

Full Length Research Paper

Computational study of environmental fate of ionic liquids using conductor-like screening model for real solvents (COSMO-RS) method

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Conductor-like screening model for real solvents (COSMO-RS) method was used in screening 2106 potential ionic liquids as safer solvents to volatile n-dodecane used in plutonium and uranium extraction (PUREX). The octanol-water partition coefficient K_{OW}, Bioconcentration factors (BCF) and Bioaccumulation of the ionic liquids were determined. From the results obtained, 111 of them have lower toxicity than the maximum permissible limits. The ionic liquids have very low K_{OW} of less than 700 which is far lower than the maximum permissible limit of 104. The ionic liquids have lower value of the BCF than the maximum permissible limit of 250 µmol/L. n-dodecane on the other hand has a very high value of 93, 756.20 µmol/L which is far greater than the maximum permissible limit. A solvent with a BCF greater than 250 µmol/L is considered to have high bio-accumulation potential in organisms and therefore considered not eco friendly.

Key words: Ionic liquids, conductor-like screening model for real solvents (COSMO-RS), plutonium uranium extraction (PUREX), COSMOtherm, octanol-water partition coefficient.

INTRODUCTION

Volatile organic compounds (VOCs) released into the atmosphere by industrial chemical processes contribute to environmental pollution, climatic changes and human health-related problems (Sonia, 2011). The growing environmental and health concerns have led to the creation of more stringent regulation of their emissions. This is spurring a growing interest in more environmentally friendly technologies, among which there is a major interest in identifying alternative solvents. In the last few years, ionic liquids (ILs) have been looked upon as one of the most promising alternatives to traditional solvents (Rogers and Seddon, 2003). They are expected to help reduce the use of hazardous and polluting organic solvents in separation, synthesis and in the design of new products, owing to their unique

characteristics (Brennecke and Maginn, 2001). In spite of their undeniable interest, it should be noted that not all ILs are green or environment friendly hence the need to determine their environmental fate in the ecosystem. Before the unavoidable release of these ILs into the environment, due to their use in processes and products, adequate knowledge is required about the mechanisms of 'attack' of the ILs to various organisms, their biodegradability, the distribution between different environmental compartments and the bioaccumulation. One of the most widely used parameters for assessing the environmental impact of chemical specie is the octanol-water partition coefficient (K_{OW}) (Laurie, 2004).

The 1-octanol is an amphiphilic solvent whose dielectric properties are similar to those of a generalized lipid

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phase. This parameter is useful in the ecosystem risk analysis because partition coefficients in octanol-water systems display similarities to the partition of biological compounds between water and living organisms.

Correlations between environmental parameters for natural systems and K_{ow} have been successful because the 1-octanol ability to mimic a lipid phases behavior.

Since these solvents are designer solvents which can be tailored by the combination of an anion and a cation, implying the possible generation of large number of them, the empirical work for the determination of the ecosystem risk parameters, octanol-water partition coefficient (K_{ow}), bio-concentration and bioaccumulation factors may be time consuming and capital intensive for a large number of solvents, hence development of a reliable and robust non empirical approaches becomes imperative. Group contribution methods, which are the most widely used theoretical models are not applicable because group interactions parameters are not available at present for ionic liquids and the group contribution concept is not suitable to handle the long-range interactions in ionic compounds (Hamad and Sumon, 2008). Monte Carlo simulations and molecular dynamics need appropriate force-fields for the treatment of ionic liquids, which have to be developed). This work will present the application of a continuum solvation based thermodynamic prediction model, conductor-like screening model for real solvents, conductor-like screening model for real solvents (COSMO-RS) for prediction of thermo-physical data which is a computational approach independent of experimental data and with general applicability (Klamt, 1995; Eckert and Klamt, 2002).

The aim of the research is to computationally determine the eco-toxicity of 2106 ionic liquids using (COSMO-RS) method by determining their octanol-water partition coefficient. The work will be limited to the application of COSMO-RS, a thermodynamic model which uses statistical thermodynamic approach in determination of thermodynamic properties based on results obtained from quantum chemical/COSMO computation for the screening of ionic liquids for uranium extraction from spent nuclear fuel.

METHODOLOGY

The following are the methods used in carrying out the research work:

(1) The Marvin sketch software is first used in sketching the structure of each individual molecule. The environment has a drawing kit including all elements in the periodic table and heterocyclic structures for easy sketch of the molecular structures. They are sketched in two dimensions and then cleaned in three dimensions to obtain full structures, remove their strain energy and minimize their energies. Marvin sketch software operates on windows. The file generated is saved in xyz format and then used as an input file for TURBOMOLE to perform the quantum chemical/COSMO calculation. The 81 cations and 26 anions were combined to generate 2106 potential ionic liquids.

(2) The TURBOMOLE uses the xyz file generated from Marvin sketch to perform quantum chemical/COSMO calculation to generate the screening charge densities of the molecules. The screening charge is a microscopic property of a molecule like internal energy and it is the main parameter used in the COSMO-RS model. The quantum chemical/COSMO computation is parameterized using a full TURBOMOLE 5.6 BP-RI-DFT COSMO optimization of the molecular structure using the large TZVP basis set denoted BP-TZVP. The file is saved as a COSMO file and an input file to COSMOtherm to perform the statistical thermodynamics and to determine the screening charge density profiles and chemical potentials of the individual molecules. The higher the specification of the computer machine, the faster the computation of the screening charges of the molecules. A data base is created for all the COSMO files generated using the TURBOMOLE program software.

(3) The screening charge density profiles and the chemical potentials of the molecules are determined using COSMOtherm. The COSMOtherm is the software that solves the COSMO-RS model based on self consistency field (SCF) algorithm to statistically determine the screening charge density profiles and the chemical potentials of the molecules. The COSMOtherm performs statistical thermodynamic calculations. The COSMOtherm was parameterized using BP_TZVP_C21_0107.ctd. The chemical potentials are determined using COSMOtherm software.

(4) Determination of octanol-water partition coefficients from COSMOtherm using the equation:

$$\log_{10}(P) = \log_{10} \left[\exp \left(\frac{(\mu_j^{(1)} - \mu_j^{(2)})}{RT} \right) * V_1 / V_2 \right] \quad (1)$$

Where V_1 and V_2 are volume quotients of phase 1 and 2. $\mu_j^{(1)}$ = chemical potential of solvent in phase 1 in energy/mole, $\mu_j^{(2)}$ = chemical potentials of solvent in phase 2 in energy/mole, Log P = partition coefficient. It is dimensionless, T = Temperature in degree Celsius, R = molar gas constant in KJ/mol/Kelvin.

The calculation of the partition coefficient log P is accomplished via computation of the chemical potentials $\mu_j^{(1)}$ and $\mu_j^{(2)}$ of all compounds j in infinite dilution in pure compounds i_1 and i_2 , respectively.

RESULTS AND DISCUSSION

Lists of cations and anions

In this work, a total of 2106 ionic liquids were considered in the screening exercise. These were formed by combining 81 cations and 26 anions. Table 1 gives a list of the cations and anions.

Validation of COSMO-RS method

Validation using octanol-water partition coefficient data

The octanol-water partition coefficient K_{ow} , a factor for the determination of the environmental fate of solvents was determined for some solvents using COSMO-RS method and the result was compared with that of the

Table 1. List of cations and anions.

Cations	Cations
1,1-dimethyl-pyrrolidinium	4-methyl-n-butylpyridinium
1,1-dipropyl-pyrrolidinium	1-ethyl-pyridinium
1-ethyl-1-methyl-pyrrolidinium	1-butyl-pyridinium
1-butyl-1-methyl-pyrrolidinium	1-hexyl-pyridinium
1-butyl-1-ethyl-pyrrolidinium	1-octyl-pyridinium
1-hexyl-1-methyl-pyrrolidinium	1-butyl-3-ethyl-pyridinium
1-octyl-1-methyl-pyrrolidinium	1-butyl-3-methyl-pyridinium
3-methyl-imidazolium	1-butyl-4-methyl-pyridinium
1-butyl-imidazolium	1-hexyl-3-methyl-pyridinium
1,3-dimethyl-imidazolium	1-hexyl-4-methyl-pyridinium
1-ethyl-3-methyl-imidazolium	3-methyl-1-octyl-pyridinium
1-butyl-3-methyl-imidazolium	4-methyl-1-octyl-pyridinium
1-pentyl-3-methyl-imidazolium	1-butyl-3,4-dimethyl-pyridinium
1-hexyl-3-methyl-imidazolium	1-butyl-3,5-dimethyl-pyridinium
1-octyl-3-methyl-imidazolium	methyl-trioctyl-ammonium
1-decyl-3-methyl-imidazolium	tetra-methyl ammonium
1-dodecyl-3-methyl-imidazolium	tetra-ethyl ammonium
1-tetradecyl-3-methyl-imidazolium	tetra-n-butyl ammonium
1-hexadecyl-3-methyl-imidazolium	benzyl-triphenyl-phosphonium
1-octadecyl-3-methyl-imidazolium	tetrabutyl-phosphonium
1-benzyl-3-methyl-imidazolium	trihexyl-tetradecyl-phosphonium
1-ethyl-2-3-methyl-imidazolium	triisobutyl-methyl-phosphonium
1-propyl-2-3-methyl-imidazolium	guanidinium
1-butyl-2-3-methyl-imidazolium	hexamethylguanidinium
1-hexyl-2-3-methyl-imidazolium	N,N,N,N,N-pentamethyl-N-isopropyl-guanidinium
1-hexadecyl-2-3-methyl-imidazolium	N,N,N,N,N-pentamethyl-N-propyl-guanidinium
1-methyl-3-(3-phenyl-propyl)-imidazolium	N,N,N,N-tetramethyl-N-ethylguanidinium
Cations	Anions
S-ethyl-N,N,N,N-tetramethylisothiuronium	Tetrafluoroborate
O-ethyl-N,N,N,N-tetramethylisouronium	Hexafluorophosphate (vi)
O-methyl-N,N,N,N-tetramethylisouronium	methyl sulfate
N-butyl-isoquinolinium	chlorate
morpholinium	bromate
methylmorpholinium	iodide
dimethylmorpholinium	formate
N-fluoropropoxy-methylmorpholinium	toluene-4-sulfonate
O-ethyl-tetrapropylisouronium	trifluoromethane-sulfonate
O-hydro-tetraethylisouronium	tris(nonafluorobutyl)trifluorophosphate
O-hydro-tetramethylisouronium	tris(pentafluoroethyl)trifluorophosphate
O-methyl-tetraethylisouronium	bisbiphenyldiolatoborate
O-methyl-tetrapropylisouronium	bisoxalatoborate
O-propyl-tetramethylisouronium	bissalicylatoborate
O-propyl-tetrapropylisouronium	tetracyanoborate
O-butyl-tetramethylisouronium	bis(2,4,4-trimethylpentyl)phosphinate
O-ethyl-tetraethylisouronium	bis-pentafluoroethyl-phosphinate
diethyl-dimethylammonium	bis(trifluoromethylsulfonyl)methane
dimethylammonium	decanoate
ethyl-trimethylammonium	tosylate
methyl-triethylammonium	bis(pentafluoroethylsulfonyl)imide
tetra-ethyl ammonium	n-methyl-n-butylcarbamate
tetramethylammonium	n-methyl-n-propylcarbamate
trimethylammonium	Nitrate
n-methyldiazabicyclo-undec-7-enium	Thiocyanate
n-ethyldiazabicyclo-undec-7-enium	Methylphosphonate
n-hexyldiazabicyclo-undec-7-enium	

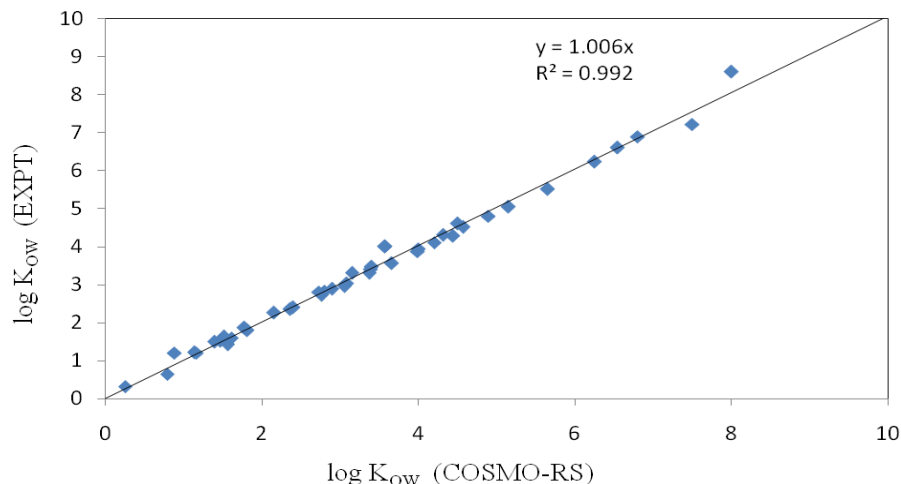


Figure 1. Comparison of experimental octanol-water partition coefficient values against COSMO-RS.

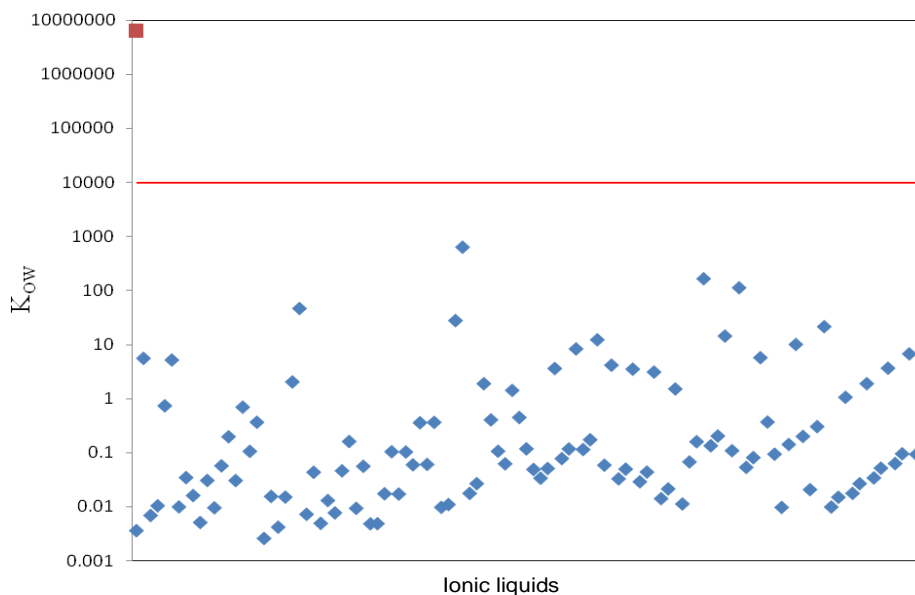


Figure 2. Octanol-water partition coefficient of n-dodecane and the screened ionic liquid n-dodecane, ◆ 111 ILs screened out of 2106.

experimental results obtained by Laurie (2004). The comparison between the experimental and the COSMO-RS method is shown in Figure 1. It can be seen from the figure that there is a very good match between prediction given by the COSMO-RS and the experimental data with coefficient correlation factor of $R^2 = 0.992$.

Environmental effects of the ionic liquids

Octanol-water partition coefficient

Figure 2 shows the octanol-water partition coefficient of

the screened ionic liquids. All of them have a very low octanol-water partition coefficient which is a surrogate for aquatic life. It is a parameter that measures the extent of effect that solvent will have for aquatic life. A solvent with K_{OW} of 10^4 and greater is considered not friendly to the aquatic life according to the U.S EPA (EPA, 1996). The 111 ionic liquids out of the 2106 screened have K_{OW} value lower than 10^4 and this makes it environmentally friendly not only having low volatility and flammability. The ionic liquids screened have very low K_{OW} of less than 700 which is far lower than the maximum permissible limit of 10^4 . On the other hand, a common solvent in separation

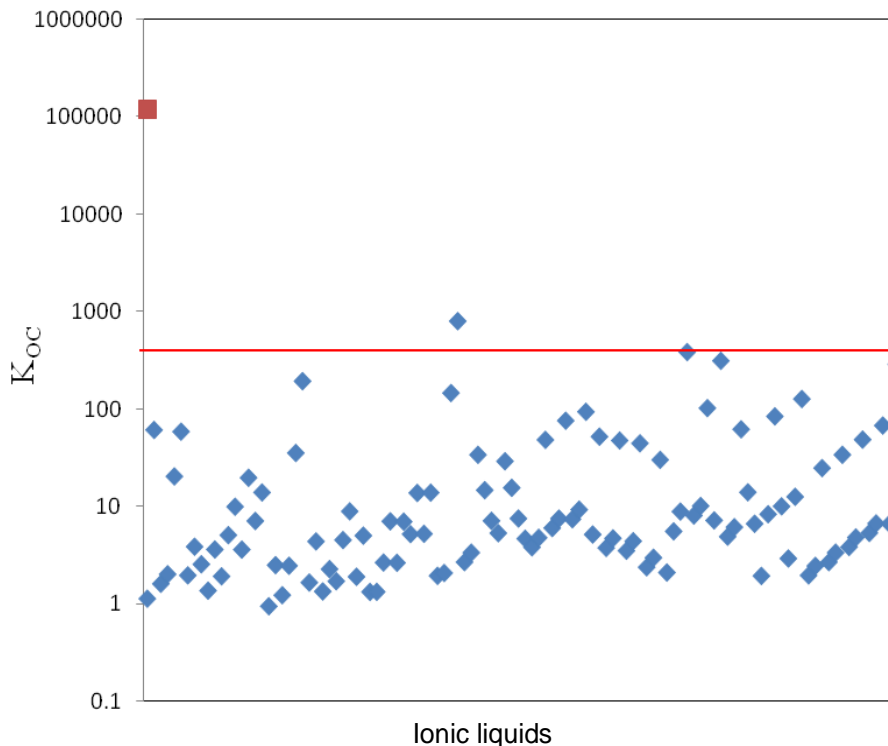


Figure 3. Soil adsorption potential values of n-dodecane and the screened ionic liquids. ■ n-dodecane, ◆ 111 ILs screened out of 2106.

process, n-dodecane has a value of 6,309,573 which is far higher than the permissible limit. This gives the ionic liquids another advantage over the conventional organic solvents used for extraction process.

Soil adsorption potential

Figure 3 shows the graphical result of soil adsorption potential of the screened ionic liquids. Two ionic liquids Methyl-trioctyl-ammonium Thiocyanate and O-ethyl-tetrapropylisouronium bis-pentafluoroethyl-phosphinate have very high K_{OC} with values 797.49 and 383.76 $\mu\text{mol/L}$ respectively. This is greater than the maximum safe limit of 316 $\mu\text{mol/L}$. n-dodecane on the other hand has a very high value of 119,179.07 $\mu\text{mol/L}$ which is far greater than the maximum permissible limit. A soil adsorption value greater than 316 $\mu\text{mol/L}$ is considered to have high sorption potential and capable of accumulating in the soil and therefore not eco friendly (Allen and Shonnard, 2002).

Bio-concentration factor

Figure 4 shows the graphical result of the bio-concentration factors (BCF) of the screened ionic liquids.

All the ionic liquids have lower value of the BCF than the maximum permissible limit of 250 $\mu\text{mol/L}$. n-dodecane on the other hand has a very high value of 93,756.20 $\mu\text{mol/L}$ which is far greater than the maximum permissible limit. A solvent with a BCF greater than 250 $\mu\text{mol/L}$ is considered to have high bio-accumulation potential in organisms and therefore not eco friendly (Allen and Shonnard, 2002).

Conclusion

There are many ionic liquids that are non-toxic to the ecosystem. This is because they have lower values of the environmental risk factor parameters: the K_{OW} , K_{OC} and BCF. 111 ionic liquids out of the 2106 screened have very low K_{OW} of less than 700 which is far lower than the maximum permissible limit of 10^4 and this makes it environmentally friendly.

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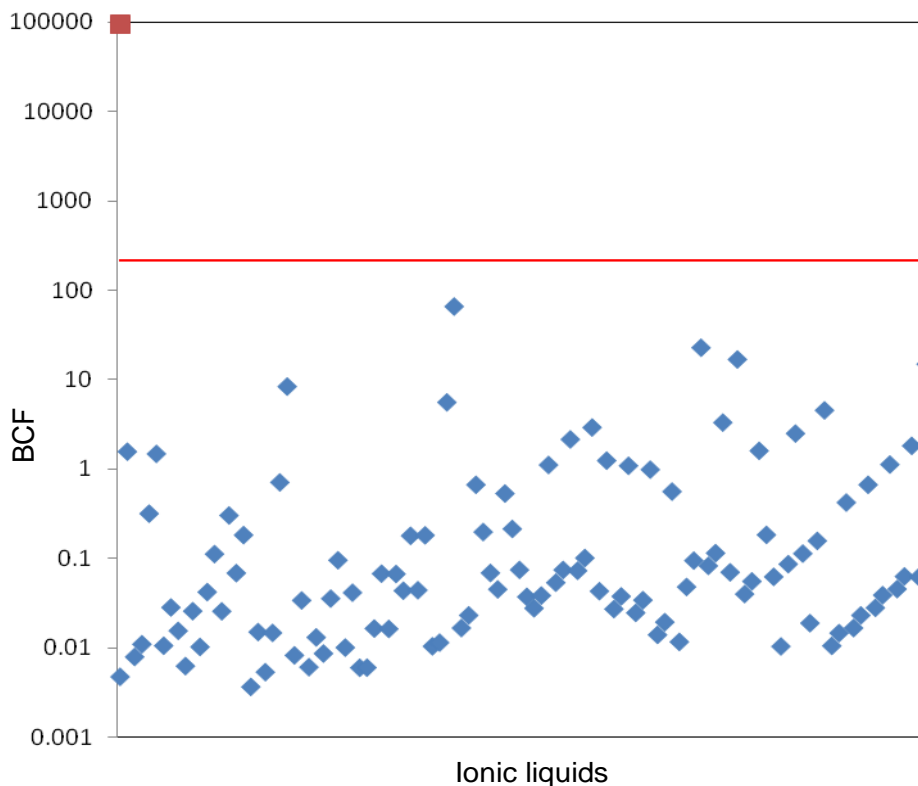


Figure 4. Bio-concentration factors of n-dodecane and the screened ionic liquids. ■ n-dodecane, ◆ 111 ILs out of 2106.

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