up to supersaturation; 2) the solution was then filtered through 0.2 μm syringe filters; 3) the saturated solution was diluted with DMSO; 4) the UV-vis absorption spectra were measured and solubility was calculated. Step 3) was modified for the alizarin and curcumin solutions, for which an acidic DMSO solution of 0.5% H_2SO_4 (vol%) was used instead, so that the spectra of the neutral forms of the dyes could be recorded. The calibration curves are reported in the Supporting Information (Figure S1).

2.3. Surface tension measurements

Gas-liquid interfacial tensions were measured using the pendant drop method in a drop shape analyzer from Krüss (model DSA30) at room temperature and under ambient conditions.

The surface tension of the aqueous surfactant solutions was measured in different concentration ranges, 0.05–5% for SLES and 0.01–0.06% for SLEG (by mass), taking into account the 0.08% solu-

bility of SLG in water. In total, 15 solutions were prepared and studied.

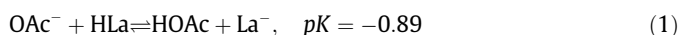
2.4. Molecular dynamics simulations

Molecular dynamics simulations were performed using the LAMMPS [35] program. The systems consisted of a single molecule of dye placed in the centre of a cubic box and surrounded by enough ionic liquid or DES and water to avoid solute–solute interactions (Table S1). The choice of the mass fraction of water for the theoretical study depended on system size, aiming for a reasonable simulation time and good statistics in the structure analysis.

Initial configurations of periodic cubic boxes were generated using *fftool* [36] and *Packmol* [37]. The CL&P force field [38–40] was used for the ionic liquid and the DES cation, while lactic and acetic acids, the lactate anion of the DES and indigo were modelled with the OPLS-AA force field [41], with partial charges obtained by *CHelpG* [42] procedure on electron densities obtained at the MP2/cc-pVTZ(-f) level of theory, with previously optimized geometries, using the Gaussian [43] program. Water was simulated with the rigid TIP4P-Ew model [44]. The net charges of ions were scaled by ± 0.8 in order to correct the dynamics of the ionic liquids [45]. A cutoff of 12 Å was considered for non-bonded interactions and tail corrections beyond this cutoff were applied for energy and pressure. The particle–particle particle–mesh (PPPM) method with an accuracy of 10^{-5} was used to evaluate electrostatic energies. Bonds terminating with hydrogen atoms and the H–O–H angle of water were constrained using the SHAKE algorithm. The time step was of 1 fs. Temperature was kept at 298 K and pressure at 1 bar using Nosé–Hoover thermostat and barostat. Equilibration runs of 2 ns in the *NpT* ensemble were followed by production trajectories of 50 ns in the *NVT* ensemble.

Radial distribution functions (RDF) were used to study the local structure, and were renormalized to the number of target ions/molecules, so as to suppress the dilution effect related to differences in system compositions and water content. Indigo was always set as a reference molecule while ions/molecules of solvent were treated as target ones. The spatial distribution functions (SDF) were kept unchanged with respect to normalization and were used for a qualitative description of the location of interacting species around indigo.

The solvation of indigo was studied in an ionic liquid, 1-ethyl-3-methylimidazolium ethyl sulfate ($[\text{C}_2\text{C}_1\text{im}][\text{C}_2\text{SO}_4]$), and in a deep eutectic solvent, tetrabutylammonium acetate + lactic acid ($[\text{N}_{4444}][\text{OAc}] + \text{HLA}$, 1:3), with 3% and 30% by mass of water. Although in practice the deep eutectic solvent is prepared by direct mixing of the salt and the hydrogen bond donor, the system composition can change due to proton transfer from lactic acid to the acetate anion ($pK_a^w(\text{HOAc}) = 4.76$; $pK_a^w(\text{HLA}) = 3.86$). Even in a fully ionic medium, lactic acid remains stronger than acetic acid, the acidity constants following the $pK_a^{\text{PIL}} = pK_a^w + 1$ linear trend [46]. Since our solvents contain up to $\omega_{\text{H}_2\text{O}} = 30\%$ ($x_{\text{H}_2\text{O}} = 0.93$), the following chemical equilibrium can be considered in DES–water medium



When building the systems for simulation, we assume full proton transfer from lactic acid to acetate, thus neglecting approximately 1 acetate per 20 lactate anions at the equilibrium composition. As such, one anion type and two hydrogen bond donor types are present in the DES system, $[\text{N}_{4444}][\text{La}] + \text{HOAc} + \text{HLA}$ (1:1:2), in MD simulations.

3. Results

The solubility of the dyes can be significantly improved in ionic media, as shown by the experimental results in Fig. 3. In pure ionic solvents, solubility decreases in order alizarin > curcumin >> indigo. The IL, $[\text{C}_2\text{C}_1\text{im}][\text{C}_2\text{SO}_4]$, is a better solvent than the DES, $[\text{N}_{4444}][\text{OAc}] + \text{HLA}$. Addition of small amounts of water leads to a remarkable solubility enhancement of alizarin in the DES and of curcumin in the IL and the DES, the latter dye becoming the most soluble among the three studied in the presence of water.

In order to explain the effect of water on the solubility of the dyes, the solvation environment of indigo in the IL or the DES with 3% and 30% water by mass was examined, using molecular dynamics. Analysis of the microscopic structure reveals significant differences in solvation patterns of indigo in these solvents.

We found that the dye is mainly surrounded by ionic liquid species and water is only found near polar C=O and N–H groups (Fig. 4), which is consistent with the negligible solubility of indigo in water. At low water content ($\omega_{\text{H}_2\text{O}} = 3\%$, $x_{\text{H}_2\text{O}} = 0.29$) both cations and anions of the IL are mainly found near the edges, forming alternating stripes characteristic of charge ordering. An increase in the concentration of water ($\omega_{\text{H}_2\text{O}} = 30\%$, $x_{\text{H}_2\text{O}} = 0.85$) results in the formation of prominent cationic layers above and below the plane of indigo, parallel to the molecular plane, as illustrated in Fig. 5. The effect of the cation- π stacking between the imidazolium ring of the cation and the oxindole fragments of indigo improves solvation of the non-polar moieties of the dye in a dominant aqueous medium.

A study of site-site interactions shows the importance of the anion in the solvation of indigo, which is not evident from spatial distribution functions. In the 3% water solution, the anion forms a medium-strength hydrogen bond with the N–H group of indigo, with the highest probability of finding the anion $\text{O}_{\text{S}4}$ at 2.1 Å from the indigo hydrogen N–H, and an associated coordination number (CN) of 0.97 O atoms around each N–H in the first coordination shell, as shown at Figs. 6 and S5, thus displacing water from the solvation shell of the dye towards the bulk. In the 30% water solution, both the anions ($r_{\text{max}}^{\text{RDF}} = 2.1$ Å) and water ($r_{\text{max}}^{\text{RDF}} = 1.9$ Å) compete for the N–H site and have a similar coordination number (CN) of 0.56 and 0.47, respectively. This competition favors formation of another hydrogen bond with water, C=O...H_w ($r_{\text{max}}^{\text{RDF}} = 1.8$ Å, CN = 0.63), at this water concentration, while at the lower water content the carbonyl group, situated next to the amine group, is shielded by the voluminous anion.

At high water content, water behaves as a strong H-bond donor, forming hydrogen bonds with indigo O (shorter H...O distance) as seen in Fig. 6. This H-bond is stronger than the one formed by indigo as a N–H donor and water O as an acceptor. The hydrogen atoms (H_{CW} and H_{CR}) of the imidazolium ring, which is a weak C–H donor, show no specific directional site-site interactions with indigo (Figure S5).

Unlike in ionic liquid, solvation in DES is more complex due to the diversity of interacting species, and in particular the presence of charge-neutral carboxylic acids alongside the ions. Ammonium cations are found above and below the indigo plane with side chains directed towards the solute (Fig. 7). Increasing water content (from $\omega_{\text{H}_2\text{O}} = 3\%$, $x_{\text{H}_2\text{O}} = 0.50$ to $\omega_{\text{H}_2\text{O}} = 30\%$, $x_{\text{H}_2\text{O}} = 0.93$) leads to accumulation of cations near indigo, stabilizing the solute in an unfavorable hydrophilic environment, here through non-polar dispersive interactions of indigo with the alkyl chains. The butyl chains of the ammonium cations are found closer to the indigo surface than the charged N atoms (Figs. 7 and 8), and this differs from the solvation structure in the IL, which has short ethyl side chains (Figs. 4 and S3).

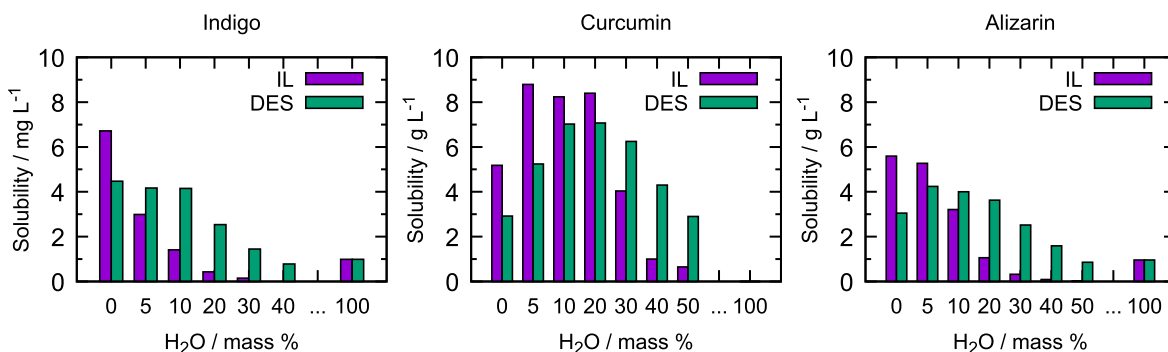


Fig. 3. Experimental solubility of indigo, alizarin and curcumin in the IL [C₂C₁im][C₂SO₄] and in the DES [N₄₄₄₄][OAc] + HLa (1:3) at room temperature and as function of mass content of water.

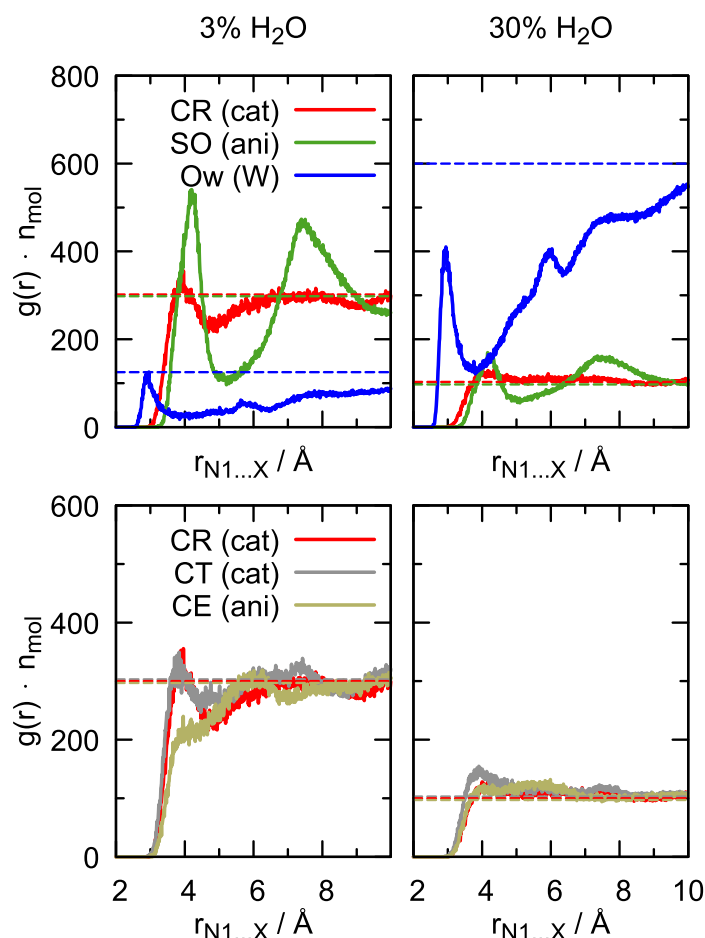


Fig. 4. Renormalized radial distribution functions of chosen atoms of solvent around the N₁ atoms of indigo in the indigo + IL + water solution. Each radial distribution function tends to a value proportional to the number of ions/molecules containing target atoms (Table S1) represented by the dashed lines.

Acids and water are found near the edges of indigo, competing for its C=O and N–H hydrogen bond sites (Figure S4). Lactic acid interacts through the hydroxyl group forming both N₁–H₁...O_H and C=O...H_O hydrogen bonds, with a typical intermolecular distance of 2.0 Å (Figs. 9, S9 and S10), and with the respective first solvation shell coordination numbers of 0.29 and 0.53, in the 3% water solution. A less marked but stronger H-bond is observed with the carboxylic hydrogen atom, C=O...H_{Ac}, at 1.8 Å with CN = 0.19 (Figures S6 and S7). These interactions disappear upon increased water content, replaced by: 1) the N₁–H₁...O₃ hydrogen bond with the carbonyl group of acetic acid at 2.1 Å

(CN_{3%H₂O} = 0.23, CN_{30%H₂O} = 0.28), as shown in Figs. 10 and S11; and 2) by the N₁–H₁...O_w and C=O...H_w interactions with water (Figures S8 and S11). The carbonyl group of lactic acid and the hydroxyl group of lactate are not involved in significant hydrogen bonding with indigo according to Figs. 9 and 10.

The important difference between solvation in the IL and the DES is the role of the anion, that acts as a main H-bond acceptor in the IL (Fig. 4) and is repelled from the solute and replaced by the neutral acids in the DES (Fig. 8). Thus the anion of the DES interacts predominantly with water and the cations, but not with the solute. In both systems, dilution in water enhances the compe-

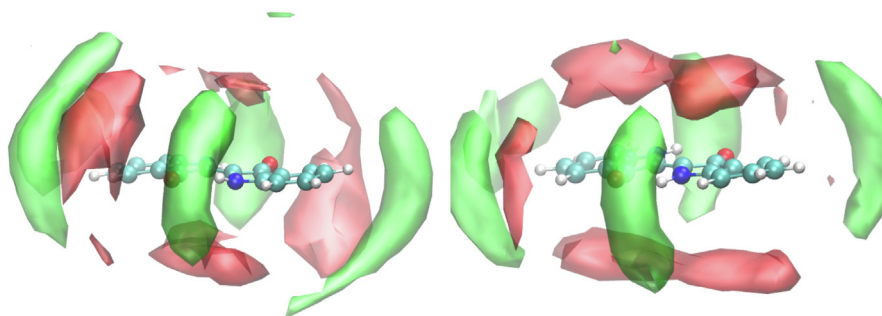


Fig. 5. Spatial distribution functions of chosen atoms of solvent around indigo in indigo + IL + water solutions at 3% (left) and 30% (right) water content. The red surface correspond to the CR atoms of cations (isodensity contours at 2.6 times the average density around indigo), the green surface to the SO atoms of anions (isodensity contours at 3.0 times the average density around indigo).

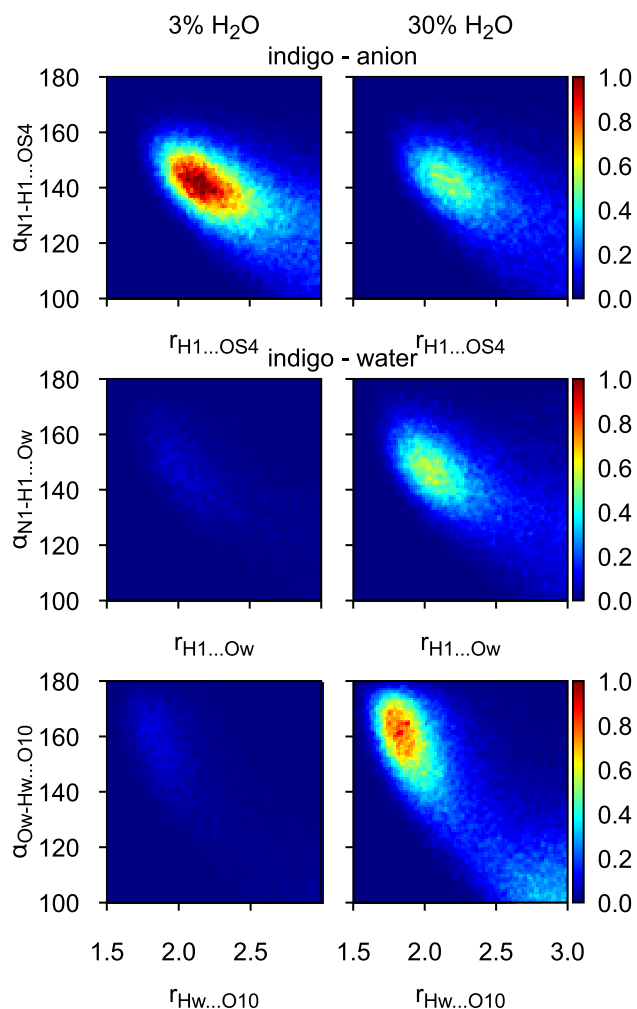


Fig. 6. Probability contours revealing hydrogen bonding in indigo + IL + water. The x-axes represent the distances between hydrogen atoms of the donor (D) and oxygen atoms of the acceptor (A). The y-axes represent the angles formed by the D-H...A hydrogen bonds, where D is a donor atom attached to hydrogen. The color bar associated with the probability of interaction is identical for the plots of each series.

tition with IL/DES for the H-bonding sites of the solute, increasing the contribution of water. However, the hydrophobic conjugated moieties of indigo are always solvated through dispersive interactions or cation- π stacking with cations, and the addition of water addition strengthens this component of solvation.

The critical micelle concentration (CMC) of SLES and SLG in water determined from the dependence of surface tension with

surfactant concentration (Figure S12) are 0.15% and 0.04%, respectively. In order to test if the solubility of the dyes in the aqueous-ionic media can be then enhanced by adding surfactants capable of dissolving hydrophobic solutes in micelles as self-aggregation takes place at surfactant concentrations above the CMC.

Pandey et al. [47] recently reported significant lowering of CMC of the surfactant in DES compared to pure water, when investigating the self-assembling of sodium dodecyl sulfate in choline chloride + urea + water solution. Relying on these results, the solutions studied here were prepared at surfactant concentrations above their CMC in water, to guarantee the formation of micelles in the ionic media.

As illustrated in Fig. 11, adding a surfactant leads to an increase of solubility of all three dyes in the DES + water mixture (40%). This effect is most pronounced for indigo, which is 1.8 and 3.6 times more soluble in the presence of SLES or SLG than in water. The increase in solubility is less marked for curcumin, with a 1.4–1.5 enhancement, and is almost absent (1.1–1.2 times) for alizarin, where the difference between SLES and SLG vanishes. Since all studied concentrations of SLES are higher than the CMC, the study of the dye solubility as a function of the surfactant concentration is not relevant.

4. Conclusion

Addition of small amounts of water to previously selected IL and DES solvents [14] can significantly enhance the solubility of the three studied dyes – indigo, alizarin and curcumin. We could understand the molecular mechanisms involved in this enhancement by the analysis of the local solvent structure around the indigo dye using molecular dynamics that revealed two different solvation patterns, in the ionic liquid, $[C_2C_1im][C_2SO_4]$, and in the deep eutectic solvent, $[N_{4444}][OAc] \equiv HLa$. In each case the modification of the composition of the mixtures was taken into account in light of the relative acidity of the constituents.

In the ionic liquid, the most prominent interaction is the cation- π stacking between the imidazolium head group and conjugated system of the dye, which become more prominent at high water content. Hydrogen bonds are formed between N–H groups of indigo and the anion, dominating over indigo-water interactions. This stabilizes the dye in solution and explains its higher solubility in the IL than in water. Increasing water content strengthens the competition between water and the anion for the hydrogen bonding sites, bringing the solubility down. In the DES, the butyl chains of the ammonium cation shield the hydrophobic moieties of indigo from the hydrophilic environment, being however less effective than the cation- π stacking in the IL (the solubility in the IL is 50% higher than in the DES). Contrary to in IL, in the DES the anion is repelled to the bulk and indigo is

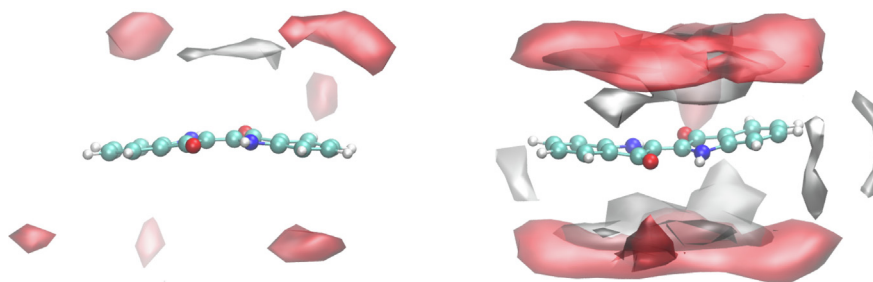


Fig. 7. Spatial distribution function of selected atoms of solvent around indigo in indigo + DES + water solutions at 3% (left) and 30% (right) water content. The red surface correspond to N_4 atoms of cations (isodensity contours at 8.0 times the average density around the indigo), the grey surface to CT atoms of cations (isodensity contours at 6.0 times the average density around indigo).

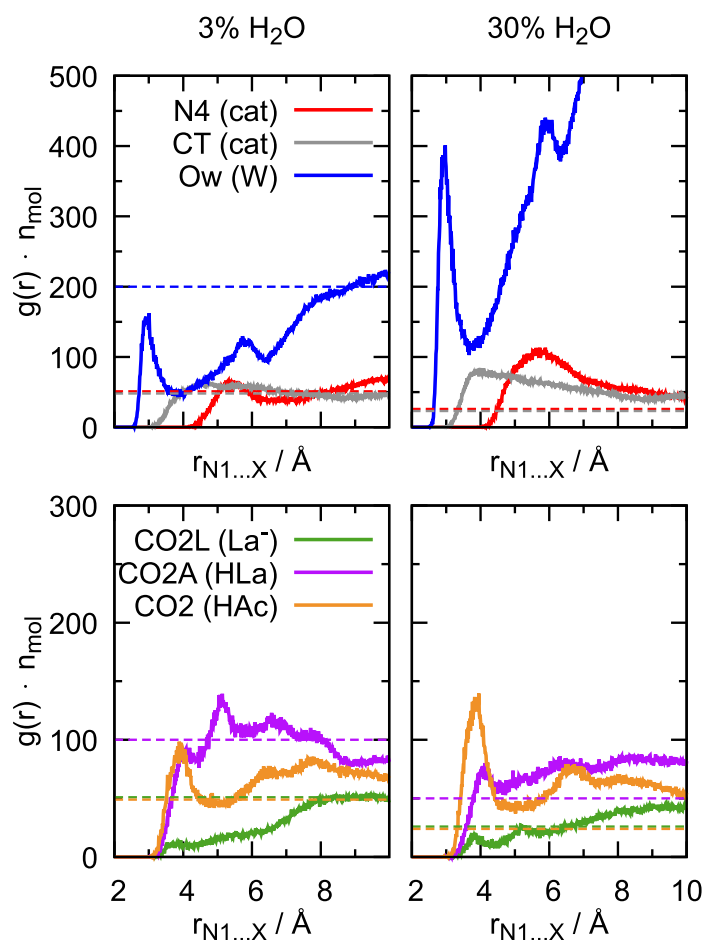


Fig. 8. Renormalized radial distribution function of selected atoms of solvent around N_1 atoms of indigo in indigo + DES + water solutions. Each function tends to a value proportional to the number of ions/molecules containing target atoms (Table S1) represented by the dashed lines. The line at 1400 for O_w atoms in the 30% water solution is not shown.

solvated by the least polar species, which are lactic and acetic acids, able to form a hydrogen bond with $N-H$ and $C=O$ groups of indigo. Water competes for these sites leading to an unfavourable effect on the solubility. These observations can also shed light on the higher solubility of curcumin and alizarin in the IL than in the DES (these are experimental results).

The distinguishing feature of alizarin and curcumin is a solubility enhancement caused by additions of small amounts of water, observed only in the DES for the former and in both solvents for the latter dye. Having easily accessible and not sterically hindered

methoxy, hydroxy and keto groups, these dyes are less hydrophobic and more soluble in water, when compared to indigo, and consequently, the presence of surfactants does not result in a remarkable solubility enhancement. Indigo dissolves well in the hydrophobic cores of micelles of SLES and SLG surfactants in ionic media, with very significant solubility enhancements of 80% and 267%, respectively. We conclude that the choice of the co-solvent or of additives to be introduced into the ionic solvent for better dye solubilization strongly depends on the nature and polarity of the solute.

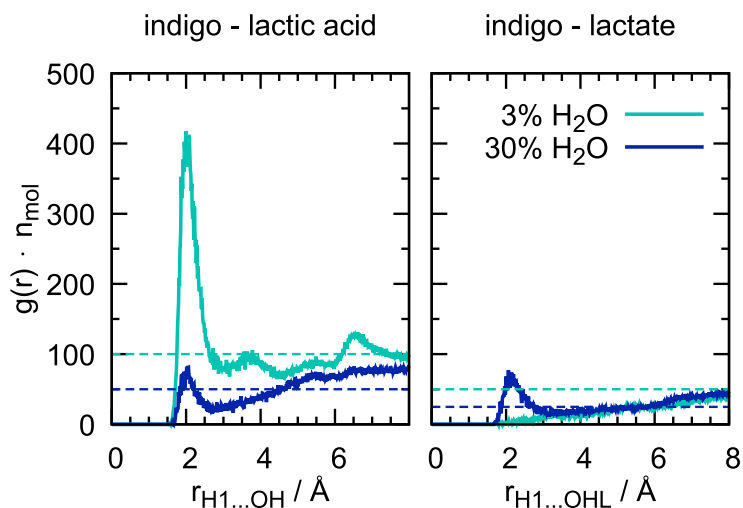


Fig. 9. Renormalized radial distribution function of hydroxyl O atoms of solvent around H atoms of indigo in indigo + DES + water solutions. Each function tends to a value proportional to the number of ions/molecules containing target atoms represented by the dashed lines.

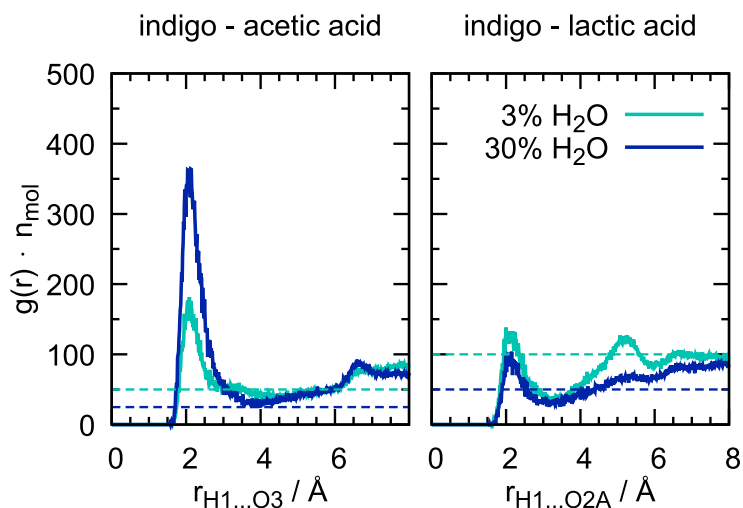


Fig. 10. Renormalized radial distribution function of carboxyl oxygen atoms of solvent around hydrogen atoms of indigo in indigo - DES - water system. Each function tends to a value proportional to the number of acid molecules containing target atoms represented by the dashed lines.

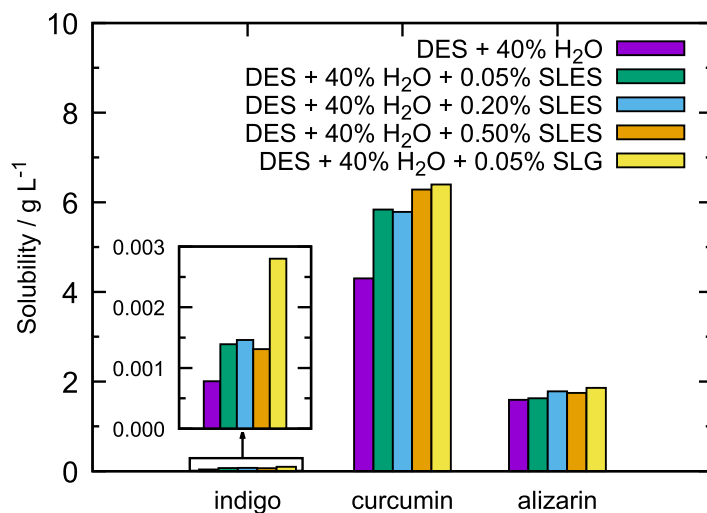


Fig. 11. Solubility of indigo, alizarin and curcumin in a DES + water mixture (40%) in the presence of surfactants: SLES (0.05%, 0.2% and 0.5%) or SLG (0.05%).

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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