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Enhancing the adsorption of ionic liquids onto activated carbon by the addition of inorganic salts

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Abstract

Most ionic liquids (ILs) are either water soluble or present a non-negligible miscibility with water that may cause some harmful effects upon their release into the environment. Among other methods, adsorption of ILs onto activated carbon (AC) has shown to be an effective technique to remove these compounds from aqueous solutions. However, this method has proved to be viable only for hydrophobic ILs rather than for the hydrophilic that, being water soluble, have a larger tendency for contamination. In this context, an alternative approach using the salting-out ability of inorganic salts is here proposed to enhance the adsorption of hydrophilic ILs onto activated carbon. The effect of the concentrations of Na₂SO₄ on the adsorption of five ILs onto AC was investigated. A wide range of ILs that allow the inspection of the IL cation family (imidazolium- and pyridinium-based) and the anion nature (accounting for its hydrophilicity and fluorination) through the adsorption onto AC was studied. In general, it is shown that the use of Na₂SO₄ enhances the adsorption of ILs onto AC. In particular, this effect is highly relevant when dealing with hydrophilic ILs that are those that are actually poorly removed by AC. In addition, the COnductor like Screening MOdel for Real Solvents (COSMO-RS) was used aiming at complementing the experimental data obtained. This work contributes with the development of novel methods to remove ILs from water streams aiming at creating “greener” processes.

Keywords

ionic liquids; adsorption; activated carbon; inorganic salt; salting-out

1. Introduction

The use of ionic liquids (ILs) as novel solvents or fluids for a diverse range of applications has become increasingly relevant [1,2]. ILs are salts with melting temperatures below 100°C, and that are usually formed by large organic cations and organic or inorganic anions. Since ILs are constituted by ionic species, most of them present particular properties not common in molecular solvents, such as a negligible vapour pressure, general non

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flammability, high thermal and chemical stabilities, among others. Moreover, the possibility of controlling their physicochemical properties by the adequate manipulation of the cation and/or the anion allows the design of these solvents for target applications [3]. This tailoring ability makes of ILs excellent alternative solvents for diverse extraction purposes [4].

The intrinsic non-volatile nature of ILs provides an opportunity to reduce, or even completely eliminate, hazardous and toxic emissions to the atmosphere. Nevertheless, although ILs cannot contribute to air pollution, some of them (even those considered hydrophobic) present a non-negligible solubility in water [5-10], and their release into aquatic media raises serious environmental concerns. Therefore, the search of novel methods/techniques to remove ILs from aqueous environments is of outmost importance. There are some previous studies regarding the removal of ILs from aqueous streams [11-31]. Amongst those, some of them use destructive methods such as advanced oxidation [11-13] or biological treatments [14,21,22]. However, when envisaging sustainable technologies, the degradation of ILs should be avoided and they should be recovered and recycled instead [32]. There are also some non-destructive methods already reported in the literature, such as distillation [23], crystallization [24], nanofiltration [25], pervaporation [26], phase separation [15] and adsorption [17]. Among the non-destructive techniques, the adsorption onto activated carbon (AC) proved to be able to remove different ILs from aqueous solutions [17,18,31]. Nonetheless, although adsorption has provide good results for hydrophobic ILs, it fails when dealing with hydrophilic ILs that have a lower affinity to AC.

It is well-known that the addition of salting-out species to aqueous media, like inorganic or organic salt ions, leads to a decrease on the solubility of hydrophobic ILs in water [33], and can even induce phase separation with hydrophilic or completely water-soluble ILs [34]. Therefore, in this work, the salting-out ability of an inorganic salt, Na_2SO_4 , was used to improve the adsorption of different ILs (hydrophobic and hydrophilic) onto AC. The adsorption of different ILs, in the presence of salt solutions at different concentrations, onto AC was investigated. The effect of the IL chemical structure and its ability to adsorb onto AC was also studied. In order to complement the experimental measurements, the COnductor like Screening MOdel for Real Solvents (COSMO-RS), a quantum chemical-based prediction model, was finally used to better evaluate the salt effect in the adsorption of ILs onto AC.

2. Experimental

2.1. Materials

The study on the adsorption onto AC was carried out for the following ILs: 1-butyl-3-methylimidazolium chloride, $[\text{C}_4\text{C}_1\text{im}]\text{Cl}$; 1-butyl-3-methylimidazolium methanesulfonate, $[\text{C}_4\text{C}_1\text{im}][\text{CH}_3\text{SO}_3]$; 1-butyl-3-methylimidazolium trifluoromethanesulfonate (triflate), $[\text{C}_4\text{C}_1\text{im}][\text{CF}_3\text{SO}_3]$; 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide, $[\text{C}_4\text{C}_1\text{im}][\text{NTf}_2]$; 1-butyl-3-methylpyridinium bis(trifluoromethylsulfonyl)imide, $[\text{C}_4\text{C}_1\text{py}][\text{NTf}_2]$. All ILs were acquired from Iolitec with a mass fraction purity of 99 %. The purity of all ILs was also confirmed by ^1H and ^{13}C NMR.

The inorganic salt sodium sulfate (Na_2SO_4) was acquired from Sigma-Aldrich with a mass fraction purity above 99 %. The commercial AC was supplied by Merck (AC-MkU) and was used as adsorbent. The AC used in this work has a BET area of $927 \text{ m}^2\cdot\text{g}^{-1}$ with high micropore volume contribution and a low concentration of surface functional groups, as reported before [31].

2.2. Method

The experiments were conducted in glass bottles (100 mL) at 308.15 K, using 50 mL of each salt solution with the IL in a concentration ranging from 100 to 500 $\text{mg}\cdot\text{L}^{-1}$. The concentrations of the different salt solutions varied between 0.28 and 1.76 $\text{mol}\cdot\text{kg}^{-1}$. The AC was then added to the aqueous solutions and placed in an orbital incubator (Julabo Shake Temp, model SW-22) at 200 rpm, and left for, at least, four days. This time proved to be the minimum time necessary to reach the equilibrium [17]. After this period, the samples were removed and the ILs content was quantified. The concentration of imidazolium- and pyridinium-based ILs were determined by UV spectroscopy (Varian, model Cary 1E) at 212 nm for the imidazolium and at 266 nm for the pyridinium aromatic ILs and using calibration curves previously established. The data obtained was fitted with the Langmuir model (Eq. (1)),

$$q_e = \frac{q_{\max} \times B \times C_e}{1 + B \times C_e} \quad (1)$$

where B ($\text{L}\cdot\text{mmol}^{-1}$) and q_{\max} ($\text{mmol}\cdot\text{g}^{-1}$) are empirical coefficients of the Langmuir equation, C_e ($\text{mmol}\cdot\text{L}^{-1}$) is the equilibrium concentration of adsorbate in the fluid phase and q_e ($\text{mmol}\cdot\text{g}^{-1}$) is the equilibrium concentration of adsorbate in the solid phase [17]. The empirical coefficients obtained and the respective correlation coefficients are reported in Table 1.

The apparent distribution coefficients (K_d , $\text{L}\cdot\text{kg}^{-1}$) of each system were calculated taking into consideration Eq. (2):

$$K_d = \frac{q_e}{C_e} \times 1000 \quad (2)$$

This coefficient evaluates the capacity of AC for the adsorption of different ILs at the same equilibrium concentration. The apparent distribution coefficients are reported in Table 1.

The AC/water/salt partition coefficient (P) of each IL at infinite dilution was calculated by COSMO-RS at 308 K. The molecular geometry of all molecular models (AC, ions of the Na_2SO_4 salt, water and ion-paired structures of ILs) were optimized at the B3LYP/6-31++G** computational level. The ideal screening charges on the molecular surface for each species were calculated by the continuum solvation COSMO model using the BVP86/TZVP/DGA1 level of theory. According to the chosen quantum method, the functional and basis sets, the corresponding parameterization (BP_TZVP_C30_1201) in the COSMOtherm code was used.

3. Results and Discussion

In Fig. 1 are represented the chemical structures of the ILs studied.

The adsorption of the ILs [C₄C₁im]Cl, [C₄C₁im][CH₃SO₃], [C₄C₁im][CF₃SO₃], [C₄C₁im][NTf₂] and [C₄C₁py][NTf₂] onto commercial AC was measured for Na₂SO₄ aqueous solutions with concentrations ranging from 0.28 to 1.76 mol·kg⁻¹. The adsorption isotherms for all ILs at 308 K onto AC-MkU are depicted in Fig. 2.

Adsorption of ILs onto AC proved to be a useful and non-destructive way to remove low concentrations of ILs from water [17,18,20,31]. However, unlike for hydrophobic ILs, for hydrophilic compounds this method is not effective due to the low polarity of the AC surface [17,31].

In a previous work [15], the formation of aqueous biphasic systems by the addition of strong salting-out species revealed to be a highly efficient methodology for removing hydrophilic ILs from water, at high concentrations. The addition of salting-out species, like inorganic salts, to a water solution containing hydrophobic ILs was previously shown to lead to a significant decrease of their solubility in water [33,34]. Therefore, with the goal of improving the adsorption of hydrophilic ILs onto AC, the salting-out ability of Na₂SO₄ was here investigated. For that purpose, several concentrations of Na₂SO₄, a strong salting-out inducing salt that does not change the medium pH when dissolved in aqueous medium [33,35], were tested. It was already shown that Na₂SO₄ can promote the phase separation when combined with hydrophilic ILs in aqueous solutions [35], and that it can decrease the solubility of highly hydrophobic and fluorinated ILs in water [33].

The results here obtained show different adsorption capacities attending to both the nature of the IL and the amount of salt in solution. For comparison purposes, *B* and *q*_{max} empirical coefficients of the Langmuir model (Eq. (1)) and the apparent distribution coefficients (*K*_d, Eq. (2)), obtained from the experimental adsorption data, are reported in Table 1.

In general, and for the imidazolium-based ILs, the anion influence on their adsorption capacity onto AC follows the order: Cl⁻ ≈ [CH₃SO]⁻ < [CF₃SO₃]⁻ < [NTf₂]⁻. This trend is in good agreement with the results already reported in the literature [17], and reveals that the adsorption of ILs onto AC is progressively more favourable with the increase on the anion hydrophobicity. On the other hand, taking into consideration the IL cation family, the pyridinium adsorbs more onto AC than the imidazolium-based counterpart. This pattern is also related to the higher hydrophobic character of the pyridinium cation that although being aromatic consists on a 6-sided ring whereas the imidazolium cation is a 5-sided aromatic ring [31].

In Fig. 3 it is shown the ratio between the *K*_d obtained in mixtures with salt to that with no salt. This ratio quantifies thus the relative influence of the salt, and salt concentration, on the adsorption of the different ILs onto AC.

It is remarkable that, in general, the presence of the inorganic and salting-out salt in aqueous solution enhances the adsorption of the different ILs onto AC. In addition, the salt influence

is much more noticeable in the systems including ILs with a more hydrophilic nature, and following the trend: $[C_4C_{1im}]Cl > [C_4C_{1im}][CH_3SO_3] > [C_4C_{1im}][CF_3SO_3] > [C_4C_{1im}][NTf_2] > [C_4C_{1py}][NTf_2]$. With the $[C_4C_{1im}]Cl$ and $[C_4C_{1im}][CH_3SO_3]$ ILs, the K_d value increases up to 5.5 times by the salt addition. Furthermore, it was also found that increasing the salt concentration leads to an increase on the adsorption of hydrophilic ILs (such as $[C_4C_{1im}]Cl$ and $[C_4C_{1im}][CH_3SO_3]$). The salting-out phenomenon, particularly for the more hydrophilic ILs, leads to a decrease on the solubility of the ILs in water and therefore favours the partition to, and enhance their adsorption onto AC [33]. Although mainly an entropic effect, the formation of salt-ion-hydration complexes leads to the dehydration of the IL solute and to an increase on the surface tension of the cavity that is responsible for the observed salting-out phenomenon of the salt over the IL [33,36]. Nevertheless, at low salt concentrations, the opposite behaviour is sometimes observed, and the adsorption of some ILs decrease in presence of the salt. This salting-in effect was previously observed before for other ILs, and is common with proteins or other charged molecules, at low salt concentrations [33]. In contrast, the presence of salt does not improve significantly the adsorption of the most hydrophobic ILs ($[NTf_2]$ -based ILs) onto AC. As reported before [19], the available pore volume of the AC-MkU adsorbent at maximum capacity should be almost nearly filled by these hydrophobic ILs. For this reason, the presence of salt does not improve the adsorption of the $[NTf_2]$ -based ILs onto this specific AC since its saturation was already reached.

To complete the current analysis and to better interpret the gathered experimental data, the COSMO-RS was used to estimate the partition coefficient (P) of the different ILs, at infinite dilution, and between AC and the diverse aqueous phases at increasing concentrations of Na_2SO_4 . The $\log(P)$ has been already reported as a reference quantitative parameter of the affinity of each IL for AC when in aqueous solutions [31]. Fig. 4 (A) depicts the $\log(P)$ values for the five studied ILs obtained by COSMO-RS while specifying in all the calculations the increasing salt concentration used in the experiments. For comparison purposes, Fig. 4 (A) also includes the experimental K_d values obtained for each IL in the absence of salt. In Fig. 4 (B) it is depicted the ratio between the P value in the presence and in absence of salt obtained by COSMO-RS.

COSMO-RS correctly predicts the influence of the IL chemical structure onto their AC adsorption capacity since $\log(P)$ values increase with the increase on the K_d values and with the hydrophobicity of the IL solute. In addition, COSMO-RS estimations reasonably reproduce the influence of the Na_2SO_4 salt on the ILs adsorption onto AC. Higher values of $\log(P)$ are obtained when increasing the salt concentration in aqueous media. However, as expectable, the COSMO-RS approach is not able to correctly describe the effects of lower salt concentrations on hydrophobic ILs ($[NTf_2]$ -based), since aspects as the available pore volume of exhausted AC adsorbent cannot be included in its respective calculations.

In summary, it is here demonstrated, for the first time, that AC can be also used as an effective adsorbent for hydrophilic ILs present at low concentrations in aqueous media if inorganic salts are concomitantly used to promote a salting-out phenomenon and enhance the partition towards the AC.

4. Conclusions

In the past years, ILs have been proposed as potential substituents for volatile organic compounds (VOCs) mainly due to their negligible vapour pressures avoiding thus the atmospheric pollution. However, they display some or even complete miscibility with water and can be dispersed by aqueous streams leading to serious environmental concerns. In this context, it is of crucial relevance to develop novel methods capable of removing ILs from wastewater streams. The adsorption onto AC proved to be a potential non-destructive method to remove low concentrations of ILs from aqueous solutions. However, this method is not so effective for hydrophilic ILs. Therefore, in this work, the addition of a salting-out inorganic salt (Na_2SO_4) is used to improve the adsorption of different ILs onto AC. The results obtained show that the K_d values of hydrophilic ILs, such as $[\text{C}_4\text{C}_1\text{im}]\text{Cl}$ and $[\text{C}_4\text{C}_1\text{im}][\text{CH}_3\text{SO}_3]$, increase up to 5.5 times in the presence of the salt. This new approach can be envisaged as a promising route for reducing the pollution of aqueous streams resulting from industrial processes where ILs are employed.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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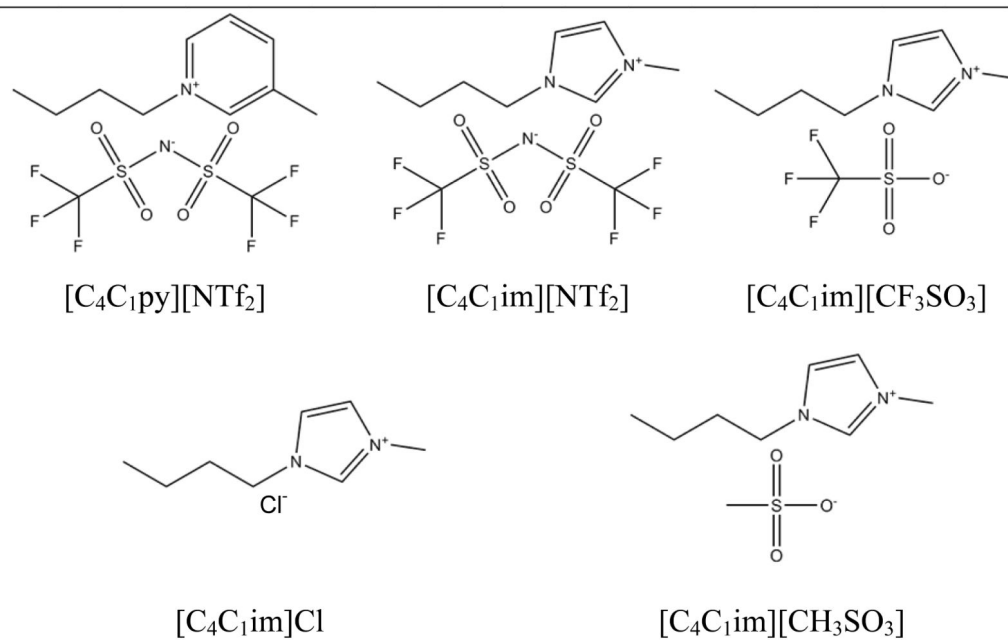


Fig. 1.
Chemical structure of the ILs studied.

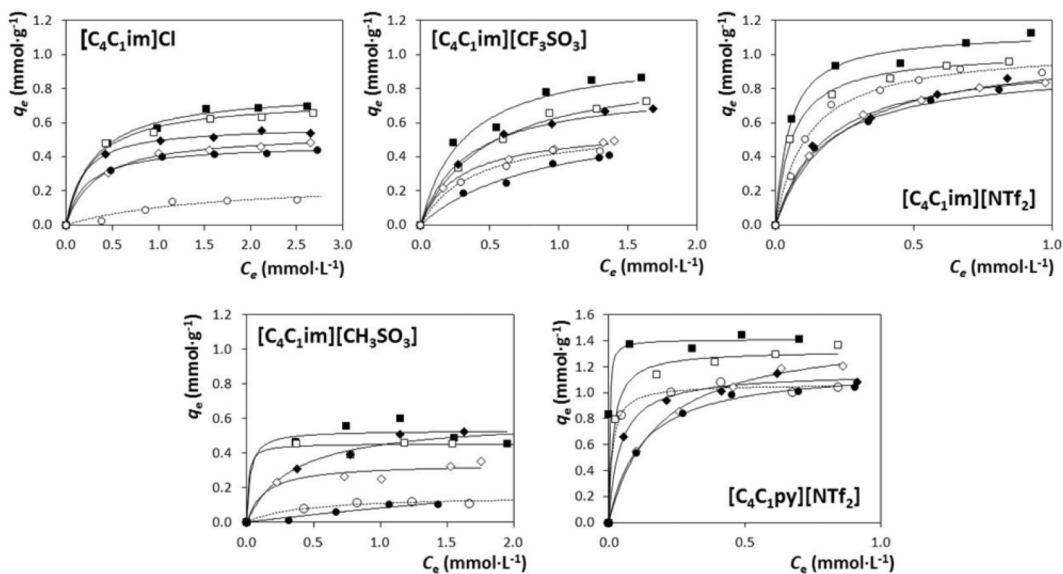


Fig. 2.

Experimental data (symbols) and Langmuir fitting (Eq. (1)) (lines) for the adsorption equilibrium of the ILs onto AC-MkU at 308 K, at several salt concentrations: (○), no salt; (●), $[\text{Na}_2\text{SO}_4] = 0.28 \text{ mol}\cdot\text{kg}^{-1}$; (◇), $[\text{Na}_2\text{SO}_4] = 0.70 \text{ mol}\cdot\text{kg}^{-1}$; (◆), $[\text{Na}_2\text{SO}_4] = 1.06 \text{ mol}\cdot\text{kg}^{-1}$; (□), $[\text{Na}_2\text{SO}_4] = 1.41 \text{ mol}\cdot\text{kg}^{-1}$; (■), $[\text{Na}_2\text{SO}_4] = 1.76 \text{ mol}\cdot\text{kg}^{-1}$.

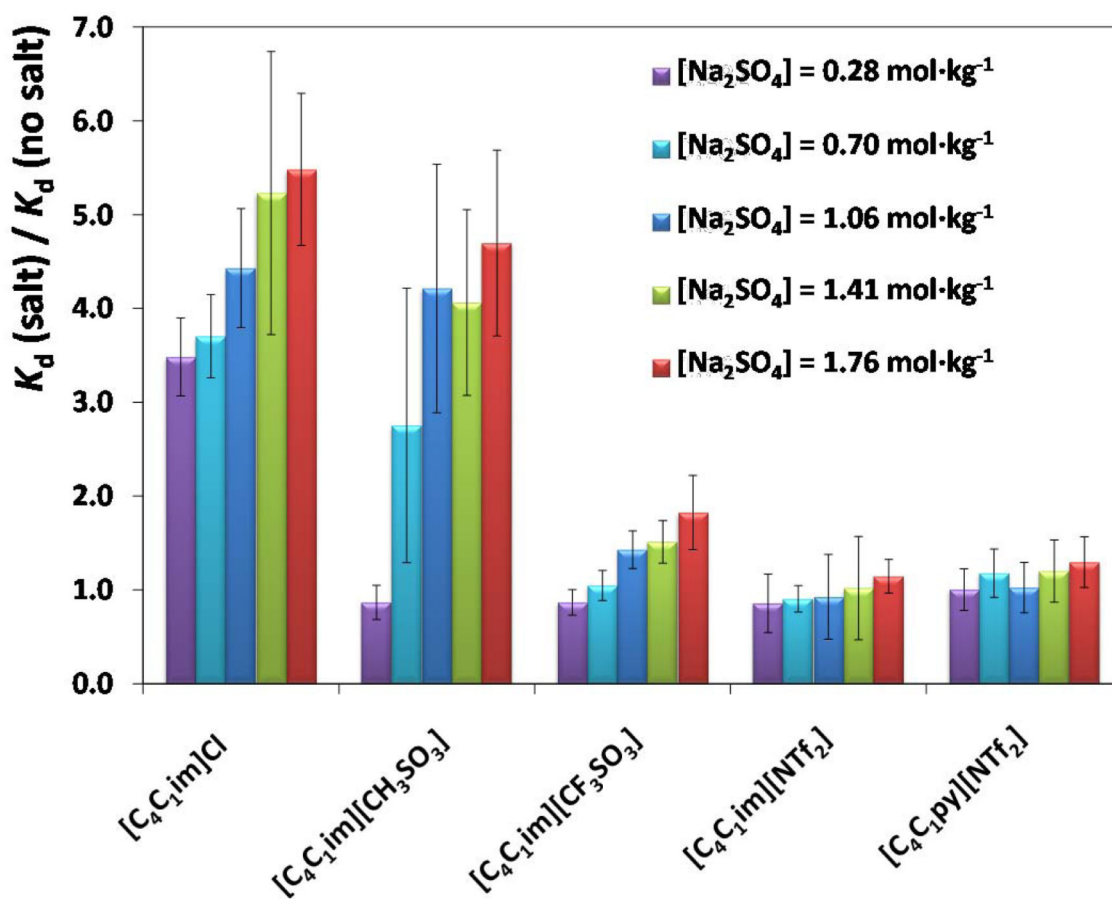


Fig. 3. Ratio between the K_d values in the presence of salt to that with no salt at different concentrations and for the several ILs investigated.

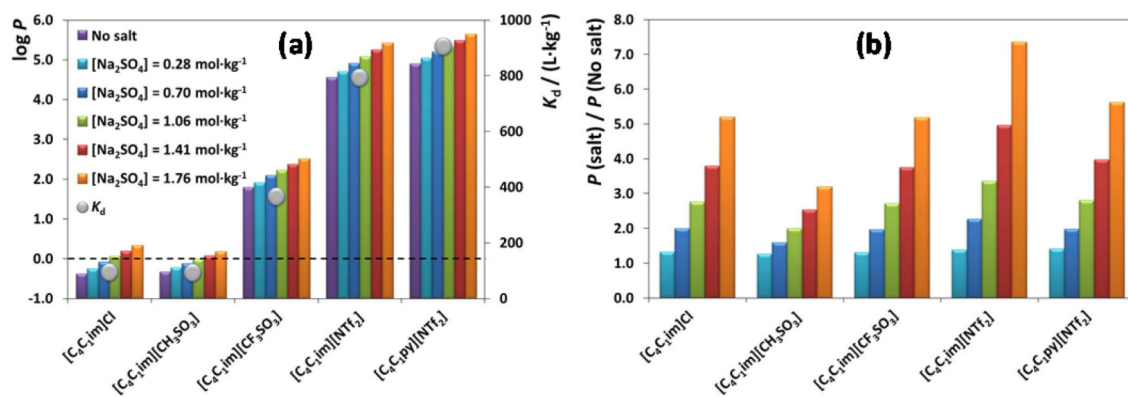


Fig. 4. (a) $\log(P)$ predicted by COSMO-RS for the ILs studied with different salt concentrations using the AC molecular model and experimental K_d values for these ILs on AC-MkU without salt; (b) effect of the salt concentration on the P ratio predicted by COSMO-RS.

Table 1

Empirical coefficients obtained from the Langmuir model fitting and K_d coefficients estimated at $C_e = 1.2$ mmol·L⁻¹ for the different ILs studied.

IL	[Na ₂ SO ₄] (mol·kg ⁻¹)	q_{\max} (mmol·g ⁻¹)	B (L·mmol ⁻¹)	R^2	K_d (L·kg ⁻¹)
C ₄ C ₁ im Cl	No salt	0.26	0.64	0.900	95
	0.28	0.47	4.52	0.999	332
	0.70	0.54	3.02	0.997	353
	1.06	0.58	5.76	0.997	422
	1.41	0.74	3.54	0.961	498
	1.76	0.78	3.31	0.993	522
C ₄ C ₁ im CH ₃ SO ₃	No salt	0.13	3.94	0.973	92
	0.28	0.72	0.13	0.924	80
	0.70	0.34	7.54	0.939	254
	1.06	0.60	2.94	0.969	388
	1.41	0.45	78.04	0.977	374
	1.76	0.53	39.79	0.899	433
C ₄ C ₁ im CF ₃ SO ₃	No salt	0.58	2.56	0.990	367
	0.28	0.67	1.12	0.988	318
	0.70	0.57	3.52	0.997	385
	1.06	0.81	2.96	0.999	525
	1.41	0.93	2.10	0.995	556
	1.76	1.02	3.17	0.978	670
C ₄ C ₁ im NTf ₂	No salt	1.04	8.71	0.992	794
	0.28	0.93	5.91	0.981	680
	0.70	0.99	5.73	0.999	719
	1.06	1.04	4.57	0.933	734
	1.41	1.02	16.99	0.964	809
	1.76	1.13	20.86	0.988	908
C ₄ C ₁ py NTf ₂	No salt	1.10	75.71	0.995	906
	0.28	1.20	8.41	0.997	909
	0.70	1.47	5.69	0.997	1068
	1.06	1.15	23.72	0.991	929
	1.41	1.32	61.70	0.989	1088
	1.76	1.41	406.48	0.458	1173