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Concentration-dependent apparent partition coefficients of ionic liquids possessing ethyl- and bi-sulphate anions†

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This study deals with the concentration dependent apparent partition coefficients log *P* of the ethyl and bisulfate-based ionic liquids. It is observed that the bisulfate-based ionic liquids show different behaviour with respect to concentration as compared to ethyl sulphate-based ionic liquids. It is significant and useful analysis for the further implementation of alkyl sulfate based ionic liquids as solvents in extraction processes. The log *P* values of the ethyl sulphate-based ionic liquids were noted to vary linearly with the concentration of the ionic liquid, whereas a flip-flop trend with the concentration for the log *P* values of the bisulphate-based ionic liquids was observed due to the difference in hydrogen bond accepting basicity and possibility of aggregate formation of these anions. The π–π interactions between the imidazolium and pyridinium rings were seen to affect the log *P* values. The alkyl chain length of anions was also observed to influence the log *P* values. The hydrophobicity of ionic liquid changes with the alkyl chain in the anion in the order; $[HSO_4]^- < [EtSO_4]^- < [BuSO_4]^-$.

1. Introduction

Recent years have witnessed an upsurge in the research activities in the area of ionic liquids. The field of ionic liquids has drawn significant interest of researchers, including those belonging to separation science as potential replacement to volatile organic compounds (VOCs). Ionic liquids possess several special physicochemical characteristics including a wide liquid range, high thermal stability, a broad solvation window ranging from water to non-polar organic solvents, low flammability, *etc.*[1–11] The most remarkable characteristic of ionic liquids is that they are highly tunable with respect to the selection of cations and anions. These properties make ionic liquids beneficial from the perspective of separation science and technology and also used in many chemical and biochemical reactions.[12–14] The overall awareness regarding greenness and sustainability in using ionic liquids as alternative reaction media to the currently used hazardous VOCs has been considered by many researchers especially for industrial applications.[15] It is normally considered that hydrophilic ionic liquid shows high miscibility with water, whereas hydrophobic ionic liquid absorbs a small amount of water. The physico-chemical properties like viscosity, conductivity, and surface tension of pure ionic liquids vary drastically in the presence of small quantity of water present in ionic liquids.[16] This necessitates rigorous studies of the physico-chemical properties akin to the miscibility and fate of ionic liquids in relation to the environment.

The determination of the octanol–water partition coefficient (K_{ow}) of a chemical compound serves as a key parameter to assess the environmental risk of that chemical and to explore the properties of solvents in the extraction processes.[17–21] The 1-octanol–water partition coefficient is a potential tool to assess the environmental acceptability of various chemical compounds because 1-octanol being an amphiphilic solvent possesses relative permittivity which is almost comparable to the comprehensive lipid phase. The relative permittivity of a compound plays a pivotal role in deciding its dissolution in any solvent. Therefore, the 1-octanol–water partition coefficient of any biological compound is comparable with its partition in water and living systems.[18]

Evaluation of the environmental acceptability of ionic liquids possessing different combinations of the cation and anion pair, through the measurements of K_{ow}, is likely to enhance their wide applications in industries, where biologically active compounds as well as medicinal compounds are being isolated from bulk reactants or solvents.[21–23]

For ionisable species such as ionic liquids, the partition coefficient is reported as the apparent partition coefficient (log *P*). Unlike ionic liquids, most of the compounds report

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the concentration-independent partition coefficient over a wide range of concentrations, whereas ionic liquids show a significant dependence on concentration[24] because of their distinct behaviour towards the water and octanol phase.

A K_{ow} value represents the distribution ratio of an ionic liquid in both water and 1-octanol. In both water and 1-octanol, an ionic liquid can acquire three forms: intact ion pair, loose ion pair and the solvent separated ions under highly dilute conditions. Under such highly dilute conditions, the precise estimation of each individual form is extremely difficult. Some reports exist on the determining K_{ow} values of ionic liquids and on the effect of alkyl chain length of the cationic group of ionic liquids on their partition in both the phases.[25–29] Brennecke *et al.* have measured the 1-octanol–water partition coefficient of dialkylimidazolium ionic liquids ranging between 0.003–11.1 at room temperature in order to describe the effect of anions on $\log P$ values.[28] The binary liquid–liquid equilibrium (LLE) data of alkylimidazolium chlorides with both water as well as 1-octanol have been measured and the solubility data used to estimate K_{ow} values.[30,31] Apart from experimental methods, many new different methods have been established to predict K_{ow} such as a sum of fragment contributions or atom derived group equivalents.[32,33] Most of the ionic liquids, the partition coefficient of which have been reported till date, contain different halides as their anions. The use of halide as an anion in an ionic liquid gives rise to great limitation in industrial applications. Recently, ionic liquids have been modified structurally for enhancing their biodegradability. It has been studied that the imidazolium-based ionic liquids are biodegradable and therefore the biodegradability of various classes of ionic liquids should be explored predominantly on the basis of modification of the anion.[34–36] The replacement of the halide-based anion by the alkyl sulfate anion, enhances their biodegradability to 54%. This is relatively close to the acceptable 60% level for a substance to be categorised as readily biodegradable.[37–39] Alkyl sulfate anion-based ionic liquids are widely used in the petrochemical field for extraction processes,[40–42] alternatives to the routine hydrodesulfurization,[43] as an azeotrope breaker in extractive distillation,[44] and can be synthesized efficiently as well as in a halide free way at reasonable costs.[45] Recent studies have shown that 1-ethyl-3-methylimidazolium ethyl sulfate possesses an acceptable level of toxicity.[46] Besides their application in extraction processes, the alkyl sulphate-based ionic liquids are used as solvents for organic reactions resulting in many remarkable and successful outcomes.[47–49] As the alkyl sulphate-based ionic liquids possess unique physico-chemical properties like biodegradability and adequate levels of toxicity, these must be further explored and analysed in depth for their better applications such as in separation, liquid–liquid extraction and for the removal of nitrogen and sulfur containing compounds from currently used fuels. The lack of partition data of alkyl sulfate anion based ionic liquids diminishes their use as alternative solvents in the industries.

No reports are available in the literature on the concentration dependent study of apparent partition coefficients of alkyl sulfate based ionic liquids. The study of the relationship between the partition coefficient and the initial concentration of alkyl sulfate based ionic liquids in the 1-octanol–water binary phase is of high interest and significance. The purpose of using the bisulfate and ethyl sulphate-based ionic liquids is: (1) their unique physicochemical properties such as biodegradability and acceptable level of toxicity, and (2) the ethyl sulphate anion ($EtSO_4^-$) possesses higher electron density as evident from the hydrogen bond acceptor ability or basicity denoted by a solvent parameter called β. The β values for $EtSO_4^-$ containing ionic liquids (≈ 0.788) is close to that of DMSO, a polar aprotic solvent (≈ 0.748).[47,49] Due to the high charge density and the basicity, DMSO can solvate the cations. Similarly, the $EtSO_4^-$ anion possesses high charge density and basicity, therefore it can interact with the imidazolium cation to a greater extent and can be present as an intact ion pair.

In this work, we present the variation in the apparent partition coefficients ($\log P$) with the variation in the substituents present in both cations and anions of ionic liquids. In this work, we have taken the ratio of total concentrations of an ionic liquid present in each phase. The ionic liquids investigated in the present study are [EMIM][$EtSO_4$], [dEIM][$EtSO_4$], [EBIM][$EtSO_4$], [EOIM][$EtSO_4$], [BMIM][HSO_4], [HMIM][HSO_4], [OMIM][HSO_4], [BPy][HSO_4], [OPy][HSO_4] and [BMIM][$BuSO_4$]. A summary of the ionic liquids, the structures of cations and anions and the acronyms used in this study are given in Table 1. In this work, first the apparent partition coefficients of these ionic liquids over a wide range of concentrations (0.01 to 0.05 M) have been described with respect to their concentrations. Then, the effect of the cationic ring as well as anions analysed on the apparent partition coefficient of ionic liquids by comparing the apparent partition coefficient data of [BPy][HSO_4], [OPy][HSO_4], [BMIM][HSO_4], [BMIM][$BuSO_4$], and [OMIM][HSO_4]. Finally we investigate the effect of the number of carbon atoms on the $\log P$ values.

2. Experimental section

2.1 Materials

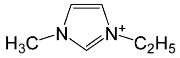
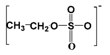
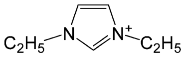
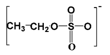
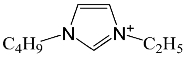
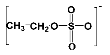
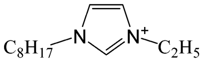
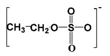
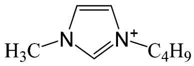
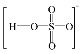
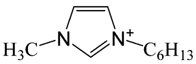
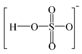
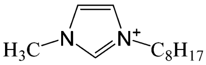
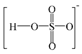
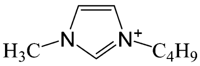
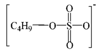
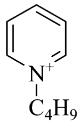
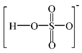
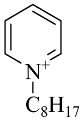
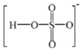
1-Methylimidazole, 1-ethylimidazole, 1-butylimidazole, 1-octylimidazole, and pyridine were procured from M/s Sigma Aldrich Co. These chemicals were distilled prior to their use in experiments. 1-Octanol (with >99.5% purity) was purchased from M/s Fluka Co. and used without further purification. Toluene, diethyl sulfate, dibutyl sulfate, sulphuric acid, and ethyl acetate were obtained from M/s Merck Co. and used as procured. Deionised water (resistivity 18.2 MΩ cm) was used throughout the work.

2.2 Synthesis of ionic liquids

All ionic liquids employed in this study, were synthesized by the following established procedures available in the literature.[45,50]

2.2.1 Synthesis of $[EtSO_4]^-$-based ionic liquids. 1-Methylimidazole (1 mol) was taken in an ice cold bath containing 10 mL of toluene; diethyl sulfate (1 mol) dropwise

Table 1 The acronyms, structures of cations and anions of ionic liquids employed in the present study

Name of ionic liquids	Structure of cations	Structure of anions	Acronym
1-Ethyl-3-methylimidazolium ethylsulphate			[EMIM][EtSO$_4$]
1,3-Diethylimidazolium ethylsulphate			[dEIM][EtSO$_4$]
1-Butyl-3-ethylimidazolium ethylsulphate			[BEIM][EtSO$_4$]
1-Ethyl-3-octylimidazolium ethylsulphate			[EOIM][EtSO$_4$]
1-Butyl-3-methylimidazolium bisulphate			[BMIM][HSO$_4$]
1-Hexyyl-3-methylimidazolium bisulphate			[HMIM][HSO$_4$]
1-Octyl-3-methylimidazolium bisulphate			[OMIM][HSO$_4$]
1-Butyl-3-methylimidazolium butylsulphate			[BMIM][BuSO$_4$]
N-Butyl-pyridinium bisulphate			[Bpy][HSO$_4$]
N-Octyl-pyridinium bisulphate			[OPy][HSO$_4$]

to pre-cooled 1-methylimidazole solution in toluene in order to maintain the temperature of reaction at 313 K. Following continuous stirring for 4 h, the upper organic layer was decanted carefully. For the removal of trace amounts of solvent impurity, the product *i.e.* the ionic liquid was dried by a rotary vacuum at the reduced pressure and 368 K. Other ethylsulfate-based ionic liquids were also prepared by the following similar procedure.

2.2.2 Synthesis of [HSO$_4$]$^-$-based ionic liquids. The synthesis involved two steps.

(1) Quaternization reaction. 1-Methylimidazole to excess haloalkane (1 : 1.2) was added into a round bottom flask fitted with a reflux condenser for 12 h and the temperature was maintained at 343 K. The unreacted starting material was removed by washing with ethyl acetate 3–4 times. The excess solvent was removed by using a rotary evaporator under the reduced pressure. Thereafter, the quaternized product was further dried in a vacuum for 10 h in order to remove trace amounts of volatile residues.

(2) Metathesis. To a stirred solution of the halogenated product of the first step (1 mol) dissolved in 10 mL of acetonitrile; sulphuric acid (1.07 mol) was added in a drop wise manner. The reaction mixture was refluxed for 48–72 h and the temperature of the reaction mixture was maintained at 343 K. The excess solvent was removed by a rotary evaporator and dried under high vacuum.

All the freshly prepared ionic liquids were dried under high vacuum for 24 h prior to each experiment. The water content of the ionic liquids was measured by the Karl–Fischer Coulometer, and was observed below to 50 ppm. The purity of all the synthesised ionic liquids was ensured with the help of ^{1}H-NMR spectra (see ESI†).

2.3 Determination of 1-octanol/water partition coefficients (log *P*)

By the definition 'octanol–water partition coefficient' represents the ratio of the solubility of a given compound between 1-octanol and water at a given temperature. If compound 'X' is dissolved in the 1-octanol/water biphasic system, an equilibrium will be reached after a certain period of time for both the phases at certain temperature. It is known that during the prevalence of equilibrium of distribution of the compound X between the 1-octanol-rich phase and the water-rich phase, activity will be the same in both the phases. Activity can be expressed as 'a' = $c \times \gamma$ *i.e.* multiplication of concentration, c and the activity coefficient, γ. Since the activity of the compound 'X' is the same in both the phases, then $X_{aw} = X_{ao}$ (X_{aw} indicates the activity at water; X_{ao} indicates activity at the 1-octanol phase of the compound X). At equilibrium,

$$X_{aw} = X_{ao} \quad (1)$$

or,

$$c_w\gamma_w = c_o\gamma_o \text{ or, } c_o/c_w = \gamma_w/\gamma_o \quad (2)$$

At constant temperature and pressure, if the compound 'X' is present in both the water and 1-octanol phases under extremely dilute conditions, the 'infinite dilute' condition activity coefficients remain invariable with small variation in the concentrations. It implies that the ratio of concentrations (c_o/c_w) at equilibrium remain constant *i.e.* $K_{ow} = c_o/c_w$ represents constant unit less value, independent of composition at constant temperature.

1-Octanol and water are not completely immiscible at 298 K. The solubility of water in 1-octanol is quite high approximately up to $x_w = 0.275$ of water, but the solubility of 1-octanol in water is $x_o = 7.5 \times 10^{-5}$.[51,52] We used the shake flask method with mutually saturated 1-octanol and water to determine the log *P* value. For estimation of log *P* of ionic liquids, 1 : 1 (v : v) ratio of water saturated with 1-octanol and 1-octanol saturated with water was taken. The solutions of ionic liquids with the known concentration (0.01–0.05 M) were made in 1-octanol and then an equal volume of water was added to the solution. The sample solution was stirred for 24 h with 170 rpm by an orbital shaker at room temperature (298 ± 2 K). The sample solutions were kept for 24 h to get the equilibrium.

Following equilibration, water and 1-octanol phases were collected separately with a syringe. The molar absorption coefficient (ε) was measured (Table S5, ESI†) in both phases (water saturated with 1-octanol and 1-octanol saturated with water) in order to calculate the concentration in both the phases by applying the Lambert–Beer Law. The UV-visible spectrophotometer (Varian make, Cary 50) was employed to measure absorbance at absorption maxima (λ_{max}) of the substances in the extracted solvents. Water saturated with 1-octanol and 1-octanol saturated with water were used in the sample cell. The concentrations of the dissolved solute was determined from the absorbance value obtained from the UV/vis spectrophotometer through a pre-calibrated graph. The accuracy of all the measurements was estimated to be ±3%. The measured data, an average of triplicate measurements, are precise to within ±1%.

3. Results and discussion

For the convenience of reporting, the log *P* data of ionic liquids has been divided into three parts.

3.1 Concentration-dependent log *P*

It is interesting to know that how the apparent partition coefficient of ionic liquids varies with the concentration of a given ionic liquid. The log *P* values as a function of concentration of the ionic liquid are shown in Fig. 1 for [EMIM][EtSO$_4$], [dEIM][EtSO$_4$], [BEIM][EtSO$_4$], [EOIM][EtSO$_4$], [BMIM][HSO$_4$], [HMIM][HSO$_4$] and [OMIM][HSO$_4$]. As seen from Fig. 1, the log *P* values of these ionic liquids depend upon their concentrations. The negative log *P* value indicates the hydrophilic nature whereas the positive log *P* value shows the hydrophobic nature of a solute. In the present study, we have observed that the hydrophobicity or hydrophilicity of an ionic liquid linearly increases by increasing the concentration of the ethyl sulphate-based ionic liquids. The ionic liquids with a lower alkyl group are hydrophilic in nature, which increases with concentration as shown in Fig. 1(a). The log *P* values vary from −2.04 to −2.82, −2.12 to −2.63, and −1.64 to −1.92 for [EMIM][EtSO$_4$], [dEIM][EtSO$_4$] and [BEIM][EtSO$_4$], respectively over a wide range of concentrations from 0.01 to 0.05 M (Table S1, ESI†). On the other hand, the hydrophobicity of [EOIM][EtSO$_4$] varies from 0.19 to 1.65 as a function of concentration in the range of 0.01 to 0.05 M as shown in Fig. 1(a). The log *P* values obtained for [HSO$_4$]-based ionic liquids demonstrated interesting results about the concentration dependent hydrophilicity or hydrophobicity. We have observed a flip-flop behaviour in hydrophobicity or hydrophilicity for [HSO$_4$]$^-$ based ionic liquids with respect to the concentration as seen in Fig. 1(b). These ionic liquids show unusual behaviour beyond a particular concentration. In the case of [BMIM][HSO$_4$], upon increasing the concentration from 0.01 to 0.03 M, the log *P* value decreases from −2.01 to −2.11 and

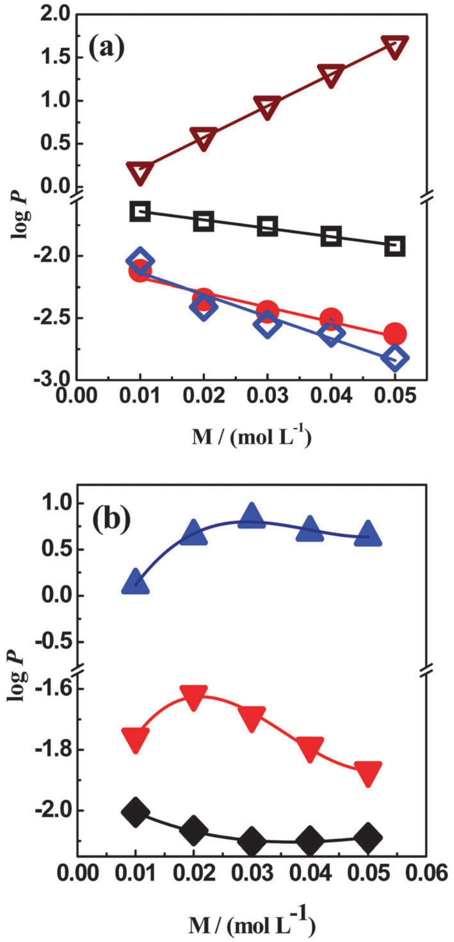


Fig. 1 Variation of log *P* with concentration (a) for [EMIM][EtSO$_4$] (◇), [dEIM][EtSO$_4$] (●), [BEIM][EtSO$_4$] (□), and [EOIM][EtSO$_4$] (▽). (b) For [BMIM][HSO$_4$] (◆), [HMIM][HSO$_4$] (▼), and [OMIM][HSO$_4$] (▲).

beyond this concentration, the log *P* value increases to −2.10 and −2.09 at 0.04 and 0.05 M, respectively (Table S2, ESI†). These results reveal that [BMIM][HSO_4] possesses hydrophilic behavior at lower concentrations and shifts towards hydrophobic behavior upon increasing concentrations (see Fig. S1(a), ESI†).

The log *P* values of [HMIM][HSO_4] increase from −1.76 to −1.62 with increasing the concentrations from 0.01 to 0.02 M and above that concentration, the log *P* values decreases up to −1.87. It is observed that up to 0.02 M concentration, the hydrophilicity decreases and beyond that concentration, the hydrophilicity of the ionic liquids increases. Similarly, in the case of [OMIM][HSO_4], the log *P* value increases from 0.12 to 0.83 upon an increase in the concentration from 0.01 to 0.03 M. Then it decreases from 0.83 to 0.64 as a concentration increases from 0.03 to 0.05 M. On moving towards [HMIM][HSO_4], the polarity of ionic liquid decreases so the interactions with water become less favorable.

[HMIM][HSO_4] shows higher log *P* values as compared to [BMIM][HSO_4] and lower to [OMIM][HSO_4] as shown in Fig. S1(b) and (c) (ESI†). The change from hydrophobic to hydrophilic nature and *vice versa* of these ionic liquids may occur due to self-aggregation. It has also been reported that self-aggregation of ionic liquids may occur in aqueous solution.[53,54]

The log *P* data obtained in the study revealed the formation of aggregates in the aqueous phase during the distribution of ionic liquids between the 1-octanol–water binary system. The [HSO_4]$^-$-based ionic liquids show different behaviour as compared to [$EtSO_4$]$^-$-based ionic liquids, because of the less basicity and the possibility of formation of aggregates. At lower concentrations, ionic liquids exist as intact ion pairs in the aqueous phase. At lower concentrations of ionic liquids, strong van der Waals interactions take place between the hydrophobic alkyl chain of ionic liquids and the hydrophobic part of the 1-octanol thereby decreasing the hydrophilicity. Moving towards the higher concentration the possibility of aggregate formation increases. The aggregate formation takes place due to the van der Waals interactions between the hydrophobic parts of ionic liquids. The flip-flopping in hydrophilicity/hydrophobicity depends on the orientation of aggregates. Orientation of the imidazolium-based ionic liquid in an aggregate form favours the hydrogen bonding between [HSO_4]$^-$ and the aqueous phase. In the case of imidazolium-based ionic liquids, the hydrophobic tail of ionic liquids reside away from the water molecules, whereas the hydrophilic head of ionic liquid and counter ions resides towards the aqueous phase due to lesser possibility of π–π stacking. The orientation of an ionic liquid above the critical aggregate concentration (cac) favors its interactions in the aqueous phase over the organic phase, leading to an increase in the hydrophilicity of the ionic liquid beyond the cac. These observations are consistent with the earlier reports that the partition coefficient of ionic species is concentration dependent.[24] A similar trend has also been observed in the case of [OPy][HSO_4] and [BPy][HSO_4] as shown in Fig. 2. The value of log *P* decreases from −2.45 to −2.63, as the concentration increases from 0.01 M to 0.02 M. However, beyond this concentration, the log *P* value increases to −2.42 at 0.05 M (Table S3, ESI†) in [BPy][HSO_4] as shown in Fig. 2(a). It is shown in Fig. 2(b) that upon increasing the concentration from 0.01 M to 0.05 M, the log *P* value increases from −0.39 to 1.22, respectively. In the case of the pyridinium-based ionic liquids, the structure of aggregates is different from those observed for the imidazolium-based ionic liquids. The pyridinium-based ionic liquids show favourable arrangement for π–π stacking between rings. At lower concentrations of [BPy][HSO_4], the ionic liquid remains as intact ion pair and thus shows favourable interactions with the aqueous phase through hydrogen bonding between [HSO_4]$^-$ and water. With an increase in the concentration of the ionic liquid, the possibility of aggregate formation also increases. The π–π stacking between rings orients the hydrophilic head reside away from the water molecules and the hydrophobic part towards it. Similarly, the orientation of aggregates of the pyridinium-based ionic liquids favours the interaction with the 1-octanol phase, as van der Waals interactions are enhanced between the hydrophobic part of aggregates and the hydrophobic tail of 1-octanol. The observed log *P* value reveals that the hydrophilicity of [BPy][HSO_4] increases in lower concentration, but beyond cac (0.02 M), the hydrophilicity of the ionic liquid decreases as the orientation of the

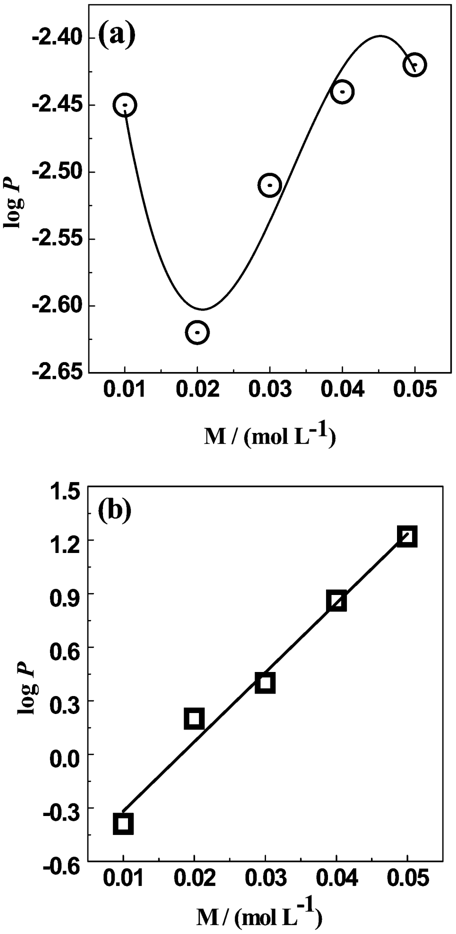


Fig. 2 Variation of log *P* with concentration for (a) [BPy][HSO_4], and (b) [OPy][HSO_4].

aggregate favours the interactions with the organic phase. The hydrophobicity of [OPy][HSO_4] increases linearly with the concentration.

At 0.01 M concentration, log *P* (−0.39) of [OPy][HSO_4] shows hydrophilic behavior but upon increasing the concentration, the hydrophobicity of ionic liquid increases linearly. In the case of [OPy][HSO_4], at a lower concentration of 0.01 M, it shows high interactions with water but as we increase the concentration of the ionic liquid, the longer alkyl group resides towards the aqueous phase due to the π–π stacking between the pyridinium ring leading to a decrease in the interaction with water. As the concentration of [OPy][HSO_4] increases, it results in favorable interaction with 1-octanol owing to the orientation of aggregates.

3.2 Effect of cationic rings and anions on log *P*

As demonstrated in the first section, the hydrophobicity of [OPy][HSO_4] increases linearly with an increase in concentration, whereas flip-flopping observed in the case of [OMIM][HSO_4]. In order to compare the effect of the cationic ring on log *P* values, we have chosen imidazolium and pyridinium cationic rings. The imidazolium ring is smaller in size and less aromatic in nature as compared to pyridinium. The imidazolium ring shows strong interactions with water as compared to pyridine. Fig. 3 shows that the log *P* value of [OPy][HSO_4] is higher than that of [OMIM][HSO_4] at the concentrations higher than ~0.035 (mol L^{-1}) indicating that pyridine is less hydrophilic as compared to that of imidazole. In the present study, effects of anions on the log *P* were also observed. The effect of anions on log *P* values has been observed in sulfate-based ionic liquids by changing the alkyl group in anions such as $[HSO_4]^-$, $[EtSO_4]^-$, and butyl sulfate ($[BuSO_4]^-$). All the alkyl sulfate anion containing ionic liquids show higher interactions with water.

The basicity of anions increases upon increasing the carbon number in anions. Upon increasing the basicity; electrostatic interactions between cations and anions increase. It was also noted that the $[EtSO_4]^-$ anion has a similar behavior as that of DMSO in terms of *β* values. Similar to DMSO, the $[EtSO_4]^-$ anion interacts with imidazolium cations to a greater extent as compared to the $[HSO_4]^-$ anion. Simultaneously, hydrophobicity of the anion also increases upon increasing the number of carbon atoms and hence $[HSO_4]^-$ anions are more hydrophilic in nature as compared to $[EtSO_4]^-$ and $[BuSO_4]^-$. As we move from $[HSO_4]^-$ to $[EtSO_4]^-$ it is noted that the ionic liquids possessing the $[HSO_4]^-$ anion shows higher interactions with water as compared to $[EtSO_4]^-$ due to the absence of the $-C_2H_5$ group and the possibility of aggregate formation. Hydrophobicity is induced by the $-C_2H_5$ group in $[EtSO_4]^-$, whereas it is not observed in the case of $[HSO_4]^-$. The electronegativity of oxygen atoms attached to the alkyl chain (hydrogen or ethyl) is increased upon increasing the alkyl group length leading to an enhanced electrostatic interaction. It is reported that upon increasing the number of carbon atoms in cations as well as, anions, a favorable interactions with 1-octanol or high solubility in 1-octanol is seen. Fig. 1 depicts that $[HSO_4]^-$ based ionic liquids behave differently as a function of concentration as compared to $[EtSO_4]^-$-based ionic liquids. Therefore the $[HSO_4]^-$ containing ionic liquids show greater ionic liquid–water interactions due to less hydrophobicity and large negative charge on the anion oxygen atom. Increasing the alkyl chain length in the sulfate anion increases the negative charge of the oxygen atom and holds a strong electrostatic interaction between cations and anions. This lowers the ionic liquid/water interaction and hence the solubility or interaction with 1-octanol increases. The log *P* values is mentioned in Table S4 (ESI†) for the ionic liquids having different anions and cationic rings. [BMIM][HSO_4] and [BMIM][$BuSO_4$] have a similar cationic ring but different alkyl groups in anions. Since both the anions possess higher capability of hydrogen bonding with water, negative log *P* values are obtained. However, in the case of the $[BuSO_4]^-$ anion, the presence of the butyl group imparts some degree of hydrophobicity in comparison to that of the $[HSO_4]^-$ anion. This enhanced hydrophobicity of the $[BuSO_4]^-$ ion is also reflected in the log *P* values of [BMIM][$BuSO_4$] *i.e.* log *P* values reside on the higher side as compared to [BMIM][HSO_4], as shown in Fig. 4.

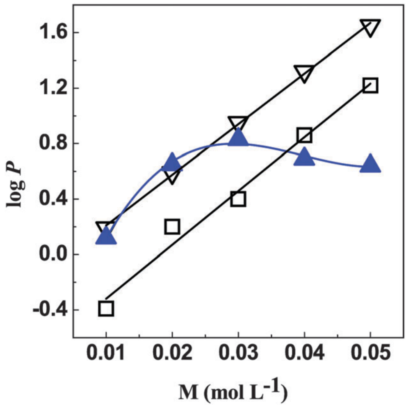


Fig. 3 A comparative study of log *P* with concentration for [OPy][HSO_4] (□), and [OMIM][HSO_4] (▲); also given [EOIM][$EtSO_4$] (▽).

3.3 Effect of the number of carbon atoms attached to the cationic ring of ionic liquids on log *P*:

As described in Fig. S2 (ESI†), the log *P* values increase with an increase in size of the alkyl chain attached to the cationic ring. $[EtSO_4]^-$ is hydrophilic in nature. A change from $[EMIM]^+$ to $[dEIM]^+$ leads to a decrease in the hydrophilicity of ionic liquids by a marginal amount as identified by log *P* values (log *P* for [EMIM][$EtSO_4$] = −2.41; log *P* for [dEIM][$EtSO_4$] = −2.35) at a particular concentration of 0.02 M. However, a value of log *P* = −1.72 for [BEIM][$EtSO_4$] indicates that the hydrophilicity again decreases (Table S1, ESI†) and shows the marginal behavior lying between hydrophobicity and hydrophilicity of these ionic liquids. From Fig. S2(a) (ESI†) it is clear that upon increasing the alkyl chain length of the cationic ring of the $[EtSO_4]^-$-based ionic liquids ([EMIM][$EtSO_4$], [dEIM][$EtSO_4$], [BEIM][$EtSO_4$] and [EOIM][$EtSO_4$]) the log *P* value changes from negative to positive. These changes occur because the non-polarity of the

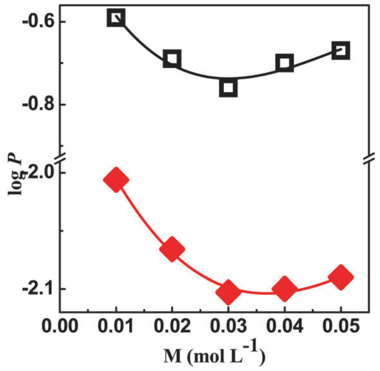


Fig. 4 A comparative study of log *P* with concentration for [BMIM][BuSO$_4$] (□), and [BMIM][HSO$_4$] (◆).

above ionic liquids increase with the introduction of additional alkyl groups, and thus, the solubility in 1-octanol of ionic liquid increases. [EOIM][EtSO$_4$] possess a positive log *P* value (0.59), whereas for [EMIM][EtSO$_4$], [dEIM][EtSO$_4$], and [BEIM][EtSO$_4$] have negative log *P* values.

[EOIM][EtSO$_4$] is hydrophobic in nature. The effect of alkyl chain length on the log *P* values for the [HSO$_4$]$^-$-based ionic liquids were obtained as shown in Fig. S2(b) (ESI†). The log *P* values of [BMIM][HSO$_4$], [HMIM][HSO$_4$], and [OMIM][HSO$_4$] are −2.01, −1.76, and 0.12, respectively at 0.01 M (Table S2, ESI†). The log *P* values indicate that hydrophilicity of ionic liquid decreases upon moving from the butyl to the hexyl group. In the case of [OMIM][HSO$_4$], due to the larger hydrophobic alkyl group, its solubility increases in 1-octanol thus showing the positive log *P* values. The [HSO$_4$]$^-$-based ionic liquids show a similar trend as noted in the case of [EtSO$_4$]$^-$-based ionic liquids. The log *P* values vary due to different behavior of anions. Upon increasing alkyl chain length of cationic ring, there is a possibility of strong van der Waals interactions between the alkyl group of ionic liquid and the hydrophobic part of 1-octanol. This behavior of hydrophobicity can also be explained by their polarity values. As the size of the alkyl group in ionic liquid increases; its polarity decreases.[55] This inhibits its ability to interact with water.[56,57] The lengthening of the aliphatic chain at positions 1 and 3 (in an imidazolium ring) on the cation also affects the interaction of ionic liquids with solvents. Many interactions like van der Waals interactions (between the hydrophobic part of ionic liquids and solvents), hydrogen bonding, coulombic interactions *etc.* are responsible for solubility. Increasing the carbon atoms on cations show the strong van der Waals interactions with the hydrophobic part of 1-octanol. Acidic C2 protons on the imidazolium cationic ring shows hydrogen bonding with water but upon increasing the alkyl chain length on the ring, the acidity of C2 proton decreases thereby increasing the hydrophobicity of cationic rings. Ionic liquids having smaller alkyl groups at 1 and 3 positions shows favorable interactions with water.[58] This supports our experimental results that upon increasing the alkyl chain length on imidazolium cation solubility of ionic liquids in water decreases (Fig. 5).

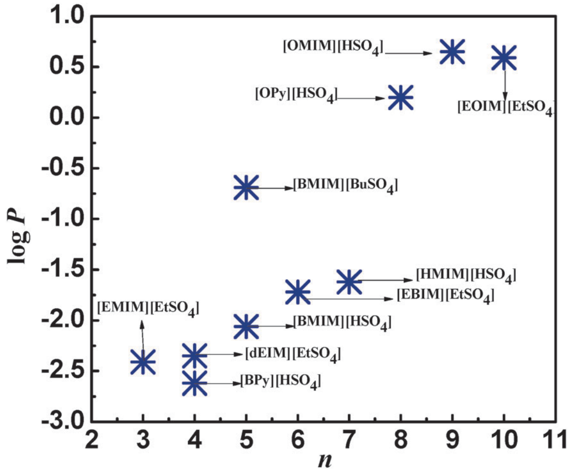


Fig. 5 Variation of log *P* with the number of carbon atoms in alkyl groups attached to the cationic ring of the ionic liquids.

The increasing order of hydrophobicity by varying the alkyl chain is as follows

$$[\mathrm{EMIM}][\mathrm{EtSO_4}] < [\mathrm{dEIM}][\mathrm{EtSO_4}] < [\mathrm{BEIM}][\mathrm{EtSO_4}] < [\mathrm{EOIM}][\mathrm{EtSO_4}]$$

Similarly, for the [HSO$_4$]$^-$-based ionic liquids hydrophobicity increases in the order as follows

$$[\mathrm{BMIM}][\mathrm{HSO_4}] < [\mathrm{HMIM}][\mathrm{HSO_4}] < [\mathrm{OMIM}][\mathrm{HSO_4}]$$

For the purpose of convenience, log *P* values for the investigated ionic liquids have been summarized in the form of adjustable parameters of a polynomial equation (Table 2).

At the end, we state that the log *P* scale may not act as a robust tool to predict hydrophobicity in ionic liquids as structural aspects of both cations and anions lead to complex properties. In an excellent review published by van Rantwijk and Sheldon[13] the miscibility aspects of ionic liquids have been discussed. The constituent anions of the ionic liquid seem to reflect on the miscibility of the ionic liquids in water.

Table 2 Values of the adjustable parameters to describe concentration dependence of log *P* by $\log P = q_0 + q_1c + q_2c^2 + \ldots$; c = molar concentration (mol L^{-1})

	Parameters			
Ionic liquids	q_0	q_1	q_2	r^2
[EMIM][EtSO$_4$]	−1.96 ± 0.09	−17.70 ± 2.89	—	0.9015
[dEIM][EtSO$_4$]	−2.06 ± 0.06	−11.8 ± 1.7	—	0.9238
[BEIM][EtSO$_4$]	−1.57 ± 0.01	−6.8 ± 0.4	—	0.9863
[EOIM][EtSO$_4$]	−0.16 ± 0.02	36.5 ± 0.7	—	0.9987
[BMIM][HSO$_4$]	−1.92 ± 0.01	−9.73 ± 0.90	128 ± 15	0.9810
[HMIM][HSO$_4$]	−1.86 ± 0.11	16.24 ± 8.59	−336 ± 140	0.6971
[OMIM][HSO$_4$]	−0.48 ± 0.22	74.2 ± 16.9	−1057 ± 277	0.8545
[BPy][HSO$_4$][a]	−1.93 ± 0.18	−76 ± 24	2679 ± 884	0.7910
[OPy][HSO$_4$]	−0.70 ± 0.09	38.80 ± 2.93	—	0.9775
[BMIM][BuSO$_4$][a]	−0.35 ± 0.07	−29.06 ± 8.24	693 ± 266	0.8679

[a] Contains q_3 for [BPy][HSO$_4$] = −27067 ± 9734, and for [BMIM][BuSO$_4$] = −4907 ± 2730.

For example, 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF_4]) and 1-butyl-3-methylimidazolium methylsulfate ([BMIM][$MeSO_4$]) are water-miscible, while 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF_6]) and 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl) imide ([BMIM][Tf_2N]) are not, though these ionic liquids possess nearly similar polarity on the Reichardt scale.[59] In addition, the coordination strengths of the [BF_4] and [PF_6] anions are also comparable.[60] Examining the $\log P$ values of the ionic liquids suggests that $\log P$ predicts the partitioning of ionic liquids between water and 1-octanol.

4. Conclusions

In short we noted that (1) the apparent partition coefficient of ionic liquids is concentration dependent and predominantly influenced by the nature of anions. (2) The $[HSO_4]^-$-based ionic liquids show flipping in $\log P$ values as a function of concentration due to the formation of aggregates, whereas $[EtSO_4]^-$-based ionic liquids possess a linear relationship of $\log P$ with concentration. (3) This different behavior of $[HSO_4]^-$ and $[EtSO_4]^-$-based ionic liquids can be correlated with the variations in hydrogen bond accepting basicity (β) of these anions as well as the possibility of aggregate formation. (4) A change in the cationic core from imidazolium to pyridinium significantly modifies the $\log P$ values due to: π–π interactions, the number of electronegative atoms present in the cationic ring and the hydrophobicity of the cationic ring. (5) The alkyl chain length in the cationic and the anionic part of ionic liquids also affects the $\log P$ values; hydrophobicity of anions increases as $[HSO_4]^- < [EtSO_4]^- < [BuSO_4]^-$. Ultimately, the apparent partition coefficients can illustrate the scale of hydrophobicity or hydrophilicity of ionic liquids.

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References

1 M. J. Earle and K. R. Seddon, *Pure Appl. Chem.*, 2000, **72**, 1391–1398.
2 R. D. Rogers and K. R. Seddon, *Ionic Liquids as Green Solvents: Progress and Prospects*, American Chemical Society, Washington, DC, 2003, vol. 856.
3 P. Wasserscheid and T. Welton, *Ionic Liquids in Synthesis*, Weinheim, Germany, 2003.
4 M. J. Earle, J. M. S. S. Esperança, M. A. Gilea, J. N. Canongia Lopes, L. P. N. Rebelo, J. W. Magee, K. R. Seddon and J. A. Widegren, *Nature*, 2006, **439**, 831–834.
5 M. Deetlefs, K. R. Seddon and M. Shara, *Phys. Chem. Chem. Phys.*, 2006, **8**, 642–649.
6 Z. Hu and C. J. Margulis, *Acc. Chem. Res.*, 2007, **40**, 1097–1105.
7 C. Hardacre, J. D. Holbrey, M. Nieuwenhuyzen and T. G. A. Youngs, *Acc. Chem. Res.*, 2007, **40**, 1146–1155.
8 S. Saha, *J. Phys. Chem. B*, 2006, **110**, 2777–2781.
9 J. F. Brennecke and E. J. Maginn, *AIChE J.*, 2001, **47**, 2384–2389.
10 J. L. Anderson, V. Pino, E. C. Hagberg, V. V. Sheares and D. W. Armstrong, *Chem. Commun.*, 2003, 2444–2445.
11 P. Attri, P. Venkatesu and T. Hofman, *J. Phys. Chem. B*, 2011, **115**, 10086–10097.
12 R. Sheldon, *Chem. Commun.*, 2001, 2399–2407.
13 F. van Rantwijk and R. A. Sheldon, *Chem. Rev.*, 2007, **107**, 2757–2785.
14 A. Shariati, R. A. Sheldon, G. Witkamp and C. J. Peters, *Green Chem.*, 2008, **10**, 342–346.
15 B. Jastorff, R. Störmann, J. Ranke, K. Mölter, F. Stock, B. Oberheitmann, W. Hoffmann, J. Hoffmann, M. Nüchter, B. Ondruschka and J. Filser, *Green Chem.*, 2003, **5**, 136–142.
16 N. D. Khupse and A. Kumar, *J. Solution Chem.*, 2009, **38**, 589–600.
17 A. Leo, C. Hansch and D. Elkins, *Chem. Rev.*, 1971, **71**, 525–616.
18 C. Hansch, *Acc. Chem. Res.*, 1993, **26**, 147–153.
19 C. Hansch, A. Leo and D. H. Hoekman, *Exploring QSAR: Fundamentals and Applications in Chemistry and Biology*, Am. Chem. Soc., Washington, DC, 1995.
20 J. Sangster, *Octanol-Water partition coefficients: Fundamentals and Physical Chemistry*, John Wiley & Sons, Chichester, 1997.
21 C. Hansch, A. Leo and D. H. Hoekman, *Exploring QSAR: Hydrophobic, Electronic and Steric Constants*, Am. Chem. Soc., Washington, DC, 1995.
22 W. M. Meylan, P. H. Howard, R. S. Boethling, D. Aronson, H. Printup and S. Gouchie, *Environ. Toxicol. Chem.*, 1999, **18**, 664–672.
23 A. T. Fisk, R. J. Norstrom, C. D. Cymbalisty and D. C. Muir, *Environ. Toxicol. Chem.*, 1998, **17**, 951–961.
24 T. Köddermann, D. Reith and A. Arnold, *J. Phys. Chem. B*, 2013, **117**, 10711–10718.
25 U. Domańska, E. Bogel-Łukasik and R. Bogel-Łukasik, *Chem. – Eur. J.*, 2003, **9**, 3033–3041.
26 S. H. Lee and S. B. Lee, *J. Chem. Technol. Biotechnol.*, 2009, **84**, 202–207.
27 S. P. M. Ventura, R. L. Gardas, F. Gonçalves and J. A. P. Coutinho, *J. Chem. Technol. Biotechnol.*, 2011, **86**, 957–963.
28 L. Ropel, L. S. Belveze, S. N. V. K. Aki, M. A. Stadtherr and J. F. Brennecke, *Green Chem.*, 2005, **7**, 83–90.
29 L. J. Ropel, *Diffusion Coefficients and 1-Octanol-Water partition Coefficients of Ionic Liquids*, University of Notre Dame, 2004.
30 U. Domańska, *Pure Appl. Chem.*, 2005, **77**, 543–557.
31 U. Domańska, A. Rękawek and A. Marciniak, *J. Chem. Eng. Data*, 2008, **53**, 1126–1132.
32 T. Fujita, J. Iwasa and C. Hansch, *J. Am. Chem. Soc.*, 1964, **86**, 5175–5180.

33 G. Kamath, N. Bhatnagar, G. A. Baker, S. N. Baker and J. J. Potoff, *Phys. Chem. Chem. Phys.*, 2012, **14**, 4339–4342.

34 N. Gathergood, M. T. Garcia and P. J. Scammells, *Green Chem.*, 2004, **6**, 166–175.

35 M. T. Garcia, N. Gathergood and P. J. Scammells, *Green Chem.*, 2005, **7**, 9–14.

36 N. Gathergood, P. J. Scammells and M. T. Garcia, *Green Chem.*, 2006, **8**, 156–160.

37 J. R. Harjani, J. Farrell, M. T. Garcia, D. Singer and P. J. Scammells, *Green Chem.*, 2009, **11**, 821–829.

38 J. R. Harjani, R. D. Singer, M. T. Garcia and P. J. Scammells, *Green Chem.*, 2008, **10**, 436–438.

39 J. R. Harjani, R. D. Singer, M. T. Garcia and P. J. Scammells, *Green Chem.*, 2008, **11**, 83–90.

40 A. Arce, M. J. Earle, H. Rodríguez, K. R. Seddon and A. Soto, *Green Chem.*, 2008, **10**, 1294–1300.

41 G. W. Meindersma, A. J. G. Podt and A. B. de Haan, *Fluid Phase Equilib.*, 2006, **247**, 158–168.

42 A. Arce, O. Rodríguez and A. Soto, *Chem. Eng. Sci.*, 2006, **61**, 6918–6928.

43 J. Eber, P. Wasserscheid and A. Jess, *Green Chem.*, 2004, **6**, 316–322.

44 A. Arce and A. Soto, *Green Chem.*, 2007, **9**, 247–253.

45 J. D. Holbrey, W. M. Reichert, R. P. Swatloski, G. a Broker, W. R. Pitner, K. R. Seddon and R. D. Rogers, *Green Chem.*, 2002, **4**, 407–413.

46 J. D. Holbrey, N. V. Plechkova and K. R. Seddon, *Green Chem.*, 2006, **8**, 411–414.

47 A. Habibi-yangjeh, Y. Jafari-tarzanag and A. R. Banaei, *Int. J. Chem. Kinet.*, 2008, **41**, 153–159.

48 A. Singh and A. Kumar, *J. Org. Chem.*, 2012, **77**, 8775–8779.

49 C. Chiappe and D. Pieraccini, *J. Phys. Org. Chem.*, 2005, **18**, 275–297.

50 A. Singh and A. Kumar, *RSC Adv.*, 2015, **5**, 2994–3004.

51 Y. Marcus, *J. Solution Chem.*, 1990, **19**, 507–517.

52 A. Alexander, *Ber. Bunsenges. Phys. Chem.*, 1983, **87**, 2–5.

53 S. Dorbritz, W. Ruth and U. Kragl, *Adv. Synth. Catal.*, 2005, **347**, 1273–1279.

54 I. Bandrés, S. Meler, B. Giner, P. Cea and C. Lafuente, *J. Solution Chem.*, 2009, **38**, 1622–1634.

55 C. Wakai, A. Oleinikova, M. Ott and H. Weingärtner, *J. Phys. Chem. B*, 2005, **109**, 17028–17030.

56 R. Lungwitz, V. Strehmel and S. Spange, *New J. Chem.*, 2010, **34**, 1135–1140.

57 J.-M. Lee and J. M. Prausnitz, *Chem. Phys. Lett.*, 2010, **492**, 55–59.

58 L. E. Ficke and J. F. Brennecke, *J. Phys. Chem. B*, 2010, **114**, 10496–10501.

59 C. Reichardt, *Green Chem.*, 2005, **7**, 339–351.

60 J. L. Kaar, A. M. Jesionowski, J. A. Berberich, R. Moulton and A. J. Russell, *J. Am. Chem. Soc.*, 2003, **125**, 4125–4131.