

Screening Ionic Solvents for Enhancing the Solubility of Water-Insoluble Natural Dyes

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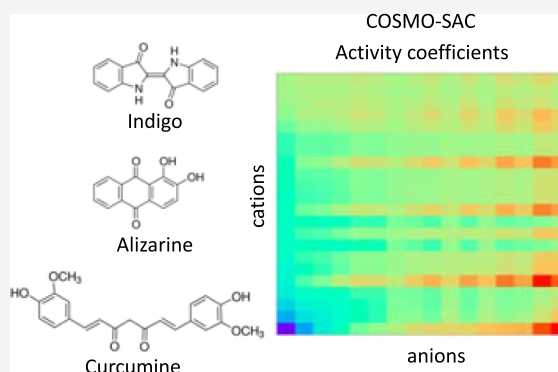


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ABSTRACT: One strategy to promote the use of natural dyes consists of developing solvents capable of increasing their solubility. Herein, *in silico* predictions of activity coefficients based on the conductor-like screening model COSMO-SAC were used to screen the most promising ionic solvents—ionic liquids or eutectic mixtures—for the dissolution of three natural dyes, namely, indigo, alizarin, and curcumin. The predicted logarithmic activity coefficients at infinite dilution, $\ln\gamma^\infty$, indicate that small ions having high charge density and capable of establishing strong hydrogen bonds appear to be the best candidates. Anions such as acetate, methanesulfonate, chloride, bromide, and methyl- or ethyl-sulfate combined with small tetraalkylammonium-based, pyrrolidinium-based, and imidazolium-based cations seem to be the best candidates for the interaction and thus possible dissolution of the natural dyes. The eutectic mixture of such small cation–anion combinations with primary amines, small carboxylic acids, and zwitterions such as betaine and carnitine can lead to ionic solvents that are liquids at room temperature. The chosen potential ionic solvents were prepared, and the experimental solubility of the three natural dyes was measured and compared with that in water.



INTRODUCTION

Color is a powerful physical phenomenon that influences and inspires human life in many aspects, from social relations to eating habits. Distinct pigments and dyes extracted from plants or animals have been used since the dawn of civilization for art, clothing, food, cosmetics, and more. However, their poor water solubility may hamper their more generalized use and the development of new dyeing processes. Therefore, new strategies to improve the solubility of some important natural dyes must be created.

One strategy to increase the solubility of natural dyes can be the use of ionic solvents such as ionic liquids (ILs) or deep eutectic solvents (DESs). ILs are salts having low melting points, many of them being liquids at room temperature.^{1,2} On the other hand, DESs are typically obtained by mixing a salt with a hydrogen-bonding neutral molecule to form an eutectic mixture close to or below room temperature.^{3,4} These solvents often confer an environmental friendly character as they have a negligible vapor pressure, can be recyclable, and/or are biocompatible according to their constituents.^{1,2,5–8} In both ILs and DESs, a subtle balance between hydrogen bonding, Coulomb interactions, and dispersion forces^{9,10} lead to their unique solvent properties. The proper choice of their constituents, cations, anions, neutral molecules, and mixture

composition, can be used to tune their properties and performance.

The possibility to tune the properties of such “designer solvents” constitutes the key advantage of using these ionic solvents^{2,4} but also leads to important difficulties linked to the enormous number of possible combinations between cations, anions, neutral compounds, and their mixture composition on the one hand and also the subtlety of the balance needed to have a liquid state at the temperature of interest. We have been confronted by these difficulties while trying to identify the most suitable solvents for the dissolution of natural dyes.

An *in silico* screening of ionic solvents can be achieved using Conductor-like Screening Model (COSMO)-based methods. COSMO-based methods, namely, the two most often used variants, COSMO-RS and COSMO-SAC, were already used for predicting the most promising ionic solvents for distinct applications such as biopolymer dissolution (keratin¹¹ and cellulose¹²), for carbon dioxide absorption,^{13–16} flavonoid¹⁷

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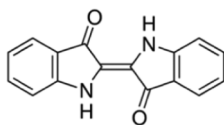
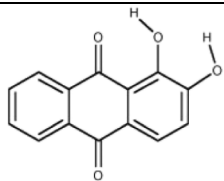
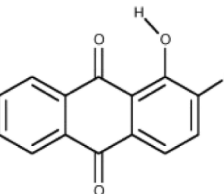
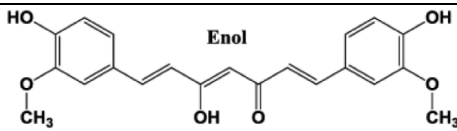
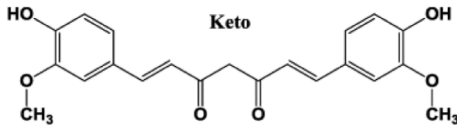
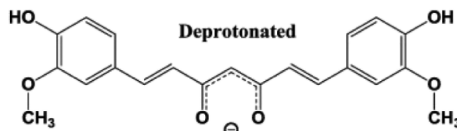
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Table 1. Chemical Structures of the Dyes Considered for COSMO-SAC Screening

Dyes	Structure	Charge
1 indigo		0
2 alizarine		0
3 alizarine-1		-1
4 curcumine-eno		0
5 curcumine-keto		0
6 curcumine-eno-1		-1

and sugar¹⁸ solubility, and more.^{19–21} As far as we know, only Govender et al.^{22–24} used COSMO-based methods for studying the solubility of dyes in water, but no literature was found for screening ionic solvents for natural dyes using COSMO calculations.

Herein, ILs and DESs were designed by means of COSMO-SAC²⁵ calculations, and experimental solubility measurements were performed in order to find the most promising ionic solvents for the dissolution of three natural dyes: indigo (blue), alizarin (red), and curcumin (yellow). These natural dyes were selected according to their different colors, their millenary use as textile dyes,^{26–32} especially indigo that is used in massive scale in denim production,^{33–37} and also due to the technological and pharmacological applications of alizarin^{38–41} and curcumin.^{6,28,41–47} Their chemical structures are displayed in Table 1.

MATERIALS AND METHODS

COSMO-SAC Calculations. We chose an improved COSMO-SAC version²⁵ for the calculation of activity coefficients. This version includes temperature-dependent electrostatic interaction parameters and a specific description

of hydrogen bonds, providing more accurate predictions of phase-equilibrium properties. The activity coefficients were computed following a three-step method. First, the geometry of solute (natural dyes) and solvent molecules (cations, anions, and neutral species) were optimized using the Gaussian 09 package at the BLYP/6-31G (d) level. Second, the optimized structures were used as input files for the GAMESS package in order to compute the σ -profile for each molecule through the LVPP open-source COSMO-SAC package.^{20,21,48,49} For the σ -profile calculations, triple zeta KTZVP basis was used for all molecules except for the Br[−] anion, where a double zeta DZV was employed. The combination of the theoretical method and basis set in the quantum calculations is the one recommended by the authors of the improved COSMO-SAC model used here.²⁰ Finally, the third step consisted of using the σ -profiles to compute the activity coefficient at infinite dilution of the dyes in the ionic solvents using the open-source JCosmo package.²⁰ The calculation temperature in JCosmo was set at 298 K.

The constituent cations and anions of the solvents were treated as independent components of the solvents when COSMO-SAC was employed to calculate the activity

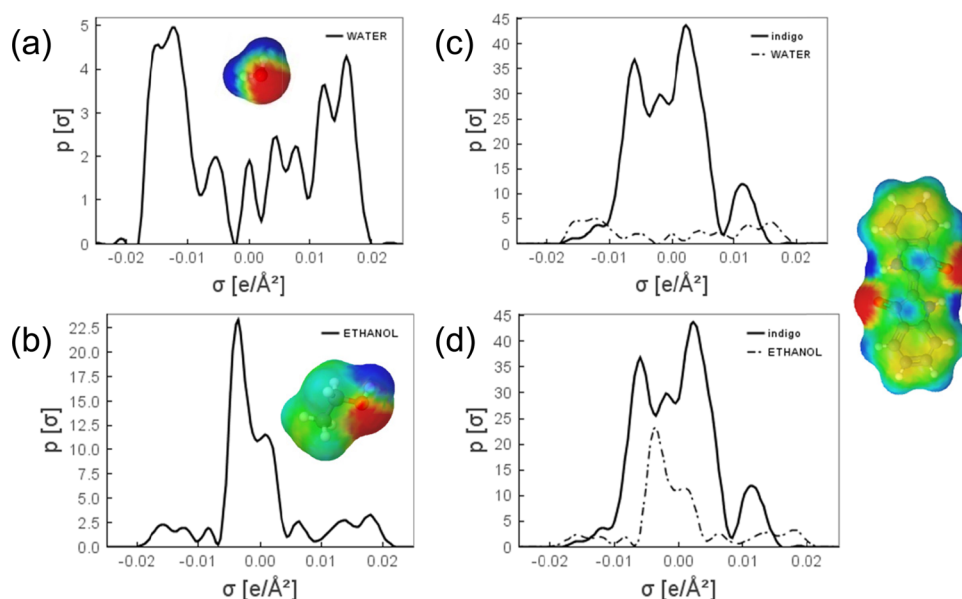


Figure 1. Sigma-profiles of (a) pure water, (b) pure ethanol, as well as the comparison between that of indigo with (c) water and with (d) ethanol. The corresponding charge distribution on the surface of (a) water, (b) ethanol, and (right) indigo molecules are displayed.

coefficients. The mole fractions of the cations and the anions were treated as in an equimolar mixture. From an experimental perspective, the best cation–anion combinations for a specific dye could render both ILs or solid salts at room temperature. Therefore, in order to find the best salts—those having promising activity coefficients—and to have them as room temperature liquids, neutral species such as carboxylic acids, primary amines, amino acids, polyalcohols, and others were selected separately for use in DES preparation.^{50,51} In total, 126 possible constituents of ILs or DESs were computed, including 88 neutral molecules, 22 cations, and 16 anions.

Structure of the Natural Dyes. Indigo, curcumin, and alizarin are natural dyes having both hydrogen bond donor and hydrogen bond acceptor sites in their structures. Concerning the hydrogen bond donor sites, indigo has secondary amine groups that establish strong intramolecular hydrogen bonds,^{52–55} while both curcumin and alizarin have hydroxyl groups that can be deprotonated according to the solvent media. Moreover, curcumin is a tautomeric compound existing in its enolic or keto form according to the solvent properties.^{45,56} Therefore, unlike indigo, distinct chemical structures have to be considered for a proper description of both curcumin and alizarin in solution. The details of their structures and charges are listed in Table 1.

Materials and Solvent Preparation. The protic ionic liquids were prepared following a synthesis protocol adapted from the work of Belieres and Angell.⁵⁷ They were obtained from a proton transfer reaction between an acid and a base. An equimolar amount of the acid was added dropwise to the base under stirring to avoid overheating of the reaction media and keep the temperature close to room temperature. The resulting mixture was stirred at room temperature for 24 h. Excess amine or excess acid can be removed, when necessary, using a rotary evaporator.

The eutectic solvents were prepared according to a synthesis protocol reported in the literature.^{51,52} The preparation is very straightforward: the mixture components are heated at 100 °C under 450 rpm stirring for 1 h. Mixtures of 2:1, 1:1, or 1:2 mole compositions for salt: (hydrogen-bonding neutral

molecule) were tested. The obtained liquids were then left at room temperature for 24 h to guarantee that they remain liquid.

The protic ILs and eutectic solvents were prepared using L-(+)-lactic acid (≥98%, Merck), betaine (98%, Acros Organics), DL-1-amino-2-propanol (>98%, TCI Europe), glycolic acid (99%, Sigma-Aldrich), and tetrabutylammonium acetate ([N₄₄₄₄][OAc], >90%, TCI Europe).

The nonprotic IL 1-ethyl-3-methylimidazolium ethyl sulfate ([C₂C₁Im][EtSO₄], 98%) was purchased from IoLiTec. The three studied dyes were indigo (95%, Sigma-Aldrich), alizarin (97%, Acros Organics), and curcumin (>98%, Acros Organics). All the chemicals were used as-received from the manufacturer.

Solubility Measurements. For measuring the solubility of the dyes in the ionic solvents at room temperature—around 298 K—a PerkinElmer Lambda 750 UV–VIS–NIR spectrophotometer was used. The dye solubility was accessed through a four-step procedure: (i) dissolution of the dye in the ionic solvent up to supersaturation; (ii) filtration of the solution using 0.2 μm syringe filters; (iii) dilution of the saturated ionic solution having the dye in DMSO; and (iv) UV–vis measurements for quantification of the solubility.

In the case of alizarin and curcumin solutions, in step (iii) an acidic DMSO solution of 0.5% H₂SO₄ (vol %) was used to guarantee that the dye molecules are kept in their neutral form prior to the UV–vis measurement.

Density and Viscosity Measurements. The density and viscosity of the ionic solvents were measured from 298 K to 353 K by an automated Anton-Paar DMA 5000 M and Lovis 2000 ME density and viscosity meter. The temperature was controlled to be ± 0.02 K, leading to an overall uncertainty of 10^{−6} g cm^{−3} of the density and of 0.5% of the viscosity.

RESULTS AND DISCUSSION

COSMO-SAC calculations use a single variable function denoted as sigma-profile, or σ -profile, for describing each molecule of a solution prior to having access to the solution's thermodynamic properties.²¹ The σ -profile represents a

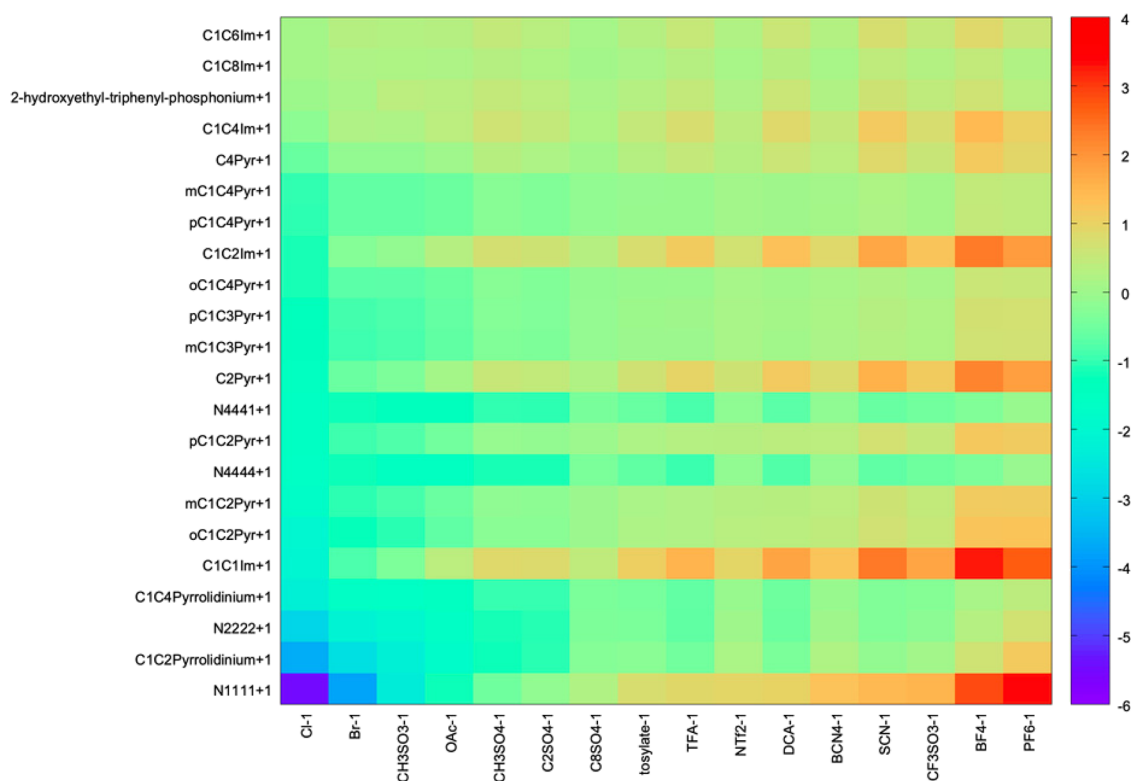


Figure 2. Logarithmic activity coefficients of indigo at infinite dilution ($\ln \gamma^\infty$) in 352 potential ILs calculated by COSMO at 298 K.

histogram of the charge density distributed on the molecule surface thus establishing the relationship between the fraction of a molecule surface and its corresponding charge density. The σ -profile of a molecule can be calculated from its electronic structure using quantum chemistry calculations.

Figure 1 shows some examples of the calculated σ -profiles for typical solvents, water and ethanol, and for one dye, indigo. Since ethanol has a nonpolar ethyl chain, its σ -profile is completely different from that of water, higher probability being observed around zero charge, 0.00 e/Å. Indigo and water have completely different σ -profiles, suggesting low affinity, as one could expect from the low solubility of indigo in water.⁵⁸ Figure 1 illustrates how the superposition of the σ -profiles from different compounds provide information about their mutual solubility—for example, it is clearly seen that indigo is much less soluble in water than in ethanol, the σ -profile of the latter overlapping more the one from indigo.

Once the σ -profile of each component of the solution was obtained from quantum chemical calculations (the σ -profiles of the dyes in Table 1 are included in the Supporting Information), the COSMO-SAC method used them to predict the solubility of a solute by computing its activity coefficient at infinite dilution, γ^∞ . The γ^∞ values are directly related to the solubility. According to Smith et al.,⁵⁹ the reciprocal of the activity coefficient is related to the solubility of a solid i in a liquid solvent L as displayed in eq 1:

$$x_i^L = \exp \left[\frac{\Delta h_{m,i}}{RT} \left(\frac{T}{T_i^m} - 1 \right) \right] \frac{1}{\gamma_i^L} \quad (1)$$

where x_i^L denotes the mole fraction of the dissolved component i in a saturated solution in equilibrium with the solid of i . The symbols $\Delta h_{m,i}$ and T_i^m stand for the melting

enthalpy and the melting temperature of component i , respectively.

Since the activity coefficient at infinite dilution (γ^∞) is linked to the solubility of a solute in a solvent, it is possible to use the COSMO-SAC method to perform a virtual screening of the affinity of the natural dyes for solvents constituted by distinct ionic species. Although the COSMO-SAC method makes it possible to calculate the activity coefficients for any composition, we have chosen to consider the activity coefficient at infinite dilution to be able to screen the different solvation media. Obviously, the computed activity coefficient does not consider the state of the pure solute, which would be necessary for an accurate calculation of the solubility. Thus, on the basis of $\ln \gamma^\infty$, it is possible to compare solvents for the same solute, but in general, it is not possible to compare the different solutes because their solubilities are dependent on the cohesion energy in their solid (crystalline) phase. To link the activity coefficient of the solute to the solubility, it would be necessary to consider other thermodynamic quantities (enthalpies or entropies of fusion, heat capacities, etc.) of the pure solute.

Therefore, the logarithmic activity coefficients of the natural dyes at infinite dilution ($\ln \gamma^\infty$) were computed aiming to screen potential ionic solvents where the natural dyes may have the best solubility. A value of $\ln \gamma^\infty = 0$ corresponds to an equivalent solute–solvent and solvent–solvent interactions. A value of $\ln \gamma^\infty < 0$ indicates an increased affinity between the solute and the solvent, whereas a positive value, $\ln \gamma^\infty > 0$, indicates unfavourable solute–solvent interactions.

The computed $\ln \gamma^\infty$ values are shown in Figures 2–4 and Figures S2–S4 of the Supporting Information. The cations and anions are organized according to their dye dissolution ability, increasing gradually from top to bottom for the cations and from right to left for the anions. The most promising ion pair

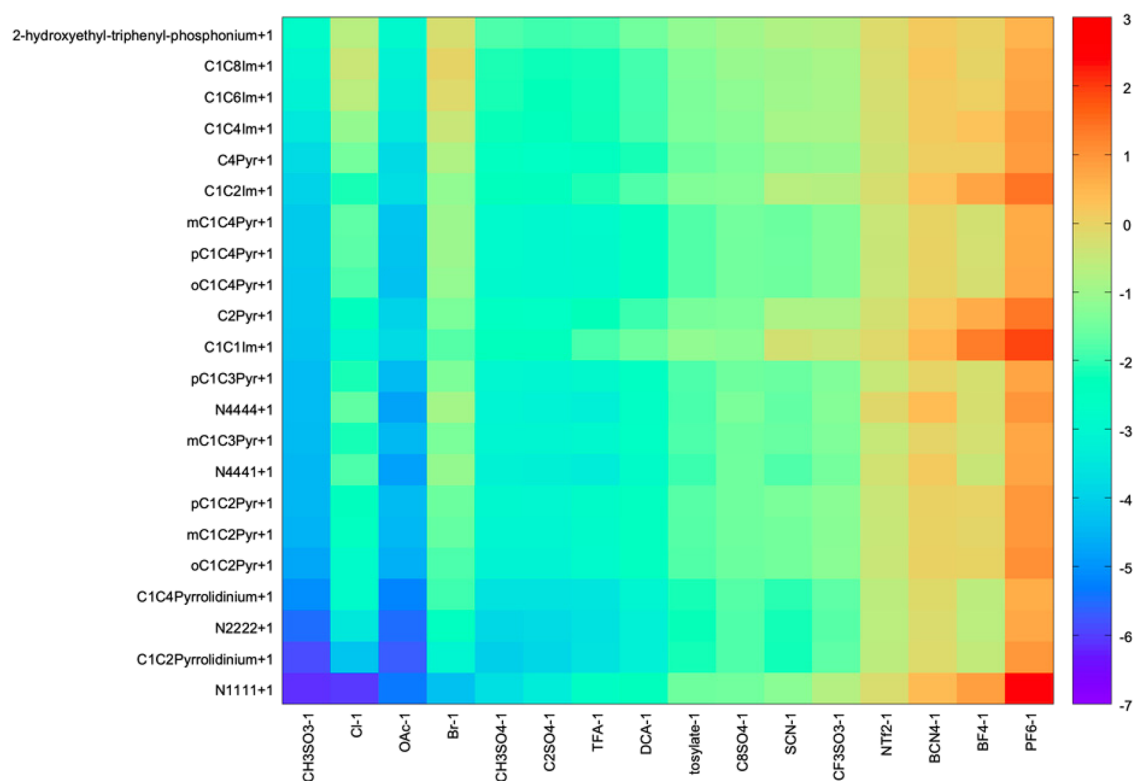


Figure 3. Logarithmic activity coefficients of alizarin at infinite dilution ($\ln \gamma^\infty$) in 352 potential ILs calculated by COSMO at 298 K.

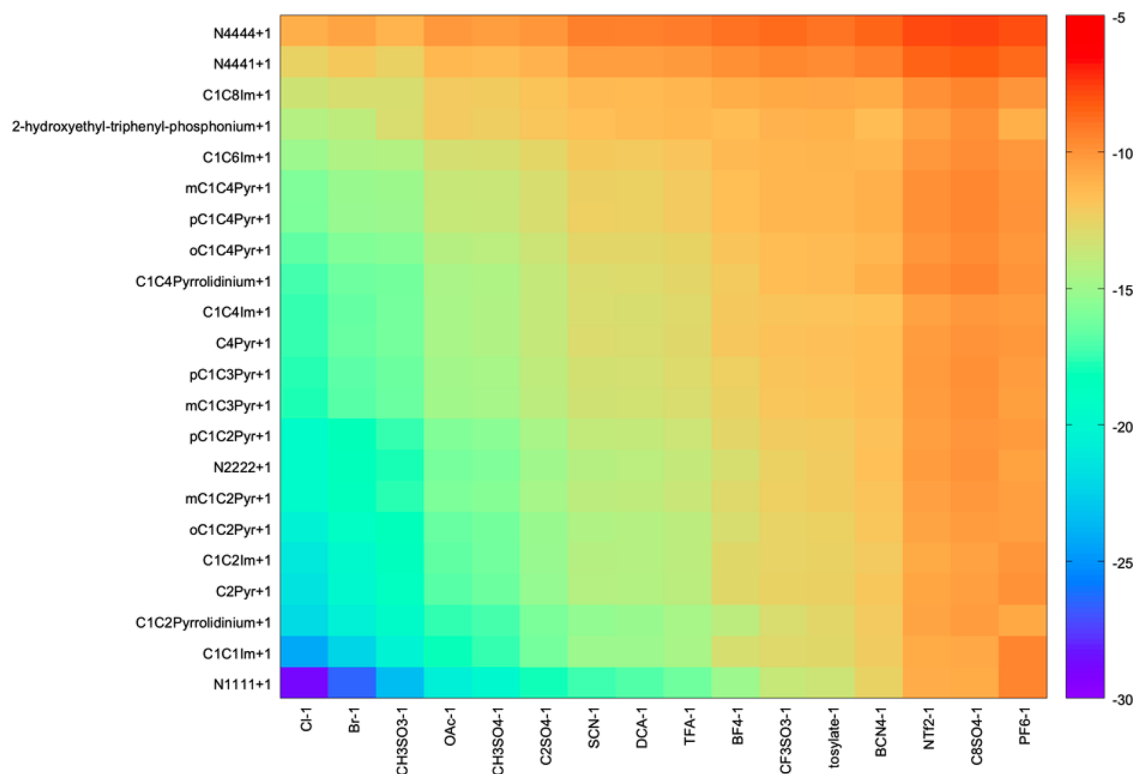


Figure 4. Logarithmic activity coefficients of deprotonated alizarin at infinite dilution ($\ln \gamma^\infty$) in 352 potential ILs calculated by COSMO at 298 K.

for dye dissolution is placed at the lower-left corner of each figure.

In Figure 2, the computed $\ln \gamma^\infty$ values for indigo are displayed for all the 352 ion pairs, which arise from combinations of the 22 cations and 16 anions (their structures

are included in the Supporting Information). Considerable differences are observed between the different ion pair combinations. Small anions such as chloride, bromide, methanesulfonate, acetate, methylsulfate, and ethylsulfate are predicted to dissolve indigo in combination with a variety of

cations. For the cations, it is observed that the most promising candidates are tetraalkylammonium such as N_{1111}^+ , N_{2222}^+ , N_{4444}^+ , and N_{4441}^+ , dialkylpyrrolidinium such as 1-ethyl-1-methylpyrrolidinium and 1-butyl-1-methylpyrrolidinium and alkylimidazolium with short alkyl chains such as 1-methyl-3-methylimidazolium.

A distinct trend is observed for neutral alizarin where the best solubility seems to be anion-dependent (Figure 3). The color code in Figure 3 shows that $\ln\gamma^\infty$ becomes more negative from right to left, according to the anion. Even if the lower values of $\ln\gamma^\infty$ suggest that it is easier to dissolve neutral alizarin in comparison to indigo, anions capable of establishing strong hydrogen bonds such as methanesulfonate, acetate, chloride, and bromide could be recognized as the most promising anions for the dissolution of neutral alizarin.

Considering possible proton exchanges between the ionic solvents and alizarin, the anionic form of alizarin was also considered. Figure 4 shows that for the deprotonated alizarin (negatively charged), the color trend becomes more organized in relation to its neutral structure (Figure 3). One possible explanation is that the interactions of the anionic alizarin are dominated by electrostatic terms so that they have more favorable interactions with ions having higher charge density (N_{1111}^+ and Cl^- , for example) and become progressively less favorable as the charge density decreases. The more complex color distribution observed for the neutral alizarin (Figure 3) reveals that COSMO-SAC is able to detect specific combinations of ions that are promising (or not) for the natural dye dissolution based on subtler effects.

Among the three natural dyes studied herein, curcumin can be considered the most complex one due to its tautomeric equilibrium and its enolic group that can be deprotonated in solution. Both *keto* and *eno* tautomers of curcumin were considered and no significant differences were observed in their color maps of $\ln\gamma^\infty$ (Figures S2 and S3). Slight differences were observed in the values of $\ln\gamma^\infty$, suggesting that the enolic tautomer is harder to dissolve in ionic solvents than its keto tautomer. As well as for neutral alizarin (Figure 3), the solubility of both curcumin tautomers (Figures S2 and S3) seems to be anion-dependent. $\ln\gamma^\infty$ becomes more negative from right to left, according to the anion (Figures S2 and S3). The anions capable of establishing strong hydrogen bonds such as methanesulfonate, acetate, chloride, bromide, and methyl- or ethyl-sulfate appear as the most promising candidates for the dissolution of curcumin.

The deprotonation of curcumin in solution was also considered so that the anionic curcumin was also computed. A comparable trend observed for the deprotonated alizarin (Figure 4) was obtained for the deprotonated curcumin (Figure S4), pointing toward ions with higher charge density as the most promising candidates for the dissolution of curcumin.

The present COSMO-SAC screening allowed the identification of the most promising cation–anion combinations for the dissolution of indigo, alizarin, and curcumin in ionic solvents. It is interesting to notice that small ions having high charge density and capable of establishing strong hydrogen bonds, appear to be the best candidates. Anions such as acetate, methanesulfonate, chloride, bromide, and methyl- or ethyl-sulfate combined with small tetraalkylammonium, pyrrolidinium, and imidazolium cations seem to be the best combinations for the dissolution of the natural dyes. Even if these ordinary cation–anion combinations can be cheap and

easily accessed, they are not necessarily liquids at room temperature.

One possible strategy to render these selected salts liquid at room temperature is to prepare eutectic mixtures with compounds capable of establishing hydrogen bonds.⁴ Therefore, chemicals such as carboxylic acids, amines, amino acids, glycols, and zwitterionic species such as betaine and carnitine were also computed so that those presenting the best affinity toward the natural dyes could be selected for preparing DESs.

Figure 5 shows the values of $\ln\gamma^\infty$ for indigo in the distinct chemicals. It is observed that for most of the chemicals a

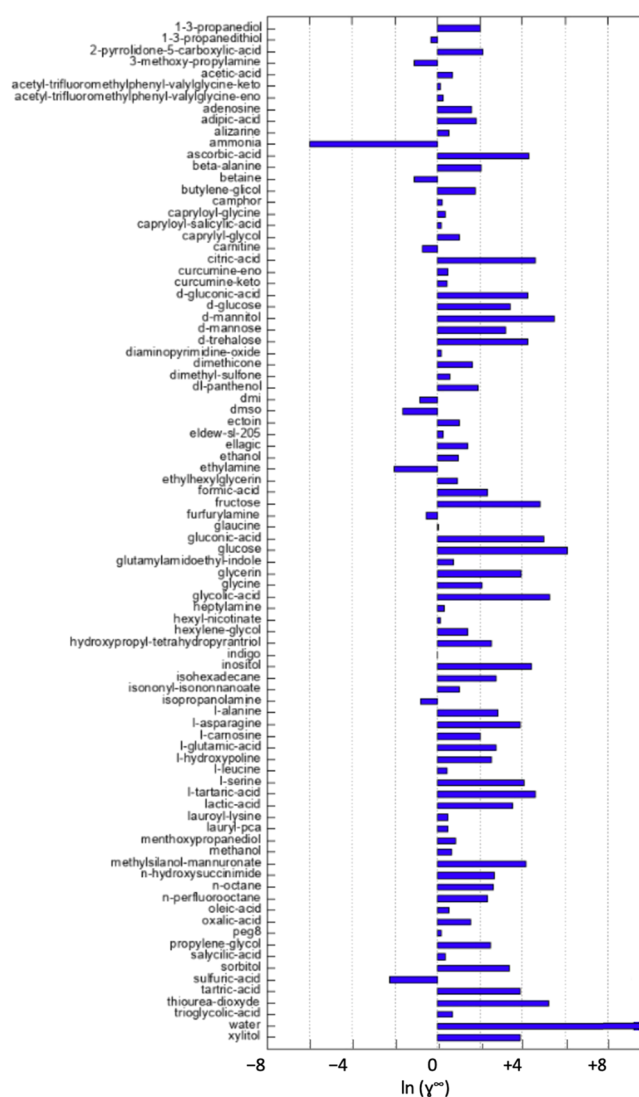


Figure 5. Logarithmic activity coefficients of indigo at infinite dilution ($\ln\gamma^\infty$) in 88 chemical compounds calculated by COSMO at 298 K.

positive value of $\ln\gamma^\infty$ was obtained (among water), as one could expect from the millenary chemical stability of indigo conferred by its large π -conjugated system and intramolecular hydrogen bond.^{60,61} However, for a few compounds such as 1-amino-2-propanol, 3-methoxypropylamine, betaine, ammonia, ethylamine, and sulfuric acid, the computed $\ln\gamma^\infty$ are negative values which might indicate an affinity of these chemicals toward indigo.

For alizarin, Figure 6 shows that it is easier to dissolve alizarin than indigo in such chemicals. Moreover, it is shown in

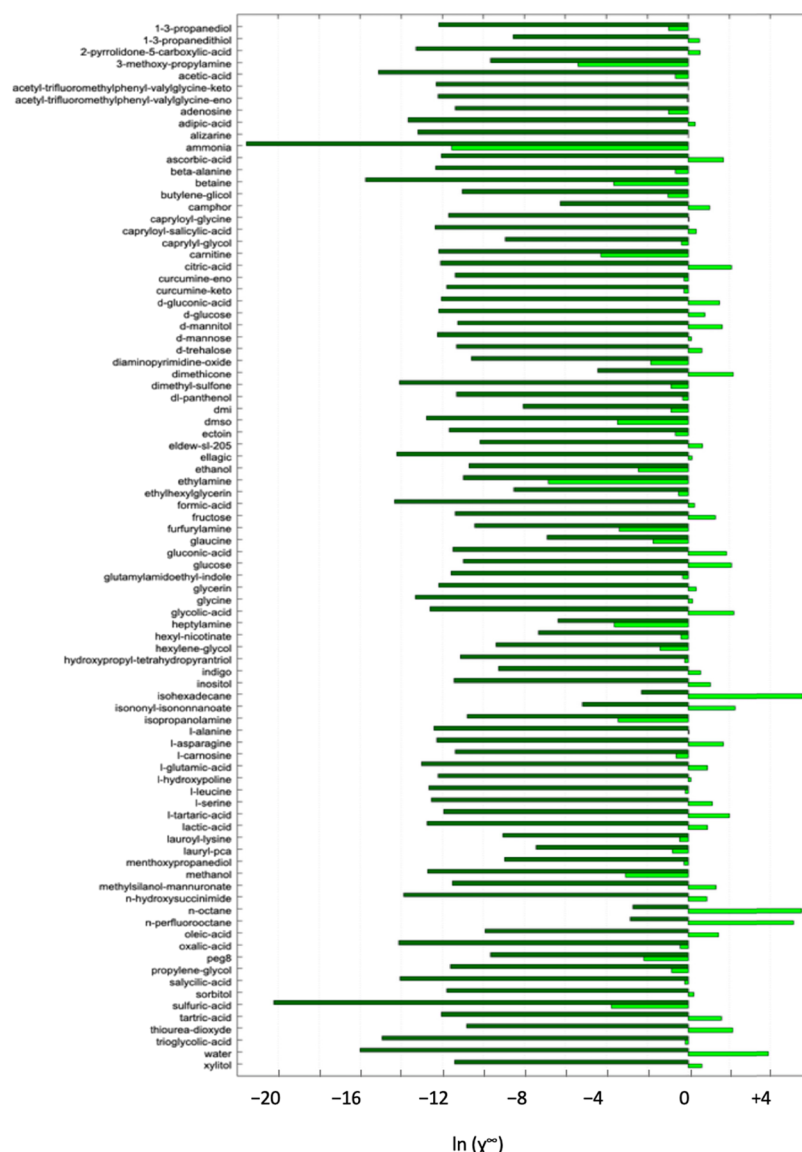


Figure 6. Logarithmic activity coefficients at infinite dilution ($\ln \gamma^\infty$) of alizarin (light green) and deprotonated alizarin (dark green) in 88 chemical compounds calculated by COSMO at 298 K.

Figure 6 that deprotonated alizarin presents more negative values of $\ln \gamma^\infty$ in comparison to its neutral form, revealing that deprotonation increases the affinity of alizarin to these chemicals. In addition to the negative $\ln \gamma^\infty$ values observed for volatile or toxic chemicals such as ammonia, ethylamine, and sulfuric acid, other compounds having less negative $\ln \gamma^\infty$ but are more environmental friendly comes out as possible ionic solvent components, namely, betaine, carboxylic acids (acetic, formic, glycolic, or lactic), and primary amines (1-amino-2-propanol and 3-methoxypropylamine).

The $\ln \gamma^\infty$ values computed for curcumin in the neutral chemicals are displayed in Figure S5. As in the cation–anion color map shown in Figures S2 and S3, these results show that the deprotonation of curcumin facilitates its dissolution (Figure S5) since more negative values of $\ln \gamma^\infty$ are observed. It is interesting to notice that some of the chemicals showing good affinity for indigo or alizarin also comes up as the most interesting ionic solvent components for the dissolution of curcumin: betaine, carnitine, carboxylic acids (acetic, formic,

glycolic, lactic, oxalic, or salicylic), and primary amines (3-methoxypropylamine, heptylamine, and 1-amino-2-propanol).

It should be noted that the $\ln \gamma^\infty$ computed herein revealed that the most promising chemicals and cation–anion combinations for the dissolution of the three natural dyes are comparable in structure: small cation–anion combinations, primary amines, small carboxylic acids, and zwitterions such as betaine and carnitine. Some of the ionic solvents studied in this screening could be prepared to measure the solubility of the natural dyes experimentally.

Four potential ionic solvents were considered for the experimental solubility measurements: two ILs and two DESs. For the ILs, the commercially available 1-ethyl-3-methylimidazolium ethylsulfate ($[\text{C}_2\text{C}_1\text{Im}][\text{EtSO}_4]$) and the new 1-ammonium-2-propanol lactate were considered. The two DESs betaine:glycolic acid (1:2) and $[\text{N}_{4444}][\text{OAc}]$:lactic acid (1:3) were prepared as described in the Materials and Methods section.

Density and viscosity of the screened ionic solvents were experimentally determined as a function of temperature. The

Table 2. Experimental Solubility of the Natural Dyes in the Screened Ionic Solvents at Room Temperature (~ 298 K)

solubility (S)	S/mg L ⁻¹	S/g L ⁻¹	S/g L ⁻¹
ionic solvent	indigo	alizarin	curcumin
betaine:glycolic acid (1:2)		0.74	0.18
[N ₄₄₄₄][OAc]:lactic acid (1:3)	4.47	3.05	2.92
1-ammonium-2-propanol lactate + 50% H ₂ O		3.54	0.33
[C ₂ C ₁ Im][EtSO ₄]	6.72	5.59	5.18
water	0.97 ^a	0.96 ^a	6 × 10 ^{-4b}

^aRef.⁵⁹ ^bRef.⁶²

experimental data are available in Tables S1 and S2. It is observed that density increases as [N₄₄₄₄][OAc]:lactic acid (1:3) < 1-ammonium-2-propanol lactate + 50% H₂O < [C₂C₁Im][EtSO₄] < betaine:glycolic acid (1:2). The high viscosity of the protic IL 1-ammonium-2-propanol lactate hampered its viscosity measurement as well as the natural dye solubility measurements, so a 50% w/w water solution was used instead. The viscosity of the ionic solvents increases as 1-ammonium-2-propanol lactate + 50% H₂O < [C₂C₁Im][EtSO₄] < [N₄₄₄₄][OAc]:lactic acid (1:3) < betaine:glycolic acid (1:2).

Prior to the solubility measurements by UV–vis spectrophotometry, the molar attenuation coefficient of indigo, alizarin, and curcumin was determined and the experimental calibration curves are displayed in Figure S6. The experimental results obtained herein as well as the solubility in water obtained from the literature are listed in Table 2 and displayed in Figure 7.

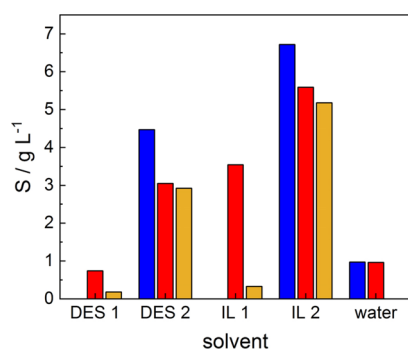


Figure 7. Experimental solubilities of indigo × 10⁻³ (blue bars), alizarin (red bars), and curcumin (yellow bars) in the screened ionic solvents betaine:glycolic acid (1:2) (DES 1), [N₄₄₄₄][OAc]:lactic acid (1:3) (DES 2), 1-ammonium-2-propanol lactate + 50% H₂O (IL 1), and [C₂C₁Im][EtSO₄] (IL 2) at 298 K. The solubility of indigo,⁵⁹ alizarin,⁵⁹ and curcumin⁶³ in water was taken from the literature.

Figure 7 shows that the solubility of the natural dyes in the screened ionic solvents are significantly higher than that in water. In comparison to the values found in the literature for water solubility, Figure 8 shows the ratio between the solubility in the ionic solvents and that in water using data from Table 2, $S_{\text{ionic}}/S_{\text{water}}$. A solubility enhancement of around 7, 6, and 8700 times is observed for indigo, alizarin, and curcumin in the IL 1-ethyl-3-methylimidazolium ethylsulfate, [C₂C₁Im][EtSO₄], respectively. A solubility enhancement of around 4.5, 3, and 4800 times was also observed in the DES [N₄₄₄₄][OAc]:lactic acid (1:3) when compared with water for indigo, alizarin, and curcumin, respectively. These impressive results could be qualitatively anticipated by the COSMO calculations that predicted large negative values of $\ln \gamma^\infty$ for these ionic solvents.

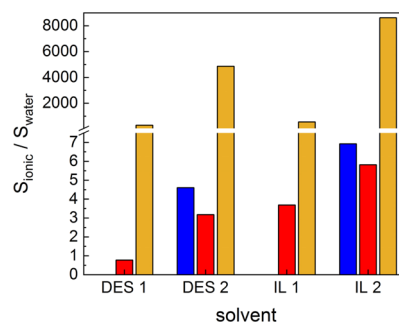


Figure 8. Enhancement of indigo (blue bars), alizarin (red bars), and curcumin (yellow bars) solubility in betaine:glycolic acid (1:2) (DES 1), [N₄₄₄₄][OAc]:lactic acid (1:3) (DES 2), 1-ammonium-2-propanol lactate + 50% H₂O (IL 1), and [C₂C₁Im][EtSO₄] (IL 2) in comparison to their water solubility at 298 K. Solubility enhancement is represented as the ratio $S_{\text{ionic}}/S_{\text{water}}$.

Even if the high viscosities of the DES betaine:glycolic acid (1:2) and the IL 1-ammonium-2-propanol lactate—2998 mPa.s and $\gg 2998$ mPa.s at 298 K, respectively—hampered a proper experimental measurement of the solubility, these results show that ionic solvents such as ILs and DESs can be used to enhance the solubility of natural dyes that are insoluble in water. Any solubility enhancement is a significant contribution for the development of greener dyeing processes using natural dyes. It is shown that COSMO-SAC is a useful method for in silico screening potential ionic solvents for the dissolution of natural dyes even if the viscosity of the solvent candidates, not available from this predictive tool, should also be considered in the screening process.

CONCLUSIONS

COSMO-SAC was used to screen the most promising ionic solvents—ILs or DESs—for the dissolution of three natural dyes having poor water solubility, namely, indigo, alizarin, and curcumin. The predicted results for the logarithmic activity coefficient at infinite dilution, $\ln \gamma^\infty$, indicate that small ions having high charge density and capable of establishing strong hydrogen bonds appear to be the best candidates to dissolve these natural dyes. Anions such as acetate, methanesulfonate, chloride, bromide, and methyl- or ethyl-sulfate combined with small tetraalkylammonium, dialkylpyrrolidinium, and 1-alkyl-3-methylimidazolium cations were found to be the best candidates. Eutectic mixtures of such small cation–anion combinations with primary amines, small carboxylic acids, and zwitterions such as betaine and carnitine allow the preparation of liquid solvents specifically for the chosen dyes. These ordinary in silico selected chemicals were thus experimentally further combined and selected to prepare ILs and DESs that can be cheap, easily accessed, and environmentally friendly.

The experimental solubility of indigo, alizarin, and curcumin was experimentally tested in the screened ionic solvents, indicating that ionic solvents are in fact capable of increasing the solubility of these natural dyes. In comparison to the solubility in water, an enhancement was observed in the IL [C₂C₁Im][EtSO₄] of up to 7, 6, and 8700 times for indigo, alizarin, and curcumin, respectively. These results may contribute to the development of better solvents for the dissolution of natural dyes and thus for developing greener dyeing processes.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.iecr.1c00785>.

Structure of the cations and anions studied in this work; σ -profiles of the dyes; charts with the logarithmic activity coefficients at infinite dilution of the dyes in the ILs; experimental densities and viscosities of the ILs; and UV–vis calibration curves of the dyes (PDF)

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Notes

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