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Ionic liquid as a novel partitioning media

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ABSTRACT

The partition coefficients of large number of organic solute including macrocyclic crown ethers in different water-ionic liquid (IL) bi-phasic systems based on Hartree-Fock (HF) and density functional theory (DFT) are presented here. The structure of imidazolium cation based ILs were optimized at HF-6-311G (d,p) level of theory and then surface charge density were calculated at BP-TZVP level of theory using novel conductor like screening model for real solvents (COSMO-RS) approach. The calculated value of density is decreased with increasing alkyl chain length for all the ILs considered here. The calculated values of partition coefficient for various organic solutes obtained from the first principle based COSMO-RS theory are reasonably in good agreement with the available experimental results. The predicted values of partition coefficient will help in the screening and thus selection and design of suitable ILs prior to solvent extraction experiments.

Keywords: Crown ether; Ionic liquids; Partition coefficients; Extraction; Density functional theory; Molecular modeling

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1. Introduction

Chemical reactions are generally carried out in molecular organic solvents. Also, as traditionally practiced, solvent extraction experiments involve water-immiscible organic solvents, many of which are highly volatile, toxic and flammable. These demerits along with their adverse impact on the environment demand the replacement of these molecular organic solvents. Recently, IL has emerged as an alternative to the traditional organic solvents. These solvents composed of entirely of ionic species and some of them even remain liquid in room temperature popularly known as room temperature IL. Both the thermodynamics and kinetics of reactions are different in ILs than those in conventional molecular organic solvents which make them highly fascinating to the users in different field of chemical reactions, catalysis, separation and electrochemical cell. ILs exhibit several remarkable properties that make them highly attractive as a potential solvent medium for efficient extraction processes due to their wide range of liquid density, good thermal stability, and the ability to solubilize a large variety of organic and inorganic molecules, viscosities above those of most common organic solvents, almost zero vapor pressure and high degree of tunability [1,2] (for more details see the nice review by Poole et al. [3]). Advantage of working with ILs is that one can easily functionalize the cations and anions to obtain the properties desired, and when that is insufficient, suitable functional groups can be attached to the ions to meet the desired property. Recently, toxicity has also being considered before its use in practical application [4,5].

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To date, there has been a great deal of progress in IL design; however, much of that progress has been achieved through an empirical approach to property modification that would benefit greatly from a better physical understanding of the structure and interactions within ILs.

It has been reported that ILs are suitable for liquid–liquid extraction due to high partitioning of organic solutes in this benign medium [6]. Solute partitioning in these diluents was found to be comparable to that of much used octanol-water system.

Although numerous studies have appeared describing the application of ILs as partitioning medium in the extraction of various solute molecules, the theoretical estimation of partitioning of solutes molecules in this novel medium is very scarce [7–23].

From theoretical point of view, viscosity of ILs has been predicted using DFT derived charge level moment [24]. Earlier, DFT methods in combination with vibrational spectroscopy have been used to investigate molecular structure of several imidazolium-based ILs [25]. The gas phase structure and energetic of BMIMPF6 has been reported using semi-empirical (AM1 and PM3) and ab initio methods [26]. Correlations between melting point and interaction energy were investigated using ab initio method with basis sets [27].

The structures of cations, anions, and cation-anion ion-pairs of 1,3-dialkylimidazolium based ILs has been reported at the level of DFT theory [28]. Ab initio methods have been used to gain insight into the parameters determining the liquid range and conductivity of ILs [29]. Recently, spectral characteristics of ILs has been reported using DFT level of theory [30].

A COSMO-RS descriptor has been used in quantitative structure–property relationship studies by a neural network for the prediction of empirical solvent polarity scale of neat ILs and their mixtures with organic solvents [31]. Partition coefficients of organic solute between water and room-temperature ILs have been correlated with Abraham's solute descriptors to predict the values of logP [32,33]. This solute descriptor model is solvent system specific and experimental data is needed to generate the descriptors for a new system through a regression analysis. This approach is totally different than ours, where no experimental data is needed in the prediction stage.

To the best of our knowledge, so far, no attempt has been made to calculate the partition coefficients of aromatic organic solutes and macrocyclic crown ethers in water-ILs biphasic system using first principle based molecular orbital theory. But the calculation of partition coefficients without any aid of experimental means is highly desirable for the fast screening of the ILs.

Thus, we have undertaken a novel COSMO-RS based approach for the estimation of partition coefficients of different organic solutes in imidazolium-based ILs with different alkyl chain length and anions using HF and DFT level of theory.

The present work will help in the molecular level understanding of the partition processes as well as in the synthesis of tailor-made new suitable solvent like ILs for better and selective separation of the organic solute/extractant and thus complexed metal ions. The outline of the paper is organized as follows. The computational protocols are described in section II. The COSMO-RS theory developed by Klamt [34–36] is presented briefly in Section II. The computation protocol is described in Section III. In Section IV, we discuss the calculated results and the present work is finally concluded in Section V.

2. Theory

The distribution ratio at infinite dilution of a solute between IL and water is calculated from the ratio of its concentration in the IL phase (C_{IL}) to that in the aqueous phase (C_W):

$$D = C_{\mathrm{IL}}/C_{\mathrm{W}}$$

In quantum electronic structure calculation the solvent effect is incorporated through the most popular COSMO-RS real solvent model [34–36]. The basic idea behind this model is to divide the solute surface segment into a large number of discrete smaller surfaces. Each surface segment is characterized by its area a_i and the screening charge density (SCD, it is the screening of the solute's charge by virtual conductor, i.e., the surrounding environment along with the back polarization) is characterized by σ_i. When two such molecular surfaces come into contact they lead to some electrostatic interaction energy. These microscopic surface interaction energies can be used to predict the macroscopic thermodynamic properties using statistical thermodynamics. The probability distributions ($p^X(\sigma)$) of σ for any compound X_i is called σ profile and the corresponding chemical potential for a surface segment with SCD σ is called σ-potential and is described by:

$$\mu_S(\sigma) = -\mathrm{RT}\ln\left[\begin{array}{l}\int p_S(\sigma')\exp\{(\mu_S(\sigma')\\ -\,a_{\mathrm{eff}}e(\sigma,\sigma'))/\mathrm{RT}\}d\sigma'\end{array}\right] \tag{1}$$

The chemical potential of compound X_i in system S is given by:

$$\mu_S{}^{Xi} = \mu_{C,S}{}^{Xi} + \int p^{Xi}(\sigma')\mu_S(\sigma')d\sigma \tag{2}$$

Here $\mu_{C,S}{}^{Xi}$ is a combinatorial contribution to the chemical potential. The chemical potential $\mu_S{}^{Xi}$ is used for the evaluation of the activity coefficients of the solute in the solvent or solvent mixture by the expression as [37]:

$$\gamma_S{}^X = \exp\{-(\mu_S{}^X - \mu_X{}^X)/K_B T\} \tag{3}$$

Similarly the partition coefficients of a solute j between two solvent (aqueous, w and organic, o) can be written as:

$$\log K_j\,(o, w) = \log\{\exp[(\mu_j{}^w - \mu_j{}^o)/\mathrm{RT}] * V_w/V_o\} \tag{4}$$

where V_w/V_o is volume quotient and can be evaluated either from experiment or COSMO-RS prediction [37,38].

3. Computational experiments

The partition coefficients of a large number of organic solute including crown ethers in different IL at BP-TZVP level of theory are calculated using Eq. (4) as implemented in COSMOtherm molecular modeling package [39]. The COSMO input for ILs are generated using optimized coordinates from GAMESS-US electronic structure calculation code at HF/6-311G (d,p) level of theory [40]. These optimized coordinates are then used for COSMO file generation using Turbomole [41] quantum chemistry package at BP-TZVP level of theory. Only single point energy is calculated both at gas phase and COSMO phase. The initial guess structures are first calculated based on PM3 semi-empirical calculations and subsequently used for input in HF/DFT calculation. We have used MOLDEN program for the visualization of various molecular geometry [42]. The average computer time in 32 processors based computer cluster for generating the optimized structure and hessian calculation for all the ILs with varied alkyl chain length are within 1–4 h. The COSMO input file generation in PIV PC takes around another 1–2 h. The COSMO input file has to be prepared only once.

4. Results and discussions

The fully relaxed equilibrated geometries of the ILs studied here are obtained based on HF-6-311G (d,p)//BP-TZVP level of theory. Though multiple conformers are possible for a particular ILs based on the orientation of the anion for a given cation, we have considered only one for the present calculation. We have considered here the imidazolium based cation and three different type of anions namely, hexafluoride phosphate anion (PF6), dimethyl phosphate (DMP) anion and bis (trifluromethyl sulphonyl) imides anion (TF2N). The structures of all the ILs studied here, have been verified from the density and vapor pressure calculation. The relative errors are presented for density and partition coefficients, where the experimental data are available.

4.1. Structure

The molecular structures of the cation-anion pair has been optimized together instead of optimizing separately at HF-6-311G (d,p) level of theory. First, we have considered here 1-methyl-3-methyl imidazolium cation (MMIM) and PF6 and then we have gradually increased the methyl chain at position to ethyl (EMIM), butyl (BMIM), hexyl (HMIM), octyl (OMIM) and decyl (DMIM) group to study the effect of alkyl chain length on energetic, density and partition coefficients of different aromatic and polycyclic crown ethers (PCEs) in to it. The minimum energy structures of the ILs are displayed in Fig. 1. From the figure it is seen that the PF6 anion is positioned over the imidazolium cation ring in non-planar fashion.

In order to study the effect of anion we have considered the DMP anion for the above mentioned series

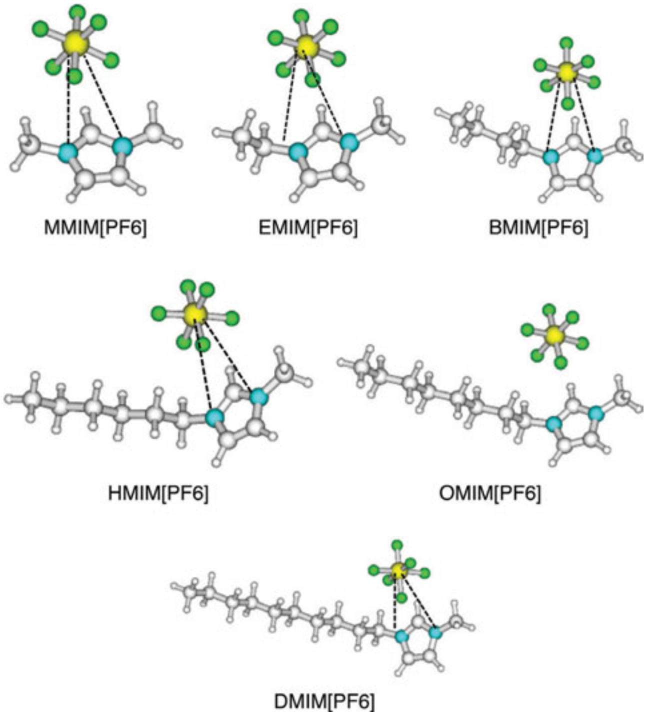


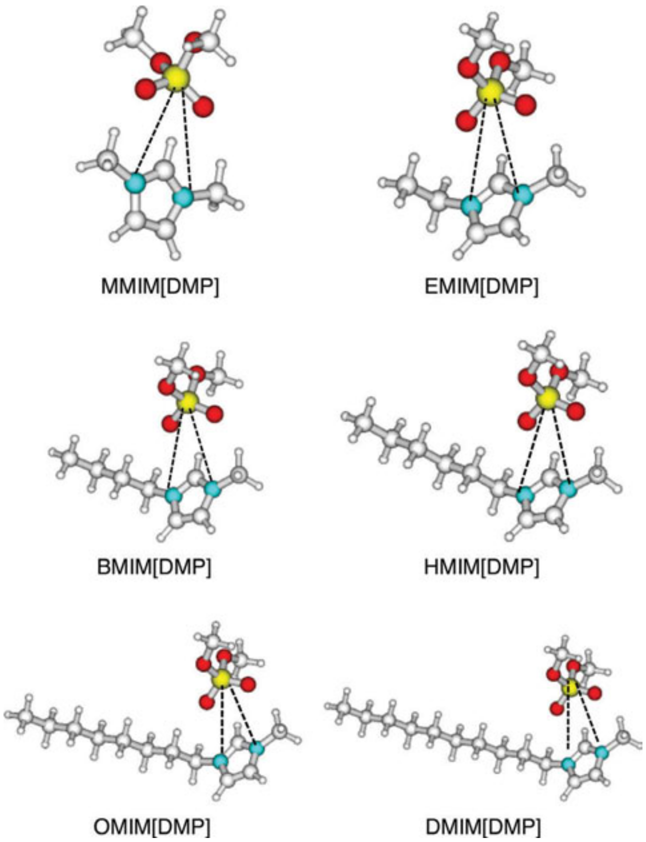
Fig. 1. Optimized minimum energy structure at HF level of theory using split valence 6-311G (d,p) basis function for PF6 based imidazolium ionic liquids. The green spheres, medium sized grey spheres and smallest grey spheres refer to F atom, C atom and H atom respectively. The cyan and yellow sphere represents the N and P atom respectively.

of imidazolium cation and the minimum energy structures of DMP based anion are given in Fig. 2. Here, also the DMP anion is positioned over the imidazolium cation ring in non-planar fashion. Two methyl group of DMP are projected away in the opposite direction of the cation ring.

Another important anion, bis (trifluromethyl sulphonyl) imides anion (TF2N) with various alkyl substituted imidazolium cation are also optimized and the equilibrated structures are presented in Fig. 3. The TF2N anion is positioned over the imidazolium cation ring in non-planar fashion. Two trifluoro methyl group of TF2N are projected away from the cation ring.

4.2. Bond distance and energy

The calculated values of various bond distances and total energy of PF6 anion based imidazolium ILs with varied alkyl chain length at position 1 are presented in Table 1. From the calculated values of P–N bond distance it is observed that the P–N bond distance with nitrogen in the 3-methyl side is gradually increased and with nitrogen in 1-alkyl side is decreased with increase in the alkyl chain length due to shifting of the anion to the 1-alkyl chain side. This may be due to the hydrogen bonding between H of alkyl chain and the F of the anion.

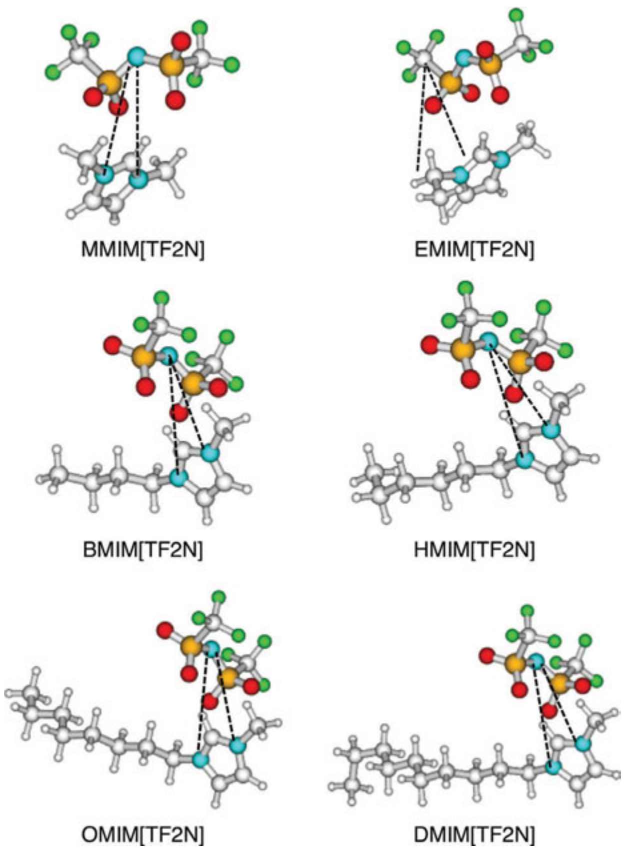


MMIM[DMP] EMIM[DMP]

BMIM[DMP] HMIM[DMP]

OMIM[DMP] DMIM[DMP]

Fig. 2. Optimized minimum energy structure at HF level of theory using split valence 6-311G (d,p) basis function for DMP based imidazolium ionic liquids. The red sphere represents the O atom. The key for all other symbol as in Fig. 1.



MMIM[TF2N] EMIM[TF2N]

BMIM[TF2N] HMIM[TF2N]

OMIM[TF2N] DMIM[TF2N]

Fig. 3. Optimized minimum energy structure at HF level of theory using split valence 6-311G (d,p) basis function for TF2N based imidazolium ionic liquids. The brown sphere represents the O atom. The key for other symbol as in Fig. 1.

Table 1
Calculated values of structural parameters and total electronic energy of the various ILs alkyl substituted imidazolium cation with PF6 as anion at HF-6-311G (d,p) level of theory

S. No.	IL	P–N distance (Å)		E_{tot} (a.u)
		$-CH_3$	$-(CH_3)_n$	
1	MMIM(PF6)	4.2067	4.3701	−1240.6209962
2	EMIM(PF6)	4.2437	4.3121	−1280.3061898
3	BMIM(PF6)	4.2780	4.3181	−1358.3954172
4	HMIM(PF6)	4.2839	4.3199	−1436.4836863
5	OMIM(PF6)	4.2870	4.3214	−1514.5717530
6	DMIM(PF6)	4.2857	4.3213	−1592.6597841

The total electronic energy of the IL is increased with increase in the alkyl chain length as displayed in Table 1.

The calculated values of various bond distances and total energy of DMP anion based imidazolium ILs are presented in Table 2. The calculated value of P–N bond distance linked with the N atom in the 3-methyl side is greater than the P–N bond distance linked with the N atom in the 1-alkyl side. In both the cases the P–N bond distance is decreased with increase in the alkyl chain length. The DMP anion is shifted to 1-alkyl side with increase in the alkyl chain length with enhanced hydrogen bonding with phosphate O atom and the H atom of alkyl chain. The total electronic energy of the IL is increased with increase in the alkyl chain length as displayed in Table 2.

The calculated values of various bond distances and total energy of TF2N anion based imidazolium ILs are presented in Table 3. The calculated values of N–N bond distance linked to N atom in the 3-methyl and 1-alkyl side are increased with increase in alkyl chain length. The total electronic energy of the IL is increased with increase in the alkyl chain length as displayed in Table 3. The P–N bond distance of DMP and PF6 anion based IL is substantially shorter than the N–N bond distance in TF2N anion based IL due to the bulky structure of the later, which prevent its to come near to the imidazolium cation.

Table 2
Calculated values of structural parameters and total electronic energy of the various ILs alkyl substituted imidazolium cation with DMP as anion at HF-6-311G (d,p) level of theory

S. No.	IL	P–N distance (Å)		E_{tot} (a.u)
		$-CH_3$	$-(CH_3)_n$	
1	MMIM(DMP)	4.3855	4.4112	−1023.1478652
2	EMIM(DMP)	4.3162	4.3137	−1062.1954321
3	BMIM(DMP)	4.3195	4.2975	−1140.2845716
4	HMIM(DMP)	4.3241	4.3010	−1218.3727672
5	OMIM(DMP)	4.3248	4.3012	−1296.4608064
6	DMIM(DMP)	4.3180	4.2973	−1374.5488288

Table 3
Calculated values of structural parameters and total electronic energy of the various ILs alkyl substituted imidazolium cation with TF2N as anion at HF-6-311G (d,p) level of theory

S. No.	IL	N–N distance (Å)		E_{tot} (a.u)
		$-CH_3$	$-(CH_3)_n$	
1	MMIM(TF2N)	4.9012	5.0987	−2124.9783060
2	EMIM(TF2N)	4.9474	5.1913	−2164.0256716
3	BMIM(TF2N)	5.0217	5.1507	−2242.1142357
4	HMIM(TF2N)	5.0630	5.1394	−2320.2008903
5	OMIM(TF2N)	5.0628	5.1399	−2398.2889043
6	DMIM(TF2N)	5.0669	5.1409	−2476.3753545

4.3. Density

The calculated values of density of imidazolium based IL with three different types of anions are plotted in Fig. 4. The density of the IL is decreased with increase in the alkyl chain length for all the ILs considered here due to increased molecular weight with increase in alkyl chain length. The IL consist of DMP anion has the lowest density and the IL consist of TF2N anion has the highest density due to the low molecular weight of DMP based IL in comparison to the TF2N based IL. The density of the IL consists of PF6 anion stands in between DMP and TF2N with intermediate molecular mass. The calculated values of density of the IL consist of PF6 anion is in excellent agreement with the experimental results (within 1.1% of the experimental results). The calculated value of density of TF2N based IL is also well in agreement with the reported experimental results (within 5.5%) [3]. The calculated density for 3-methyl-1-methyl-imidazolium di-methyl phosphate (1.279 gm cc^{-1}) is very close to the reported experimental value of 1.277 gm cc^{-1}. The calculated value of density of 3-methyl-1-ethyl-imidazolium-di-methyl phosphate (1.22 gm cc^{-1}) is within 6% of the experimental value of 1.157 gm cc^{-1}.

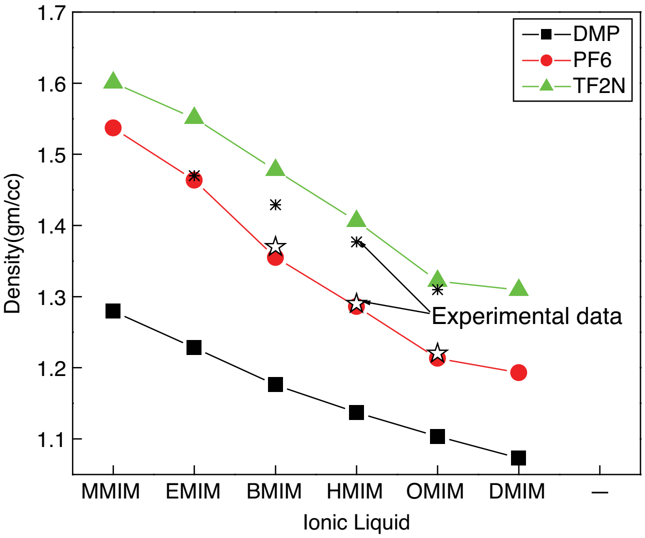


Fig. 4. Plot of calculated values of density of ionic liquids consists of imidazolium cation and anions (PF6, DMP and TF2N) at BP-TZVP/COSMO-RS level of theory.

The higher the density better will be phase separation with aqueous medium. In view of density, TF2N based IL is the suitable extracting medium.

4.4. Partition coefficients

The quantum chemistry based calculated structures are then used for the generation of COSMO input file to be used in the statistical thermodynamics based COSMOtherm code for calculation of thermodynamic parameters. We have calculated the partition coefficients of various organic solutes in ILs of wide range of alkyl chain length and anion. Types of organic solutes we have considered are polycyclic aromatic hydrocarbon (PAH) and PCE. The calculated values of partition coefficients in water and PF6 anion based imidazolium ILs are presented in Table 4. The present calculated values of partition coefficients for polycyclic aromatic compounds and dicyclohexano-18-crown-6 are in excellent agreement with the reported experimental results [43,44]. The partition coefficients of PAH compounds is higher than the PCE compound. This is due to the presence of O atom in the un-substituted crown ether, which enhances its solubility in water and hence reduces the partition coefficients. In case of PAH, the value of partition coefficient is increased with increase in the number of hydrophobic benzene ring. The predicted partition coefficients of PAH follows the order: Fluoranthene > pyrene > anthracene > phenanthrene > fluorene. The same trend was also reported in the experimental findings. The calculated values are within 4% of the experimental results except fluoranthene and pyrene, where it is 8.45% and 6% respectively. In case of crown ether, the predicted order of partition coefficients follows: dch18c6 > 12-crown-4 > 15-crown-5 > 21-crown-7 > 18-crown-6. The calculated value of partition coefficient for dch18c6 (1.94) is within 7.6% of the experimental value (2.10). The calculated values of partition coefficients for both PAH and PCE compounds are increased with increase in the alkyl chain length of the cation. This is due to the increased density and hydrophobicity of the ILs with alky chain length. The calculated value of partition coefficient follows the order: MMIM < EMIM < BMIM < HMIM < OMIM = DMIM. As one goes from MMIM to EMIM, there is jump of 8.4% in the partition coefficient and 18.9% for OMIM. The value of partition coefficient is same for OMIM and DMIM, which means that after OMIM there is no effect of alkyl chain length in the partitioning of the solute. Interestingly, this increment in partition coefficient is nearly same for all the PAH compounds considered here. In case of dch18c6, there is a jump in partition coefficient of 83.6% as one goes from MMIM to EMIM and it is 401% in DMIM. The partition coefficient is increased by 6.15% from OMIM to DMIM, whereas it was unchanged for PAH compounds. Next, we analyze the results in DMP based ILs. The calculated values of partition coefficients in water and DMP anion based imidazolium ILs are presented

Table 4
Calculated values of partition coefficients ($\log K$) of different organic solute in water-(CnMIM)(PF6) biphasic system at BP-TZVP/COSMO-RS level of theory

Solute	MMIM (PF6)	EMIM (PF6)	BMIM (PF6)	HMIM (PF6)	OMIM (PF6)	DMIM (PF6)
Napthalene	2.85	3.09	3.28 (3.34 ± 0.06)[a]	3.36	3.39	3.39
Fluorene	3.50	3.80	4.06 (3.82 ± 0.15)[a]	4.17	4.23	4.23
Phenantherene	3.73	4.04	4.28 (4.06 ± 0.12)[a]	4.38	4.42	4.42
Anthracene	3.76	4.07	4.33 (4.15 ± 0.15)[a]	4.44	4.49	4.49
Fluoranthene	4.11	4.45	4.73 (4.20 ± 0.13)[a]	4.85	4.91	4.91
Pyrene	3.97	4.30	4.58 (4.21 ± 0.11)[a]	4.69	4.75	4.75
Iodomethane	1.69	1.68	1.68 (0.93)[b]	1.65 (0.97)	1.62	1.58
1,2,3-trichlorobenzne	2.68	2.9	3.18 (2.97)[b]	3.29 (2.74)	3.31	3.33
dch18c6	0.55	1.01	1.94 (2.10)[c]	2.38	2.59	2.76
12-crown-4	−0.36	−0.35	−0.09	−0.01	−0.02	−0.02
15-crown-5	−1.34	−1.33	−1.01	−0.81	−0.91	−0.89
18-crown-6	−3.16	−3.38	−2.94	−2.78	−2.83	−2.77
21-crown-7	−1.90	−2.10	−1.66	−1.52	−1.59	−1.57

[a] Reference [43].
[b] Reference [44].
[c] Reference [32].

Table 5
Calculated values of partition coefficients (log*K*) of different organic solutes in water-(CnMIM)(DMP) biphasic system at BP-TZVP/COSMO-RS level of theory

Solute	MMIM (DMP)	EMIM (DMP)	BMIM (DMP)	HMIM (DMP)	OMIM (DMP)	DMIM (DMP)
Napthalene	3.35	3.40	3.39	3.38	3.36	3.33
Fluorene	4.10	4.18	4.19	4.18	4.17	4.15
Phenantherene	4.42	4.48	4.47	4.45	4.42	4.39
Anthracene	4.45	4.52	4.51	4.50	4.48	4.45
Fluoranthene	4.86	4.94	4.93	4.92	4.90	4.87
Pyrene	4.72	4.79	4.79	4.77	4.75	4.72
dch18c6	1.11	1.42	1.68	1.83	1.92	1.99
12-crown-4	−0.64	−0.58	−0.55	−0.55	−0.57	−0.59
15-crown-5	−1.69	−1.61	−1.57	−1.56	−1.57	−1.60
18-crown-6	−4.28	−4.17	−4.09	−4.07	−4.08	−4.10
21-crown-7	−3.07	−2.97	−2.91	−2.91	−2.94	−2.98

in Table 5. The calculated values of partition coefficients for PAH compounds are almost constant with increase in the alkyl chain length of the cation. The calculated value of partition coefficient for PAH follows the same order as was observed in HFP ILs. The calculated value of partition coefficient of PAH in DMP is higher than HFP up to HMIM, after that it is reversed. In case of unsubstituted crown ether, the effect of alkyl chain length on the crown ether partition is very small as seen in case of PAH partitioning. But, in case of substituted dch18c6, there is a jump of 79.23% in the value of partition coefficient as one goes from MMIM to DMIM. The calculated value of partition coefficient of dch18c6 in DMP is higher than HFP up to EMIM, after that it is reversed. Now we will pay attention to the high density TF2N based ILs. The calculated values of partition coefficients in water and TF2N anion based imidazolium ILs are presented in Table 6. The calculated value of partition coefficient for PAH follows the same order as was observed in HFP and DMP ILs. The calculated values of partition coefficients of PAH compounds in TF2N are greater than that in the HFP but smaller than the DMP based ILs. The calculated values of partition coefficients for polycyclic aromatic compound and crown ethers are increased with increase in the alkyl chain length of the cation but the increment is not as high as was in HFP. The increment in partition coefficient of PAH compound considered here is 2.15–4.0% as one goes from MMIM to EMIM and is 5.2–6.6% for MIMIM to OMIM. The increment in partition coefficient of dch18c6 is quite substantial but for

Table 6
Calculated values of partition coefficients (log*K*) of different organic solutes in water-(CnMIM)(TF2N) biphasic system at BP-TZVP/COSMO-RS level of theory

Solute	MMIM (TF2N)	EMIM (TF2N)	BMIM (TF2N)	HMIM (TF2N)	OMIM (TF2N)	DMIM (TF2N)
Napthalene	3.18	3.25	3.31	3.34	3.35	3.34
Fluorene	3.93	4.03	4.11	4.16	4.19	4.18
Phenantherene	4.17	4.26	4.34	4.37	4.39	4.37
Anthracene	4.22	4.32	4.40	4.44	4.47	4.45
fluoranthene	4.62	4.73	4.82	4.86	4.89	4.87
Pyrene	4.47	4.58	4.67	4.71	4.74	4.72
dch18c6	1.49	1.73	2.10	2.33	2.49	2.57
12-crown-4	−0.35	−0.34	−0.26	−0.24	−0.25	−0.26
15-crown-5	−1.32	−1.30	−1.20	−1.16	−1.17	−1.18
18-crown-6	−3.30	−3.27	−3.13	−3.08	−3.13	−3.11
21-crown-7	−2.09	−2.10	−1.98	−1.94	−2.01	−2.02

other unsubstituted crown ethers it is not varied much with alkyl chain length. The increment in partition coefficient of dch18c6 is 16.1% from MMIM to EMIM and is 67.1% from MMIM to OMIM. After OMIM, the effect of alkyl substitution is negligible as seen in DMIM. The calculated value of partition coefficient of dch18c6 is higher in TF2N than that in DMP for all the size of alkyl substituted IL and up to BMIM in HFP ILs. The value of partition coefficient of dch18c6 is smaller in TF2N than HFP after HMIM. The optimized other crown ether structures are taken from our earlier reported results [45–47]. The calculated values of partition coefficients of iodomethane and 1,2,3 trichloro benzene in water-HFP ILs are also presented in Table 4. The value of partition coefficient of iodomethane is nearly independent of the alkyl chain length as observed in the experiment but the partition coefficient of 1,2,3 tricholoro benzene is increased with the length of the alkyl chain up to octyl group. The calculated results are little off from the experimental data. To further test the predicting ability of the present formalism, the partition coefficients of dibenzothiophene in dodecane-IL biphasic system were also evaluated. The calculated values of partition coefficients of dibenzothiopehne in (BMIM)(HFP) and (BMIM)(TF2N) are of 1.6 and 1.5 respectively, which are found to be in moderate agreement with the experimental results of 1.2 and 1 respectively [48]. Among the ILs studied here, TF2N anion based IL has the lowest solubility loss in water. In view of low solubility loss and moderately high partition coefficient TF2N IL can be the suitable IL medium for extraction of solutes.

5. Conclusions

The optimized geometries, total energy and density of imidazolium based ILs with different anions at HF/6-311G (d,p) level of theory are demonstrated. The COSMO input file for all the ILs and the organic solutes are generated at BP-TZVP/COSMO-RS level of theory. The calculated values of density are decreased for all the ILs as molar volume of the IL increases and are in good agreement with the experimentally predicted data. The calculated values of partition coefficients are in excellent agreement with the reported experimental results. In case of PAH, the value of partition coefficient is increased with increase in the number of hydrophobic benzene ring. The predicted partition coefficients of PAH follows the order: fluoranthene > pyrene > anthracene > phenanthrene > fluorine in all the ILs considered here. The calculated value of partition coefficient follows the order: MMIM < EMIM < BMIM < HMIM < OMIM = DMIM for all the PAH compounds considered here. The calculated values of partition coefficients of PAH solutes follows the order (CnMIM)(DMP) > (CnMIM)(TF2N) > (CnMIM)(PF6) for *n* = 4, that is, 3-methyl-1-hexyl. The calculated values of partition coefficient of PAH is higher than the PCEs in all the ILs due to more hydrophobic nature of PAH than crown ethers. The calculated value of partition coefficient of dch18c6 is higher in TF2N than that in DMP for all the size of alkyl substituted IL and up to BMIM in HFP ILs. The present molecular level understanding of the partitioning of organic solutes in the novel media like ILs will help in the screening of existing ILs as well as in the tailor made design of new ILs for better and selective separation of the metal ions based on ab initio and DFT based molecular modeling calculation.

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