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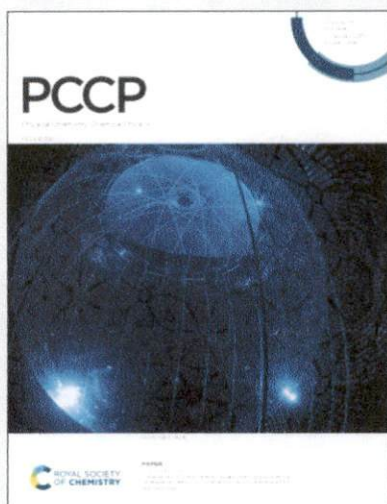
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ARTICLE

Understanding the adsorption of ionic liquids onto Zeolite ZSM-5 from aqueous solution: Experimental and Computational Modelling

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Ionic liquids are considered as emergent pollutants as these compounds possess high persistence in aqueous solution and toxicity toward aquatic organism. In this work, the adsorption equilibrium of 27 ionic liquids, with different cation head group, alkyl chain length, and anion, onto ZSM-5 were measured experimentally at several composition and at temperature 298.15 K and 0.1 MPa. The extensive number of the studied ionic liquids allows a comprehensive study on the impact of adsorbate chemical structures toward their adsorption process. The gathered experimental results show that anion have a dominant effect, when compared to the cation head group and the alkyl chain length, in ruling the adsorption of ionic liquids from aqueous solution onto ZSM-5. The adsorption isotherms reveal that the adsorption process is a combination between Langmuir and Freundlich behaviors, with the later leading the general process. Moreover, computational modelling using COSMO-RS demonstrate the existence of several molecular forces that rule the adsorption process, reinforcing the idea that the ionic liquids anion rules the adsorption. The results collected in the present work provide new understanding on the molecular mechanism for development of efficient adsorbent for removal and recovery of ionic liquids from aqueous solution.

Introduction

Ionic liquids are an innovative class of compound that have received huge interest from both academic and industrial field. Their exceptional chemical and physical properties, such as wide liquidus range, high chemical and thermal stability, and negligible vapor pressure at room temperature, making these fluids attractive as an alternative to the hazardous volatile organic solvents currently used in the industry.¹ In the first decade of ionic liquids evolution, circa 2000-2010, these room temperature molten salts have found themselves various applications, especially as solvent for removal of Pb(II),^{2,3} Cr (III IV),⁴ Zn(II),^{5,6} Cd(II),⁵ Fe(III),^{5,6} Cu(II),⁷⁻¹¹ Ni(II),⁷ Co(II),^{3,7} Ce(IV),^{12,13} Eu(III),¹⁴⁻¹⁶ Am(III),¹⁵ Au(III),^{17,18} and iron and boron,¹⁹ platinum,^{20,21} actinide,²² lanthanide,²³ anionic azo dyes,^{24,25} 2-phenylethanol,²⁶ alcohol^{27,28} and other organic compounds,²⁹⁻³⁸

from aqueous solution. In general, most of these authors reported the successful elimination of the target compound from aqueous solution, without proper assessment of the fate of ionic liquids used in the process. They assumed that ionic liquids were sufficiently hydrophobic, therefore their solubility in aqueous solution were neglected. However, and unfortunately, it was later shown that even the most hydrophobic ionic liquids present a small solubility in aqueous solutions that should not be ignored.³⁹ This condition is worsened with the fact that many ionic liquids possess high stability and substantial toxicity,⁴⁰ thus when the fluids accumulate in aqueous media, they could harm aquatic organisms.^{41,42} Consequently, proper treatment of wastewaters containing ionic liquids before entering natural water streams, must be strictly imposed.

Several methods are proposed for the removal of ionic liquids from aqueous solution. To this end, these methods can be divided into destructive and non-destructive approaches.⁴³ In the first approach, ionic liquids are removed by altering its original structure, mostly through degradation reaction, using electrolysis,⁴⁴ sono- and photoelectrocatalytic process,⁴⁵ ultrasonic irradiation,⁴⁶ and the popular advance oxidation processes (AOPs).⁴⁷⁻⁵³ However, it should be highlighted that due to its destructive style, these methods do not allow the recovery of these expensive compounds. The non-destructive method is then preferred as it allows the recovery and reuse of these ionic liquids for further use. Among numerous non-

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[†]Electronic Supplementary Information (ESI) available: List of ionic liquids, experimental adsorption equilibrium, The obtained Langmuir and Redlich-Peterson parameters, predicted activity coefficient, predicted excess enthalpy. See DOI: 10.1039/x0xx00000x

destructive methods,⁵⁴ adsorption has been widely investigated due to its convenient operation, non-toxic, and most important, permitting the recovery and reuse of ionic liquids. Current studies on the adsorption of ionic liquids is mainly focused on the use of carbonaceous materials,⁵⁵⁻⁶² with little attention being given to other adsorbents, such as bentonite,⁶³ bacterial biosorbent,⁶⁴ three dimensional crumpled graphene oxide/cellulose nanocrystals (GO/CNCs) composite,⁶⁵ and zeolites.⁶⁶ These researchers seek to understand the interaction between ionic liquids and adsorbent, as it could lead to a better control of their fate in aqueous solution.⁵⁸⁻⁶¹ For example, Palomar and co-workers demonstrated that the van der Waals forces dominate the interaction between ionic liquids and activated carbon, and consequently, this particular adsorbent is more useful for the removal and recovery hydrophobic ionic liquids than hydrophilic ones.⁵⁹ This example clearly shows that a better knowledge of the molecular interactions between ionic liquids and adsorbent, is crucial for the selection of adsorbent material for the removal and recovery of these fluids from aqueous solution.

Very recently, Zhang and co-workers showed that Zeolite Socony Mobil-5 (ZSM-5) have superior removal efficiency compare to silica-based and carbon-based adsorbent due to its regularly shaped inner channel and homogenous pore size distribution, which can control the accessibility of the internal space for a given adsorbate.⁶⁶ In addition, ZSM-5 can be regenerated and reused for ten consecutive adsorption-desorption cycles, while the adsorbed ionic liquid can be recovered by thermal treatment at temperature circa 773 K.⁶⁶ It is, however, their study was limited to few number of ionic liquids and most importantly, the fundamental knowledge on the ionic liquid – ZSM-5 is yet to be studied.⁶⁶ Gaining an understanding of the molecular interactions driving the adsorption of ionic liquids onto ZSM-5 is fundamental to produce improved adsorbents for wastewater treatment. However, adequate description of the molecular mechanism driving the adsorption of ionic liquids onto ZSM-5 from aqueous solution is still absent.

In the present work, aiming at understanding the molecular mechanism that controls the adsorption of ionic liquids onto ZSM-5 from aqueous solution, the adsorption equilibrium for an extensive number of ionic liquids in aqueous solution onto ZSM-5 were measured at various concentration ranges and at ambient temperature (298.15 K) and pressure (0.1 MPa). The selected ionic liquids consist of 6 different common studied cation families, namely imidazolium, pyridinium, piperidinium, pyrrolidinium, ammonium, and phosphonium that combine with 14 diverse anions. The obtained results are discussed throughout by considering the impact of cation head group, alkyl chain length, and anion toward the adsorption of ionic liquids onto ZSM-5 from aqueous solution. The influence of anion was assessed by examining several anions paired with [C_nC₁im]-cation. Whereas, the dependence of alkyl chain length was investigated by fixing the cation head group and anion, [C_nC₁im]Cl, where n = number of alkyl chain length. Similarly, the impact of cation head group was evaluated by fixing alkyl chain length and anion, [C4C1X]Cl, where X = imidazolium,

pyridinium, piperidinium, or pyrrolidinium. Several adsorption isotherm models were used to get insight on the adsorption process. In addition, the experimental measurement is also accompanied with Conductor-like Screening Model for Real Solvent (COSMO-RS), a quantum-based thermodynamic model to forecast the molecular interaction occur between ionic liquids and ZSM-5 in aqueous solution. The obtained experimental and computational data allows us to investigate the driving forces on ionic liquids toward their adsorption onto ZSM-5 from aqueous solution and ultimately, to screen and select the best adsorbent for removal of ionic liquids from aqueous solution.

METHODOLOGY

Chemicals

A commercial ZSM-5 (CAS Number 1318-02-1) supplied by Alfa Aesar was used as adsorbents. Table S1 in the ESI[†] provides a list of wide variety of ionic liquids used in this study along with their general information. Both ZSM-5 and ionic liquids were used as received from the supplier without any further purification. Double distilled water was used throughout the experimental measurement.

Experimental Measurement

The adsorption of ionic liquids onto ZSM-5 were determined in 100 mL glass vials equipped with polytetrafluoroethylene lined screw caps at 298.15 K, using 50 mL of an ionic liquid solution with concentrations ranging from 100 to 2000 mg·L⁻¹. Then, circa 1 gram of ZSM-5 was added into the ionic liquid solution, sealed tightly, and the vials were placed in a thermostated shaker bath with constant speed of 200 rpm for 48 hours to ensure that adsorption equilibrium were achieved, when there was no significant uptake of ionic liquids onto ZSM-5. After that time, aqueous solutions were taken carefully using syringe. The concentration of imidazolium- and pyridinium-based ionic liquids were determined using Biochrom Libra S60 Double Beam Spectrophotometer at wavelength of 212 and 266 nm, respectively. While the concentration of piperidinium-, pyrrolidinium-, ammonium- and phosphonium-based ionic liquids were determined using Starter 3100M pH & Conductivity Bench, Ohaus. The measurement was repeated three times and the average value was reported.

Computational Modelling

COSMO-RS is unimolecular quantum-based thermodynamic model developed by Klamt and co-worker.^{67,68} The advantage of using COSMO-RS is the most only required chemical structure of the studied compounds. COSMO-RS is not only able to predict the thermophysical properties of compounds, but also can be used to understand the molecular interaction occur in the given system.^{69,70} The computational modelling consists of two major steps. In the first steps, the continuum solvation COSMO calculation of electronic density and molecular geometry of ionic liquids cation, anion, water, and ZSM-5 were optimized using TURBOMOLE V7.3 2018 software program package on the

density functional theory level, utilizing the BP functional B88-P86 with a triple- ζ valence polarized basis set (TZVP) and the resolution of identity standard (RI) approximation.⁷¹ Once the COSMO file is produced, it can be stored in the database and ready to be used for the next step. Figure 1 shows the optimized structure of ZSM-5 used in this work that consists of two 10-member rings with chemical formula of $\text{Si}_{20}\text{O}_{40}\text{H}_{20}$ and molecular formula $1381.4 \text{ g}\cdot\text{mol}^{-1}$.

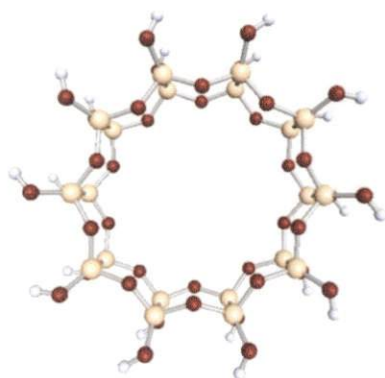


Figure 1. The optimized structure of ZSM-5 used in this work

In the second step, the thermophysical properties, namely activity coefficient of ionic liquids at infinite dilution in water and in ZSM-5, and excess enthalpies were determined by means of COSMOtherm software using parameter BP_TZVP_C30_1701 (COSMOlogic, Levekusen, Germany).⁶⁸ Otherwise stated, the ionic liquids are always treated as a one to one cation/anion mixture, and the ions are treated at the quantum chemical level separately, and therefore, it is possible to analyse the contribution of cation and anion to the predicted properties. The detail of the COSMO-RS calculation on estimating the chemical potential is given in the COSMOtherm User's Manual.⁶⁸ In brief, the activity coefficient of component i is related to its chemical potential μ_i through the following equation,

$$Y_i = \exp\left(\frac{\mu_i - \mu_i^0}{RT}\right) \quad (1)$$

where μ_i^0 is the chemical potential of the pure compound i , R is the ideal gas constant, and T is the absolute temperature.

The most important output from COSMO-RS model is the interaction energies in pure ionic liquids, water, and ZSM-5. Thus, the COSMO-RS model allows both chemical structure and interactions to be probed on a molecular level providing vital information on the impact of structural changes upon adsorption process. In the molecular approach, COSMO-RS

model focuses on three specific interactions, namely the electrostatic – misfit energy, H_{MF} , hydrogen-bonding energy, H_{HB} , and van der Waals energy, H_{vdW} . These energies are described in Equations 3-5, respectively:

$$H_{MF} = a_{\text{eff}} \frac{\alpha}{2} (\sigma + \sigma')^2 \quad (2)$$

$$H_{HB} = a_{\text{eff}} c_{\text{HB}} (0; \min(0; \sigma_{\text{donor}} + \sigma_{\text{HB}}) \times \max(0; \sigma_{\text{acceptor}} - \sigma_{\text{H}}) \quad (3)$$

$$H_{vdW} = a_{\text{eff}} (\tau_{vdW} + \tau'_{vdW}) \quad (4)$$

where a_{eff} is the effective contact area between two surface segments, α is the interaction parameter, σ_{HB} is the hydrogen bond strength that the threshold for hydrogen bonding, and the last two τ_{vdW} and τ'_{vdW} are elements of specific van der Waals interaction parameters.

In addition, interaction energies between ionic liquids – water and ionic liquids – ZSM-5 were also estimated by COSMO-RS using the excess enthalpies as the difference in the enthalpy of the studied cation, anion, or water molecules in its mixture and pure state, according to the following equation:

$$H_{E,i}(\text{interaction}) = H_{\text{mixture}}(\text{interaction}) - H_{\text{pure}}(\text{interaction}) \quad (5)$$

The $H_{E,i}(\text{interaction})$ in the COSMO-RS model originates from summing the three specific interactions as described in Equations 3-5. Thus, it can be expressed as,

$$H_{E,m} = H_{E,MF} + H_{E,HB} + H_{E,vdW} \quad (6)$$

Therefore, the COSMO-RS model could provide the information required for the evaluation of molecular interactions of ionic liquids in the pure state, as well as in the aqueous solution, as contribution of cation, anion, and water molecules.

Adsorption Isotherm

Several adsorption isotherm models, namely Langmuir, Freundlich, and Redlich-Peterson were used to describe the adsorption behaviour of ionic liquids onto ZSM-5 from an aqueous solution that expressed in Equations 7-9, respectively.

$$Q_e = \frac{Q_m K_L C_e}{1 + K_L C_e} \quad (7)$$

$$Q_e = K_F C_e^{1/n_F} \quad (8)$$

$$Q_e = \frac{K_{RP} C_e}{1 + \alpha C_e^{\beta}} \quad (9)$$

where C_e is concentration of ionic liquids at equilibrium ($\text{mmol}\cdot\text{L}^{-1}$), Q_e is equilibrium adsorption capacity ($\text{mmol}\cdot\text{g}^{-1}$), K_L is Langmuir adsorption constant ($\text{L}\cdot\text{g}^{-1}$), K_F is Freundlich constant ($\text{L}\cdot\text{g}^{-1}$), n_F is heterogeneity factor of adsorption sites (dimensionless), K_{RP} is a Redlich-Peterson constant ($\text{L}\cdot\text{g}^{-1}$), α is

constant ($\text{mg}\cdot\text{L}^{-1}$) ^{β} , and β is Redlich-Peterson exponent (dimensionless).

The evaluation of best fit is calculated using average absolute relative deviation, as expressed in Equation 10,

$$AARD = \sum_{i=1}^N \frac{|Q_{e,pred} - Q_{e,exp}|}{N} \quad (10)$$

Results and Discussions

The experimental adsorption equilibrium between ionic liquids on ZSM-5 in aqueous solution at temperature 298.15 is given in Table S2 in the ESI.[†] The effectiveness of adsorbent in removing the adsorbate from aqueous solution can be evaluated using distribution coefficient and %removal. The distribution coefficient, K_D , is an important parameter for estimating the affinity of ZSM-5 for ionic liquids in aqueous solution. The K_D values were calculated using Equation 11,

$$K_D = \frac{Q_e}{C_e} \times 10^3 \quad (11)$$

where Q_e is the amount of ionic liquids adsorbed on ZSM-5 at equilibrium and C_e is concentration of ionic liquids in aqueous solution at equilibrium. The K_D values for all studied ionic liquids on ZSM-5 in aqueous solution is given in Table S2 in the ESI.[†] It can be seen that with an increase in initial concentration, as expected, the values of K_D decreased for all studied ionic liquids.

The percentage removal of ionic liquids from aqueous solution at different initial concentration using ZSM-5 was calculated using the following equation:

$$\% \text{removal} = \frac{C_0 - C_e}{C_0} \times 100 \quad (12)$$

The calculated percentage removal is also given in Table S2 in the ESI.[†] The results show that ZSM-5 could remove the ionic liquids from aqueous solution, in general, close to 90%. The gathered results also reveal that the decrease in initial concentration lead to increase in the %removal. Based on the result described, ZSM-5, indeed, could be used as potential adsorbent to remove ionic liquids from aqueous solution. Thus, in the next section, the impact of the ionic liquids structure on their adsorption onto ZSM-5 from aqueous solution is described in detail.

Effect of Ionic Liquids Structure

The large number of experimental data obtained allows a systematic assessment on the impact of ionic liquids structural features, such as cation head group, alkyl chain length, and anion, towards their adsorption on ZSM-5 from aqueous solution. Figure 2 shows the adsorption isotherm of six ionic liquids with different head groups and common anion, Cl⁻. The cation head group seem to have a small influence on the

adsorption of ionic liquids onto ZSM-5. Nevertheless, remarkable effect of the cation head group is observed when comparing phosphonium-based and ammonium-based ionic liquids. The results reveal that the phosphonium-based structure, with four alkyl chains, leads to higher adsorption capacity than those observed for other cation head groups, followed by remaining nitrogen-based ionic liquids, following the order $[\text{P}_{4444}]\text{Cl} > [\text{N}_{4444}]\text{Cl} > [\text{C}_4\text{C}_{1\text{im}}]\text{Cl} > o\text{-}[\text{C}_4\text{C}_{1\text{py}}]\text{Cl} > [\text{C}_4\text{C}_{1\text{pyrr}}]\text{Cl} \approx [\text{C}_4\text{C}_{1\text{pip}}]\text{Cl}$. The higher adsorption equilibrium capacity of the first two aliphatic-based cation could be addressed due to their higher molar volume compare to remaining cyclic-based ionic liquids that translate to higher van der Waals forces between adsorbate and adsorbent.⁵⁹ Among the cyclic nitrogen-based ionic liquids, aromatic-cation (imidazolium and pyridinium) presents higher adsorption capacity compared to the non-aromatic cation (pyrrolidinium and piperidinium). Thus, it can be projected that the presence of π molecular orbitals is more relevant than the size in defining adsorption capacity of these ionic liquids onto ZSM-5.

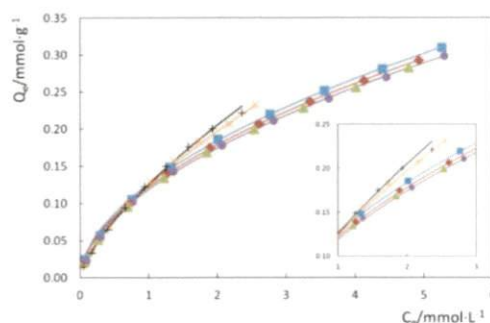


Figure 2. Adsorption isotherm of ionic liquids with different head group on ZSM-5 at 298.15 K. Symbols and lines represent experimental and Freundlich fits, respectively. (●), $[\text{C}_4\text{C}_{1\text{im}}]\text{Cl}$; (▲), $o\text{-}[\text{C}_4\text{C}_{1\text{py}}]\text{Cl}$; (▲), $[\text{C}_4\text{C}_{1\text{pip}}]\text{Cl}$; (◆), $[\text{C}_4\text{C}_{1\text{pyrr}}]\text{Cl}$; (×), $[\text{N}_{4444}]\text{Cl}$ and (○), $[\text{P}_{4444}]\text{Cl}$.

The impact of ionic liquid alkyl chain length on their adsorption onto ZSM-5 is depicted in Figure 3. It is shown that the ionic liquids alkyl chain length nature has a slight influence on their adsorption onto ZSM-5 and similar to that presented before with the ionic liquids head group. Nevertheless, it is worth to note that the adsorption capacity increases with increasing cation alkyl chain length. This trend is also observed for the adsorption of ionic liquids with different alkyl chain length on silica⁶⁶ and activated carbon.⁵⁹ Palocz and co-workers⁵⁹ reported that the adsorption capacity for a series of $[\text{Tf}_2\text{P}_6\text{P}_6]$ -based ionic liquids on activated carbon, increased with the cation alkyl chain length. The authors related this behaviour to the molar volume of ionic liquids cation.⁵⁹ It should, however, be highlighted that the effect of the ionic liquids alkyl chain length on the adsorption capacity onto ZSM-5 seems to vary with the aluminium-silica ratio.⁶⁶ The authors described that the electrostatic interactions in this case could be the dominant forces for the adsorption of ionic liquids on high aluminium

content zeolites, while hydrophobic partition would be responsible for the adsorption of long chain ionic liquids onto low aluminium content zeolites.⁶⁶ Thus, since the ZSM-5 used in the present work has a ratio of 13:1 for $\text{SiO}_2:\text{Al}_2\text{O}_3$, making it a low aluminium content, it is believed that the adsorption of ionic liquids with different alkyl chain could be attributed to the subtle balance between hydrophobicity and molar volume of ionic liquids cation. This molecular mechanism is further supported by the COSMO-RS results discussed below.

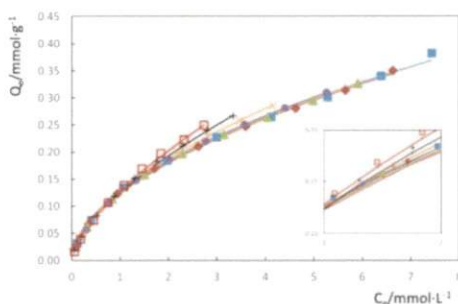


Figure 3. Adsorption isotherm of ionic liquids with different cation alkyl chain length on ZSM-5 at 298.15 K. Symbols and lines represent experimental and Freundlich fits, respectively. (■), $[\text{C}_4\text{C}_{1\text{im}}]\text{Cl}$; (♦), $[\text{C}_6\text{C}_{1\text{im}}]\text{Cl}$; (▲), $[\text{C}_8\text{C}_{1\text{im}}]\text{Cl}$; (●), $[\text{C}_{10}\text{C}_{1\text{im}}]\text{Cl}$; (×), $[\text{C}_{12}\text{C}_{1\text{im}}]\text{Cl}$; (+), $[\text{C}_{14}\text{C}_{1\text{im}}]\text{Cl}$, and (□), $[\text{C}_{16}\text{C}_{1\text{im}}]\text{Cl}$.

In contrast with ionic liquids cation head group and alkyl chain length, the anions have a significant impact on their adsorption onto ZSM-5 in aqueous solution, as depicted in Figures 4 and 5. The adsorption capacity varied dramatically from most basic anion $[\text{C}_4\text{C}_{1\text{im}}][\text{Ac}]$ to mediocre basicity $[\text{C}_4\text{C}_{1\text{im}}][\text{N}(\text{CN})_2]$ (cf. Figure 4). The variation of adsorption capacity indicated that ionic liquids anions have a huge impact on their adsorption onto ZSM-5 in aqueous solution. However, care must be taken as a different rank of ionic liquids is observed on the lower and higher adsorption isotherm region. For example, at lower concentration (cf. insert at Figure 4), it can be determined that the adsorption capacity can be ranked as follow $[\text{C}_4\text{C}_{1\text{im}}][\text{Ac}] < [\text{C}_4\text{C}_{1\text{im}}][\text{DMP}] < [\text{C}_4\text{C}_{1\text{im}}]\text{Cl} < [\text{C}_4\text{C}_{1\text{im}}][\text{CH}_3\text{SO}_3] < [\text{C}_4\text{C}_{1\text{im}}]\text{Br} < [\text{C}_4\text{C}_{1\text{im}}][\text{TFA}] < [\text{C}_4\text{C}_{1\text{im}}][\text{N}(\text{CN})_2]$. This rank follows the extended basicity scale proposed by Cláudio et al.⁷² It indicates that the anion basicity plays an important role on the initial adsorption of ionic liquids on ZSM-5 at lower concentration range. Nevertheless, at higher concentration range, the tendencies are changed, especially for the first four anions with higher basicity. This change may indicate a different molecular mechanism that rules the adsorption isotherm at higher concentration regions.

Similar behaviour is also observed in Figure 5, where the different trends in adsorption capacity at lower and higher concentration range are observed. At low concentration, yet again, the adsorption capacity rank follows the anion basicity,⁷² and the trend is changed when moving to the higher concentration region. A possible explanation for this

phenomenon could be that at low concentration range, the basicity of anion plays important role on the adsorption isotherm of ionic liquids on ZSM-5, whereas at higher concentration there is subtle balance between anion basicity and hydrophobicity, among many other, that translated into different uptakes.

The experimental results gathered in this work clearly demonstrate that several molecular mechanisms govern the adsorption of ionic liquids onto ZSM-5 in aqueous solution, such as π - π interaction, molecular size, hydrophobicity, and anion basicity, with the later having the most significant impact. To get a better understanding on the molecular level, the equilibrium modelling and quantum-chemical based computational modelling using COSMO-RS are discussed below.

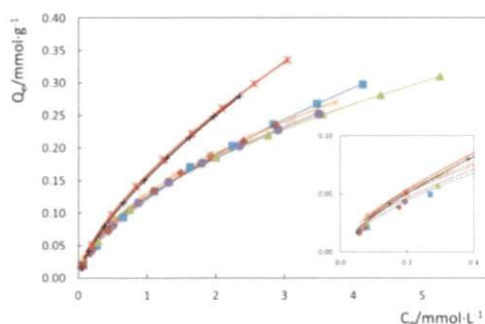


Figure 4. Adsorption isotherm of $[\text{C}_4\text{C}_{1\text{im}}]$ -based ionic liquids with different anion on ZSM-5 at 298.15 K. Symbols and lines represent experimental and Freundlich fits, respectively. (■), $[\text{C}_4\text{C}_{1\text{im}}][\text{Ac}]$; (♦), $[\text{C}_4\text{C}_{1\text{im}}][\text{DMP}]$; (▲), $[\text{C}_4\text{C}_{1\text{im}}]\text{Cl}$; (●), $[\text{C}_4\text{C}_{1\text{im}}][\text{CH}_3\text{SO}_3]$; (×), $[\text{C}_4\text{C}_{1\text{im}}]\text{Br}$; (+), $[\text{C}_4\text{C}_{1\text{im}}][\text{TFA}]$, and (□), $[\text{C}_4\text{C}_{1\text{im}}][\text{N}(\text{CN})_2]$.

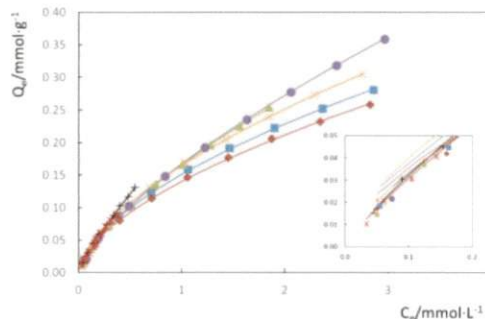


Figure 5. Adsorption isotherm of $[\text{C}_4\text{C}_{1\text{im}}]$ -based ionic liquids with different anion on ZSM-5 at 298.15 K. Symbols and lines represent experimental and Freundlich fits, respectively. (■), $[\text{C}_4\text{C}_{1\text{im}}][\text{HSO}_4]$; (♦), $[\text{C}_4\text{C}_{1\text{im}}][\text{MeSO}_4]$; (▲), $[\text{C}_4\text{C}_{1\text{im}}][\text{CF}_3\text{SO}_3]$; (●), $[\text{C}_4\text{C}_{1\text{im}}][\text{SCN}]$; (×), $[\text{C}_4\text{C}_{1\text{im}}][\text{BF}_4]$; (+), $[\text{C}_4\text{C}_{1\text{im}}][\text{PF}_6]$, and (□), $[\text{C}_4\text{C}_{1\text{im}}][\text{Tf}_2\text{N}]$.

Adsorption Equilibrium Modelling

In order to describe the adsorption isotherm (Figures 2-5), initially Langmuir and Freundlich models were used. The detail calculation is given in Table S2 in the ESI,[†] whereas the obtained parameters, values of correlation coefficients (R^2), average absolute relative deviation (AARD) are summarized in Tables S3 in the ESI.[†] In general, values of R^2 and AARD of the Freundlich

model (cf. Table 1) were found to be better than those of the Langmuir model to describe the adsorption of ionic liquids onto ZSM-5 in aqueous solution. However, the difference in the experimental and calculated values of the ionic liquids adsorbed, particularly at lower equilibrium concentrations, cannot be explained on the basis of the Freundlich model (cf. inserts in Figure 5). The adsorption isotherm model based on Redlich-Peterson equation⁷³ provides a better AARD than either Langmuir or Freundlich models. Redlich-Peterson model combines elements from both Langmuir and Freundlich equations, consequently, the molecular mechanism of adsorption is a mix between these two original models. Thus, the scenario for adsorption of ionic liquids onto ZSM-5 in aqueous solution may be described as follow (i) initially, due to the anion basicity, the attractive interaction of very high affinity at low equilibrium concentration, adsorption of ionic liquids molecules tend to form a homogenous monolayer, obeying the Langmuir model, while (ii) at higher equilibrium concentrations, a subtle balance between anion basicity and hydrophobic nature of the ionic liquids resulted in the surface heterogeneity, and in this region, the adsorption isotherms follow the Freundlich model. The presence of two molecular mechanisms is also observed from the experimental results described hitherto, where both the anion basicity and hydrophobicity play delicate roles on the adsorption of ionic liquids onto ZSM-5. Thus, it can be concluded that the adsorption of ionic liquids onto ZSM-5 consist of two mechanisms, where it obeys Langmuir model at low equilibrium concentrations, and at higher equilibrium concentration it follows the Freundlich model, with the latter having a more dominant influence.

The Freundlich model consists of two parameters, namely K_f and n_f that indicate the adsorption capacity and intensity, respectively. The value of n_f is used to determine the type of adsorption, where if $n_f < 1$, the adsorption is chemisorption; if the value for $n_f = 1$, the adsorption is linear; and for $n_f > 1$, the adsorption is a favourable physical process. The obtained n_f values in this work are higher than 1, indicating the favourable physical adsorption of ionic liquids onto surface of ZSM-5 in aqueous solution. Thus, while the adsorption isotherm validate that the adsorption is spontaneous, the question remain is the type of molecular mechanism that play role in this process.

COSMO-RS

In order to get better understanding on the adsorption behaviour of ionic liquids from aqueous solution onto ZSM-5, a detail analysis based on the COSMO-RS was carried out. In the first approach, the affinity of ionic liquids toward water and ZSM-5, in terms of activity coefficient at infinite dilution (γ_{il}^∞), were predicted using COSMO-RS at 298.15 K. The estimated activity coefficient at infinite dilution of ionic liquids in water and ZSM-5 are given in Table S4 in the Supplementary Material. As can be seen, the γ_{il}^∞ in water, in general, is lower than unity that indicating favourable interaction between the ionic liquids and the water molecules. The exception is observed for $[C_4C_1im][CF_3SO_3]$ ($\gamma_{il}^\infty = 0.57$), $[C_4C_1im][PF_6]$ ($\gamma_{il}^\infty = 1030$), and $[C_4C_1im][TF_2N]$ ($\gamma_{il}^\infty = 21495$), which are known already as

hydrophobic ionic liquids. The estimated γ_{il}^∞ using COSMO-RS demonstrates the capability of the model to predict the behavior of ionic liquids in aqueous solution, in good agreement with the experimental observations. Surprisingly, the γ_{il}^∞ in ZSM-5 is much lower than in water, an indication that all the studied ionic liquids favourably partition to the adsorbent. This behavior might explain the high %removal of ionic liquids from aqueous solution using ZSM-5, as discussed previously.

We attempted to correlate the partition coefficients (Log P) of ionic liquids between water and ZSM-5 phases at infinite dilution and the experimentally obtained apparent adsorption coefficient (K_D) values onto ZSM-5 at 298.15 K. The plot of Log P versus K_D is given in Figure S1 in the ESI.[†] Unfortunately, the plot only produces R^2 circa 0.75 that indicates inadequate correlation between these two parameters. The plot of Log P with other experimental parameters, such as K_f and n_f (from Freundlich model), Q_m and K_L (from Langmuir model), and K_{RP} , α , and β (Redlich-Peterson model) also produce unsatisfying correlations. It should be highlighted that the γ_{il}^∞ values, either in water or ZSM-5, are predicted by taking into account all types of interactions in the systems. Thus, in the second approach, a focus is given to more specific interaction, namely electrostatic misfit, hydrogen bond, and van der Waals forces, between ionic liquid – water and ionic liquid – ZSM-5.

In the second approach, COSMO-RS was then used to predict the interaction energy, in term of excess energy, between ionic liquids – water ($H_{E,IL-H_2O}$) and ionic liquids – ZSM-5 ($H_{E,IL-ZSM-5}$) and the values are given in Tables S5 and S6 in the ESI.[†] The hydrogen bonding between anion and water, as expected, plays a dominant role in the interaction between ionic liquids and water.⁷⁰ In regard toward ionic liquids and ZSM-5, all the species, namely ionic liquids cation, anion, and ZSM-5, in general, have negative values, with the hydrogen bond between anion and ZSM-5 contributing significantly to the exothermicity of the mixture. The electrostatic between cation – ZSM-5 and anion – ZSM-5 are also found to be negative, indicating that both counterion of ionic liquids have high attraction towards the adsorbent. The only positive value is observed from hydrogen bonding contribution of cation. This can be addressed due to rupture of hydrogen bonding between ionic liquids cation and anion, with the latter forming stronger hydrogen bonds with ZSM-5. Interestingly, the plot of $H_{E,IL-ZSM-5}$ against K_f , a Freundlich constant, produces a satisfying correlation coefficient, 0.9541, as depicted in Figure 6. Accordingly, two major conclusions can be drawn as follow (i) the hydrogen bonding between anion and ZSM-5 plays a dominant role toward the adsorption of ionic liquids onto adsorbent from aqueous solution. This explain the significant influence of anion on the adsorption of ionic liquids onto ZSM-5 when compare to cation head group and alkyl chain length; and (ii) the adsorption of ionic liquids onto ZSM-5 follows the Freundlich assumption, as previously described above. The obtained result from computational modelling undeniably support the gathered experimental data

Table 1 The obtained adsorption constant, K_f , and adsorption capacity, n_s , using Freundlich model

No	Ionic liquids	K_f	n_s	R^2	AARD
1	[C ₆ C ₁ im][Ac]	0.1220	1.5867	0.9784	0.0021
2	[C ₆ C ₁ im]Cl	0.1264	1.8522	0.9626	0.0025
3	[C ₆ C ₁ im][DMP]	0.1243	1.6592	0.9740	0.0027
4	[C ₆ C ₁ im]Br	0.1308	1.8126	0.9656	0.0031
5	[C ₆ C ₁ im][CF ₃ SO ₃]	0.1656	1.4410	0.9870	0.0013
6	[C ₆ C ₁ im][N(CN) ₂]	0.1586	1.4854	0.9841	0.0011
7	[C ₆ C ₁ im][SCN]	0.1674	1.4257	0.9872	0.0011
8	[C ₆ C ₁ im][HSO ₄]	0.1515	1.6931	0.9727	0.0025
9	[C ₆ C ₁ im][MeSO ₃]	0.1401	1.6834	0.9725	0.0023
10	[C ₆ C ₁ im][CH ₃ SO ₃]	0.1256	1.7849	0.9664	0.0026
11	[C ₆ C ₁ im][TFA]	0.1548	1.4445	0.9857	0.0006
12	[C ₆ C ₁ im][PF ₆]	0.2158	1.2115	0.9973	0.0013
13	[C ₆ C ₁ im][BF ₄]	0.1644	1.6353	0.9770	0.0024
14	[C ₆ C ₁ im][Tf ₂ N]	0.2070	1.2107	0.9973	0.0013
15	[C ₂ C ₁ im]Cl	0.1270	1.8798	0.9629	0.0046
16	[C ₂ C ₁ im]Cl	0.1233	1.8420	0.9645	0.0035
17	[C ₂ C ₁ im]Cl	0.1249	1.8462	0.9639	0.0025
18	[C ₂ C ₁ im]Cl	0.1257	1.7272	0.9705	0.0028
19	[C ₂ C ₁ im]Cl	0.1247	1.5767	0.9781	0.0021
20	[C ₁₀ C ₁ im]Cl	0.1284	1.5184	0.9818	0.0028
21	[C ₆ C ₁ pip]Cl	0.1188	1.8067	0.9661	0.0023
22	o-[C ₆ C ₁ py]Cl	0.1219	1.8242	0.9651	0.0024
23	p-[C ₆ C ₁ py]Cl	0.1239	1.8239	0.9652	0.0025
24	[C ₆ C ₁ pyrr]Cl	0.1187	1.8084	0.9660	0.0021
25	[Ch]Cl	0.1340	1.9454	0.9583	0.0041
26	[N ₄₄₄₄]Cl	0.1237	1.4963	0.9829	0.0030
27	[P ₄₄₄₄]Cl	0.1258	1.4192	0.9866	0.0025

Other ⁷¹ finding can also be observed, for example, favourable van der Waals interaction between ionic liquids and ZSM-5, $H_{E,IL-ZSM-5}$, supported the postulation that higher adsorption capacity of [P₄₄₄₄]Cl and [N₄₄₄₄]Cl when compared to

other ionic liquids presented in Figure 2. Inspection at Table S6 in the ESI[†] reveal that the contribution of $H_{E,IL-ZSM-5}$ for [P₄₄₄₄]Cl and [N₄₄₄₄]Cl are -8.17 and -8.09 kJ mol⁻¹, respectively. While these values are higher than other cation head group, yet again, the hydrogen bond interaction between anion and ZSM-5 are significantly higher, circa -41.2 kJ mol⁻¹. Thus, anions have the dominant role, while van der Waals play marginal role toward adsorption of ionic liquids onto ZSM-5 from aqueous solution. The subtle balance between hydrogen bond interaction and van der Waals forces also responsible for enhancing the adsorption capacity with increasing alkyl chain length (cf. Figure 3). Thus, COSMO-RS model is capable to provide a thoughtful understanding on the molecular mechanism that rule the adsorption of ionic liquids onto ZSM-5 from aqueous solution.

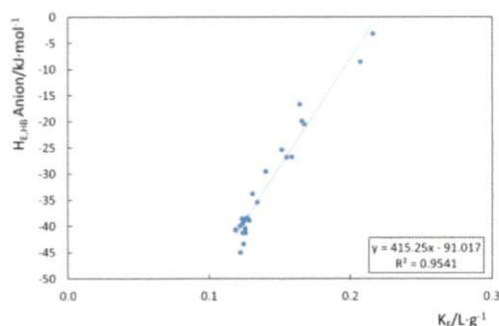


Figure 6 Plot of experimentally calculated Freundlich constant, K_f , for the adsorption of ionic liquids onto ZSM-5 from aqueous solution versus excess enthalpy for hydrogen bonding between ionic liquids anion and ZSM-5 predicted using COSMO-RS at 298.15 K.

Conclusions

The present work focuses in getting enhanced understanding in the molecular level mechanisms that drive the adsorption of 27 ionic liquids onto ZSM-5 from aqueous solution. The extensive number of the ionic liquids studied covers a wide variety of cation head group, alkyl chain length, and anions. It permitted to assess the impact of the ionic liquids structure on their adsorption onto ZSM-5 from aqueous solution. The newly obtained adsorption equilibrium curves reveal that the anion has ¹¹ more significant impact in the adsorption process than the cation head group ³⁶ or the alkyl chain length. In addition, the results ⁴⁹ also show that the adsorption of ionic liquids onto ZSM-5 from aqueous solution obey the Langmuir and Freundlich adsorption isotherm, with the latter being dominant impact, in particular at high concentrations. The computational modelling using COSMO-RS also revealed the existence of several molecular interactions that control the adsorption of ionic liquids onto ZSM-5 from aqueous solution, namely electrostatic misfit, van der Waals and hydrogen bonding interactions with the latter having the foremost impact in the adsorption process.

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Conflicts of interest

There are no conflicts to declare.

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