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Hydrogen bond basicity of ionic liquids and molar entropy of hydration of salts as major descriptors in the formation of aqueous biphasic systems

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Abstract

Aqueous biphasic systems (ABS) composed of ionic liquids (ILs) and conventional salts have been largely investigated and successfully used in separation processes, for which the determination of the corresponding ternary phase diagrams is a previous requirement. However, due the large number of ILs that can be prepared and their high structural versatility, it is impossible to experimentally cover and characterize all possible combinations of ILs and salts that may form ABS. The development of tools for the prediction and design of IL-based ABS is thus a crucial requirement. Based on a large compilation of experimental data, a correlation describing the formation of IL-based ABS is here shown, based on the hydrogen-bonding interaction energies of ILs (E_{HB}) obtained by the CONductor-like Screening MOdel for Real Solvents (COSMO-RS) and the molar entropy of hydration of the salt ions. The ability of the proposed model to predict the formation of novel IL-based ABS is further ascertained.

Introduction

Aqueous biphasic systems (ABS) composed of ionic liquids (ILs) offer several advantages over typical polymer-based ABS,¹ and as such have been largely investigated as alternative liquid-liquid separation techniques. These advantages include low viscosity, high thermal stability, and a wide hydrophilic/hydrophobic range that can lead to enhanced selectivities and tailored extraction efficiencies. Moreover, these systems provide higher density differences between the coexisting phases, enabling a faster and easier phase separation than that observed in more traditional polymer-based ABS.²

Gutowski et al.³ reported the first ABS composed of an hydrophilic IL – 1-butyl-3-methylimidazolium chloride, [C₄C₁im]Cl – combined with K₃PO₄, after which a large array of ILs and conventional salts have been used in order to form novel IL-based ABS.¹ In these works, their ternary phase diagrams have been determined and their extraction ability for a wide variety of biomolecules appraised. Most studies have focused on imidazolium-based

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Conflicts of interest

There are no conflicts to declare.

ILs.¹ However, given the large number of ILs that can be prepared and their high structural versatility, their full characterization by experimental approaches is an extensive task. Therefore, tools for the a priori design of IL-based ABS is a crucial requirement while envisaging the development of more selective extraction processes.

From the many studies available in IL-based ABS,^{1,4,5} a molecular-level model for their formation has been previously proposed, suggesting that it is driven by the competition between the IL and salt ions for the formation of hydration complexes. This competition is dominated by ions with a higher charge density and, consequently, capable of stronger interactions with water,^{1,4,5} corresponding thus to salt ions. ILs, with a more diffuse charge, are thus usually salted-out by high-charge density salts. Previously, Coutinho and co-workers^{6–8} suggested the existence of a relationship between the hydrogen bond basicity (β) of ILs and their ability to form ABS. However, they failed on quantitatively describing this dependence.^{6–8}

The hydrogen bond basicity parameter, describing the ability of a given specie to accept protons, is actually one of the most important descriptors of the ILs solvation capability for a wide variety of compounds,^{9–12} and great efforts have been made to establish polarity scales for ranking ILs. Furthermore, it was already shown that the polarity of ILs reflects also their own solvation in water, which is intrinsically associated to their capability to form ABS.¹ A polarity-scale of ILs is thus of high importance as it allows the development of a framework to, at least qualitatively, predict the solubility of a given solute in ILs and also of ILs in a set of solvents.

Several dyes have been used as solvatochromic probes to experimentally determine the polarity of several solvents, including ILs.^{13–23} The multiparametric approach proposed by Kamlet-Taft^{24–27} is able to characterize a given fluid in terms of polarity, by determining specific parameters, namely the hydrogen bond (acceptor) basicity (β), the hydrogen-bond (donor) acidity (α), and the dipolarity/polarizability (π^*), being one of the best established and accepted polarity scales in the literature. Several researchers have determined these parameters in neat ILs.^{14–23} However, the determination of the solvatochromic parameters consisting on the measurement of specific solute-solvent interactions is probe dependent, meaning that different solvatochromic probes will result in different values for the same parameter, but at least can be used to rank ILs in terms of polarity if addressed by the same probes and under the same conditions. Lungwitz et al.^{16–18} and Welton and co-workers^{19–23} are the two research groups that extensively determined solvatochromic parameters of pure ILs. For the β determination, Lungwitz et al.¹⁷ used 3-(4-amino-3-methylphenyl)-7-phenyl-benzo-[1,2-*b*:4,5-*b'*]-difuran-2,6-di-one dye (1) as solvatochromic probe, while Welton and co-workers^{21–25} employed the *N,N*-diethyl-4-nitroaniline (2) and 4-nitroaniline (3) probes pair – Fig. 1. Although the ILs tendencies observed by both research groups are similar, the obtained absolute values of solvatochromic parameters are distinct. For example, for the ILs [C₄C₁im][CH₃CO₂] and [C₄C₁im][CF₃SO₃], the β values obtained are, respectively, 0.85 and 0.5717 when 3-(4-amino-3-methylphenyl)-7-phenyl-benzo-[1,2-*b*:4,5-*b'*]-difuran-2,6-di-one is used, and 1.20 and 0.4919 when the probe pair *N,N*-diethyl-4-nitroaniline/4-nitroaniline is employed. Furthermore, the Kamlet-Taft parameters are highly sensitive to impurities and water content,^{24–29} and require the use of liquid samples. Some

probes also do not allow the determination of solvatochromic parameters of aqueous solutions of ILs, for which alternative probes have been suggested.³⁰ These are significant experimental drawbacks in the determination of the ILs solvatochromic parameters.

Based on the exposed, the development of a generalized and coherent polarity β -scale for ILs is thus a major challenge. Furthermore, with the continuous reports on the synthesis of new ILs, finding simple computational tools that can provide this assessment, based only on their cation and anion structures, is of utmost importance. To overcome the drawbacks described above with experimental approaches, several attempts have been made on developing predictive methods for solvatochromic parameters.^{31–34} Hunt et al.³³ used computational simulations for predicting the Kamlet-Taft parameters α and β in neat ILs. However, this approach has a high computational cost and requires expert knowledge, being unfeasible for a routine screening. A simpler, alternative, computational method, based on COnductor-like Screening MOdel for Real Solvents (COSMO-RS), has been successfully applied for predicting solvatochromic parameters of pure ILs.^{35,36} Other authors have demonstrated the ability of COSMO-RS to evaluate and correlate the polarity of ILs.^{37,38} COSMO-RS is a computational approach well established in the literature, and commonly applied to describe properties and phase equilibria of systems involving ILs.^{39–41} Of particular relevance are the works of Freire and co-workers^{35,36} that reported the successful correlation of the experimental β and α parameters with the IL equimolar cation–anion hydrogen-bonding interaction energies, E_{HB} , electrostatic-misfit interactions, E_{MF} , and van der Waals forces, E_{vdW} , determined using COSMO-RS. The authors proposed a new and extended scale of polarities based on COSMO-RS parameters, for a variety of ILs composed of a large number of anions and cations.^{35,36}

In this work, the most extended experimental solvatochromic parameter scales available for the hydrogen-bond basicity of ILs – Lungwitz et al.¹⁷ and Welton and co-workers¹⁹ scales – are used to correlate with the ILs ability to form ABS. Due to the reduced number of experimental data reported in the literature, and aiming at finding a predictive model, the COSMO-RS hydrogen-bonding interaction energies were then evaluated as potential substitutes of β , allowing the development of a model to predict the IL-based ABS formation.

Experimental

Phase diagrams

Most IL-based ABS experimental data (solubility curves of the respective ternary phase diagrams at 25°C and atmospheric pressure) considered in this work were previously reported.^{2,4,6–8,42–55} Nevertheless, to fill gaps in the literature data, some binodal curves were additionally determined in this work through the cloud point titration method^{8,55} at 25°C and atmospheric pressure. To this end, aqueous solutions of each salt and IL under study were prepared and used for the determination of the binodal curves. Repetitive drop wise addition of the aqueous salt solution to the aqueous solutions of IL was carried out until the detection of a cloudy (biphasic) solution, followed by the drop wise addition of ultrapure water until the finding of a monophasic region (clear and limpid solution). The ternary system compositions were determined by weight quantification within $\pm 10^{-4}$ g. These novel

results are shown in the ESI[†]. Due to the size of the database used, the values of IL molality at saturation of each ABS and respective reference are given in the ESI[†].

COSMO-RS

The IL hydrogen-bonding interaction energies, E_{HB} , were calculated using the COSMO-RS (CONductor-like Screening MODEL for Real Solvents) thermodynamic model that combines quantum chemistry, based on the dielectric continuum model known as COSMO, with statistical thermodynamic calculations. The standard process of COSMO-RS calculations employed in this work was previously described by Kurnia et al.³⁶ The quantum chemical COSMO calculations were performed with the TURBOMOLE 6.1 program package on the density functional theory (DFT) level, applying the BP functional B88-P86 with a triple- ζ valence polarized basis set (TZVP) and the resolution of identity standard (RI) approximation.⁵⁶ The COSMOthermX program using the parameter file BP_TZVP_C20_0111 (COSMOlogic GmbH & Co KG, Leverkusen, Germany) was used in all calculations.⁵⁷

Results and discussion

Taking into account that the ABS (ILs + salts) formation results from all ions competition for hydration, the system composition at each binodal curve where the molality of the IL equals the molality of the salt, hereafter named “saturation solubility” as proposed by Shahriari et al.⁴, was used in this work as a relative measure of the ABS formation ability. By using all the published data^{2,4,6–8,42–55} and the new data determined in this work, shown in the ESI[†], the IL molality at saturation solubility, $[IL]_{ss}$ was plotted as function of the hydrogen bond basicity ability of pure ILs, depicted in Fig. 2. A linear correlation was found, represented by the following equation:

$$[IL]_{ss} = A \cdot \beta + B \quad (1)$$

where A and B are constants that depend on the salt used in the preparation of ABS.

Fig. 2 presents the correlations obtained for ABS composed of $[C_4C_1im]$ -based ILs and the following salts: K_3PO_4 , $K_3C_6H_5O_7$, K_2HPO_4 , Na_2CO_3 , Na_2SO_4 , and $KNaC_4H_4O_6$. Two different correlations for each salt are obtained, which depend on the set of β values used – β values determined with the solvatochromic probe (1) by Lungwitz et al.¹⁷ (β_{Lung}), or with the pair (2)/(3) by Welton and co-workers¹⁹ (β_{TW}).

The formation of ion hydration complexes depends on the IL hydrogen bond accepting ability, and therefore this parameter is highly dependent on the IL anion nature.³⁵ Thus, and as shown Fig. 2, IL anions with lower β values have a lower capacity to interact with water being more prone to be salted-out by the salt ions, and thus an easier liquid-liquid demixing is achieved at lower $[IL]_{ss}$ values. Independently of the set of β values used (β_{Lung} or β_{TW}), good correlations are obtained between this parameter and the saturation solubility of the studied ABS. Although the trends here found are based on a specific IL cation, namely

$[\text{C}_4\text{C}_1\text{im}]^+$, this is also valid for other ILs classes, since it was previously shown that the anion rank is maintained even if the cation is changed.¹

Despite the good correlations found between the ILs hydrogen bond acceptor ability and the saturation solubility in the ABS evaluated (Fig. 2), the drawbacks associated to the experimental solvatochromic parameters determination, such as the required experimental efforts given the large number of possible ILs, their sensitivity to ILs impurities and color, and the fact of being only possible to carry out measurements in liquid samples, makes the convenience of β values highly limited.³⁵ Furthermore, most ABS studies are focused on $[\text{C}_4\text{C}_1\text{im}]$ -based ILs, and there is almost no data for other types of cations which makes unfeasible the use of experimental β parameters in the development of a model that can be used to predict the IL-based ABS formation.

Taking into account the importance of the parameter β in the description of the polarity of ILs, its relation with the ILs ability to form ABS, and the previously reported correlation between the E_{HB} taken from COSMO-RS and the experimental β parameter,³⁵ E_{HB} ($\text{kJ}\cdot\text{mol}^{-1}$) was further used to correlate the ABS formation ability, according to the Eqn. (2):

$$[\text{IL}]_{ss} = C \cdot E_{HB} + D \quad (2)$$

with C and D as constants that depend on the salt employed.

The set of available data for E_{HB} from COSMO-RS can be as large as desired since this approach only requires computational information based on the chemical structure of ILs, without restrictions on the IL cation-anion combinations. This overcomes the drawbacks associated to the use of solvatochromic probes, not only by avoiding an extensive experimental determination of the β values, but also by eliminating the limitations to establish a coherent and complete polarity scale for any IL structure caused by the presence of impurities and water, or by the IL physical state. For that purpose, in Fig. 3, β values were replaced by the COSMO-RS E_{HB} values and a very diversified set of ILs included. The ILs included in the correlations shown in Fig. 3 are described in Table 1.

When replacing β by E_{HB} values, and by introducing different types of ILs cations, such as pyridinium, tetraalkylammonium- and phosphonium-based, similar linear dependencies were observed for IL-based ABS composed of the salts K_3PO_4 , $\text{K}_3\text{C}_6\text{H}_5\text{O}_7$, K_2HPO_4 , Na_2CO_3 , Na_2SO_4 and $\text{KNaC}_4\text{H}_4\text{O}_6$, with correlation coefficients ranging between 0.74 and 0.89 (*cf.* Fig. 3). As reported by Cláudio et al.³⁵, ILs with more negative values of E_{HB} present higher hydrogen bond basicities, and for these the ABS formation is only attained at higher $[\text{IL}]_{ss}$.

The ILs used in these correlations, as well as their ability to form (✓) or not (✗) ABS with each salt, are summarized in Table 1. Some ABS composed with a given IL and salt were considered as outsiders (within a 95 % confidence interval) to the tendency generated with the E_{HB} values. Despite some particular cases that may be related with experimental errors, there are two ILs, namely $[\text{C}_4\text{C}_1\text{pip}]\text{Cl}$ and $[\text{C}_4\text{C}_1\text{pyr}]\text{Cl}$ that, independently of the salt used, were always identified as outsiders. This suggests that the E_{HB} values for these two ILs

could be wrongly estimated by COSMO-RS. It is important to have in mind that COSMO-RS is a thermodynamic model that combines quantum chemistry with statistical thermodynamic calculations, and this tool is in constant upgrade trying to enhance its ability to estimate more accurate properties of ILs. However, taking into account the chemical structure of these two ILs, both cyclic amines with non-aromatic rings, the determined E_{HB} parameters are in good agreement with what is expected. Although some limitations have been identified, the obtained results demonstrate the potential of COSMO-RS hydrogen-bonding interaction energies, E_{HB} , to predict the IL + salt ABS formation.

After identifying the correlations between $[IL]_{ss}$ and E_{HB} , their ability to predict the formation of ABS constituted by other ILs, which were not considered in the establishment of these correlations, was further evaluated. The obtained results are shown in Fig. 4. Experimental data used in these correlations are reported in the ESI†. The respective average relative deviations (ARD) were determined through Eqn. (3),

$$ARD = 100 \frac{1}{NP} \sum_{k=1}^{NP} \left| 1 - \frac{Z_k^{pred}}{Z_k^{exp}} \right| \quad (3)$$

where NP is the number of experimental data points and the superscripts “pred” and “exp” are the predicted results and experimental data, respectively. Remarkably, ARD values between 11.21 and 24.17 % were obtained, indicating that previously determined correlation for each salt can be used to predict the formation of new ABS. $[C_4C_1pyr]Cl^-$ and $[C_4C_1pip]Cl^-$ -based ABS predicted results were also represented in Fig. 4 (orange circles). Since they behave as outsiders in the correlation between $[IL]_{ss}$ and E_{HB} parameters (*cf.* Fig. 3), they were not considered in the ARD calculation; even thus it is possible to observe quite good results for these systems in some of salt-based ABS considered.

It was demonstrated that for a common salt and using the ILs E_{HB} values estimated by COSMO-RS, it is possible to predict the formation of new ABS, even by providing the amount of IL/salt required to form a two-phase system, without the need of experimental data. This type of data is valuable for researchers who aim to address the possibility of using specific ABS for separation purposes. However, the correlations proposed are salt dependent, and it would be important to try to derive generic correlations that could account with both the nature of the salt and the IL.

Since each correlation presented in Fig. 3 was determined for a fixed salt, the constants C and D of Eqn (2) are salt dependent. Shahriari et al.⁴ reported that the molar entropy of hydration ($_{hvd}S$) of the salt ions is related with the IL-based ABS formation. The $_{hvd}S$ values for the cations and anions that compose the salts evaluated in this work are reported in Table 2. In fact, it was possible to find a linear dependence of the constants C and D determined for each salt and the salt ions molar entropy of hydration. These correlations are described by Eqn. (4) and (5) below.

$$C = (2.41 \times 10^{-4} \pm 4.35 \times 10^{-5}) \cdot \Delta_{hyd}S_{anion} - 0.134 \pm 0.013 \quad (4)$$

$$R^2 = 0.94; F = 31; N = 4$$

$$D = (8.08 \times 10^{-4} \pm 2.64 \times 10^{-5}) \cdot \Delta_{hyd}S_{anion} + (3.51 \times 10^{-3} \pm 1.18 \times 10^{-4}) \cdot \Delta_{hyd}S_{cation} + 0.346 \pm 0.017 \quad (5)$$

$$R^2 = 1.0; F = 3584; N = 4$$

Through Eqn. (4) and (5), it is possible to conclude that the parameter C is dominated by the molar entropy of hydration of the salt anion, while parameter D depends on both the salt anion and cation $\Delta_{hyd}S$. Unfortunately, there is no available data for the molar entropy of hydration of citrate and tartrate anions, and thus Eqn. (4) and (5) were estimated only with $N = 4$. These equations have statistical meaning and are in good agreement with Shahriari et al. 4 previous findings.

Constants C and D for the ABS constituted by the salt K_2CO_3 ,⁶¹ not used in the establishment of Eqn. (4) and (5), were here adopted to evaluate the predictive capability of these equations on IL-based ABS formation. By their direct application, the following values were calculated for K_2CO_3 -based ABS: $C = -0.075 \text{ mol}^2 \cdot (\text{kg} \cdot \text{kJ})^{-1}$ and $D = 0.28 \text{ mol} \cdot \text{kg}^{-1}$. With these parameters and ILs E_{HB} values, it was possible to predict the $[IL]_{ss}$ for ABS composed of K_2CO_3 . In Fig. 5 the values predicted by Eqn. (2) are represented as function of experimental data. Remarkably, an ARD of 19.68 % was obtained. This result demonstrates that $[IL]_{ss}$ values of K_2CO_3 -based ABS can be predicted only using the ILs E_{HB} parameters estimated by COSMO-RS and the molar entropy of hydration of both cation and anion of the salt.

Conclusions

An effective predictive model for IL-based ABS formation was successfully established. It was demonstrated that the ABS ILs saturation solubility presents a linear dependence with the ILs COSMO-RS hydrogen-bonding interaction energies, allowing to predict the ability of ILs to form ABS with a specific salt. The correlation constants obtained showed to be intrinsically related with the salt ions molar entropy of hydration, allowing to further establish a predictive model of IL-based ABS formation which considers both the nature of the IL and salt used. This type of correlation is particularly relevant due the large number of ILs that can be prepared, turning impossible to experimentally characterize all possible combinations of ILs and salts that may form ABS. The established predictive model is highly relevant for researchers dealing with the use of ABS composed of ILs and conventional salts applied in separation processes, for which the assessment of a given ABS formation ability could be previously carried out.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgements

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Fig. 1.
Chemical structures of the solvatochromic probes used by Lungwitz et al.¹⁷ and Tom Welton and co-workers¹⁹: (1) 3-(4-amino-3-methylphenyl)-7-phenyl-benzo-[1,2-*b*:4,5-*b'*]-difuran-2,6-di-one dye; (2) *N,N*-diethyl-4-nitroaniline; (3) 4-nitroaniline.

Fig. 2.

Relationship between the molality of the IL/salt at saturation solubility ($[IL]_{ss}$) and the hydrogen-bond basicity (β) of $[C_4C_{1im}]$ -based ILs determined with the solvatochromic probes: (1) by Lungwitz et al.¹⁷ (β_{Lung} , blue circles) and the pair (2)/(3) by Welton and co-workers¹⁹ (β_{TW} , green triangles) for IL-based ABS composed of: (A) K_3PO_4 ; (B) $K_3C_6H_5O_7$; (C) K_2HPO_4 ; (D) Na_2CO_3 ; (E) Na_2SO_4 ; (F) $KNaC_4H_4O_6$.

Fig. 3.

Relationship between the molality of the IL/salt at saturation solubility ($[IL]_{ss}$) and the hydrogen-bonding interaction energy in the equimolar cation-anion mixture (E_{HB}) of ILs, estimated by COSMO-RS, for the IL-based ABS composed of (A) K_3PO_4 , (B) $\text{K}_3\text{C}_6\text{H}_5\text{O}_7$, (C) K_2HPO_4 , (D) Na_2CO_3 , (E) Na_2SO_4 , and (F) $\text{KNaC}_4\text{H}_4\text{O}_6$. ILs used in each correlation (blue circles) and outsiders (orange diamonds) are identified in Table 1.

Fig. 4.

Correlation between experimental (Exp. [IL]_{ss}) and predicted (Pred. [IL]_{ss}) values of IL/salt molality at saturation solubility in ABS composed of: (A) K₃PO₄, (B) K₃C₆H₅O₇, (C) K₂HPO₄, (D) Na₂CO₃, (E) Na₂SO₄, and (F) KNaC₄H₄O₆. [C₄C₁pyr]Cl⁻ and [C₄C₁pip]Cl⁻ based ABS (orange circles). Legend: *N* – number of ABS considered; ARD – average relative deviation.

Fig. 5. Correlation between experimental and predicted values of IL/salt molality at saturation solubility ($[IL]_{ss}$) for K_2CO_3 -based ABS. Legend: N – number of ABS considered; ARD – average relative deviation.

Table 1

ABS used to evaluate the correlation between $[IL]_{ss}$ and E_{HB} : (✓) formation of ABS; (✗) no formation of ABS. ABS identified as outsiders are colored at grey.

ILs	SALTs					
	(A) K_3PO_4	(B) $K_3C_6H_5O_7$	(C) K_2HPO_4	(D) Na_2CO_3	(E) Na_2SO_4	(F) $KNaC_4H_4O_6$
(1) $[C_2C_{1im}]Cl$	✓	✗	✓	✓	✗	✗
(2) $[C_4C_{1im}][CF_3SO_3]$	✓	✓	✓	✓	✓	✓
(3) $[C_4C_{1im}][SCN]$	✓	✓	✓	✓	✓	✓
(4) $[C_4C_{1im}][N(CN)_2]$	✓	✓	✓	✓	✓	✓
(5) $[C_4C_{1im}]Br$	✓	✓	✓	✓	✓	✓
(6) $[C_4C_{1im}]Cl$	✓	✓	✓	✓	✗	✗
(7) $[C_4C_{1im}][DMP]$	✓	✓	✓	✓	✗	✗
(8) $[C_4C_{1im}][CH_3CO_2]$	✓	✓	✓	✗	✗	✗
(9) $[C_4C_{1py}]Cl$	✓	✓	✓	✓	✓	✗
(10) $[C_4C_{1pip}]Cl$	✓	✓	✓	✓	✓	✓
(11) $[C_4C_{1pyr}]Cl$	✓	✓	✓	✓	✓	✓
(12) $[C_6C_{1im}]Cl$	✓	✓	✓	✓	✗	✓
(13) $[N_{111(2OH)}]Cl$	✓	✗	✓	✗	✗	✗
(14) $[N_{4444}]Cl$	✓	✓	✓	✓	✓	✓
(15) $[P_{4444}]Cl$	✓	✓	✓	✓	✓	✓

Table 2Molar entropy of hydration ($_{hyd}S$) for ions that compose the salts under study.^{58–60}

$_{hyd}S(\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})$	
Anions	
PO_4^{3-}	-421
$\text{C}_6\text{H}_5\text{O}_7^{3-}$	<i>n.a.</i>
HPO_4^{2-}	-272
CO_3^{2-}	-245
SO_4^{2-}	-200
$\text{C}_4\text{H}_4\text{O}_6^{2-}$	<i>n.a.</i>
Cations	
K^+	-74
Na^+	-111