Computational Screening of Ionic Liquids for Aromatic Extraction Using COSMO-RS

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Introduction

Since ionic liquids (ILs) are salts composed of a cation and an anion their physical and chemical properties can be tailored by the selection of anion and cation. Therefore, it is possible to generate a huge number of different ionic liquids, each with specific properties. Despite much interest, accurate thermodynamic data of ionic liquids and their mixtures are still rare. To exploit the potential of these new substances, it would be of great value to have prediction methods that can reliably predict the thermodynamic properties of ionic liquids and their mixtures. This would help to scan the growing set of already known ILs in order to find suitable candidates for a certain task or to design new ILs for special applications [1].

Screening Method

Structure-interpolating group contribution methods GCMs presently are the most reliable and most widely accepted way of predicting activity coefficients and other thermophysical data of compounds in liquid multi-component mixtures without explicit use of experimental mixture data. However, group contribution methods are not applicable to ILs because group parameters are not available at present, and the group contribution concept is not suitable to handle the long-range interactions in ionic compounds.

COSMO-RS or 'Conductor-like Screening Model for Real Solvents', is another novel method for the prediction of thermophysical data of liquids. Only recently, it was shown, e.g. by the thesis of Clausen [2] , that COSMO-RS is a valuable tool for the handling of chemical engineering problems regarding activity coefficients and other thermophysical data of compounds in the fluid phase.

Therefore, we have applied this quantum chemically based thermodynamic prediction model to ionic liquid mixtures to calculate activity coefficients of heptane and toluene at infinite dilution in about 1500 ionic liquids.

COSMO-RS

In COSMO-RS the solute molecules are considered as embedded in a virtual conductor environment. In such an environment, the solute molecule induces a polarization charge density σ on the interface between the molecule and the conductor, that is, on the molecular surface. These charges act back on the solute and generate a more polarized electron density than in a vacuum. During the quantum chemical self-consistency algorithm SCF, the solute molecule is thus converged to its energetically optimal state in a conductor with respect to electron density.

In the second step, the polarization charge density of the COSMO calculation, which is a good local descriptor of the molecular surface polarity , is used to extend the model toward the "Real Solvents" (COSMO-RS) [3,4].The 3D polarization density distribution on the surface of each molecule X is converted into a distribution function, the so-called σ-profile $P^{X_i}(\sigma)$, which gives the relative amount of surface with polarity σ on the surface of the molecule. The σ -profile for the entire solvent of interest S, which might be a mixture of several compounds, $P_S(\sigma)$, can be built by adding the $P^{X_i}(\sigma)$, values of the components weighted by their mole fractions X_i in the mixture.

$$P_S(\sigma) = \sum_{i \in S} X_i P^{X_i}(\sigma) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

The chemical potential of compound X_i in the system S (the solvent) can now be calculated by integration of $\mu_S(\sigma)$, over the surface of the compound.

$$\mu_S^{X_i} = \mu_{C,S}^{X_i} + \int P^{X_i}(\sigma)\mu_S(\sigma)d\sigma \ldots\ldots\ldots\ldots (2)$$

To take into account size and shape differences of the molecules in the system, an additional combinatorial term, which depends on the area and volume of all compounds
in the mixture and three adjustable parameters $\mu_{C,S}^{X_i}$, is added. Details of the derivation of eq (2) can be found in ref [1].

The chemical potential of compound X_i can now be used to calculate a wide variety of thermodynamic properties, for example, the activity coefficient:

$$\gamma_S^{X_i} = \exp\{\frac{\mu_S^{X_i} - \mu_{X_i}^{X_i}}{RT}\} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

where ,
$\mu_S^{X_i}$ =chemical potential of compound X_i in the solvent
$\mu_{X_i}^{X_i}$ =chemical potential of the pure component

Computational Details

All COSMORS calculations are performed using the COSMOthermX_2.1 (Release 01.04) program, which provides an efficient and flexible implementation of the COSMO-RS method. Selectivity (S^{∞}) and capacity(C^{∞}) of different ILs at infinite dilution are calculated based on infinite dilution activity coefficient of toluene and heptane in ILs.

$$C^{\infty} = 1/\gamma_{tol}^{\infty} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(4-a)}$$

$$S, S^{\infty}, C^{\infty}$$

$$S^{\infty} = C_{tol}^{\infty} / C_{hep}^{\infty} = \gamma_{hep}^{\infty} / \gamma_{tol}^{\infty} \ldots\ldots\ldots\ldots\ldots \text{(4-b)}$$

The activity coefficients have been calculated using eq 3. The ILs have been described by an equimolar mixture of two distinct ions; that is, the cation and the anion contribute to $P_S(\sigma)$ as two different compounds. On the other hand, experimental depermination of IL thermodynamic properties is based on the assumption of a binary system consisting of the IL and the solute.The activity coefficient that is defined as binary system experimentally but calculated as a ternary system in COSMO*therm* is difined as [5]:

$$\gamma_i^{binary} = \gamma_i^{ternary} (x_i^{ternary} + x_{ion}^{ternary\infty}) \ldots\ldots\ldots\ldots\ldots \text{(5)}$$

For the calculation of activity coefficient in infinite dilution in an IL this reduces to:

$$\gamma_i^{binary} = \frac{1}{2} \gamma_i^{ternary} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(6)}$$

The calculated values are scaled with the factor 0.5 in order to reflect experimental data that takes the view of the system as a binary mixture.

Results and Discussion

The γ^{inf} values for toluene and heptane in 1508 different ionic liquids and in sulfolane at 40°C are calculated using a total of 58 cations and 26 anions .

Two most important criteria of a desired solvent are its capacity and selectivity. A higher selectivity means less extraction stages and a higher capacity requires a lower solvent to feed ratio. Figure-1 shows the position of all the pure ionic liquids in a selectivity (S) vs capacity (C) profile. We observe that a high selectivity is accompanied with a lower capacity and vice versa.

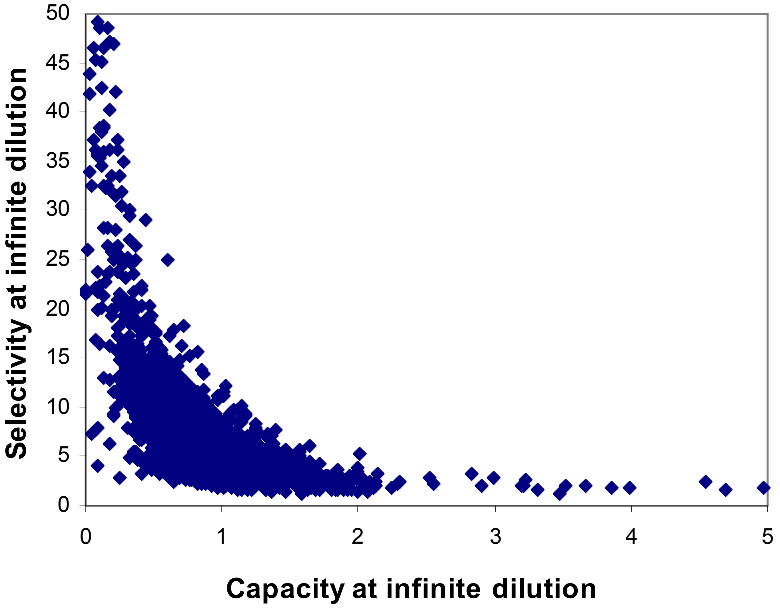

Fig-1: Selectivity vs Capacity at infinite dilution of the solvents investigated

Sulfolane is extensively used for the extraction of aromatics. Hence, we consider sulfolane to be the benchmark solvent in this study. For the extraction of toluene from heptane, the selectivity and capacity of sulfolane at infinite dilution are: $S^{\infty}=6.61$ and $C^{\infty}=0.414$. The selectivity-capacity plane is divided into four quadrants based on the position of sulfolane as shown in figure 2. The upper right portion is shown in figure 3. This portion contains 32% of all the solvents (478 out of 1507) investigated. This indicates that there many ionic liquids which may be used as potential solvents for the extraction of aromatics.

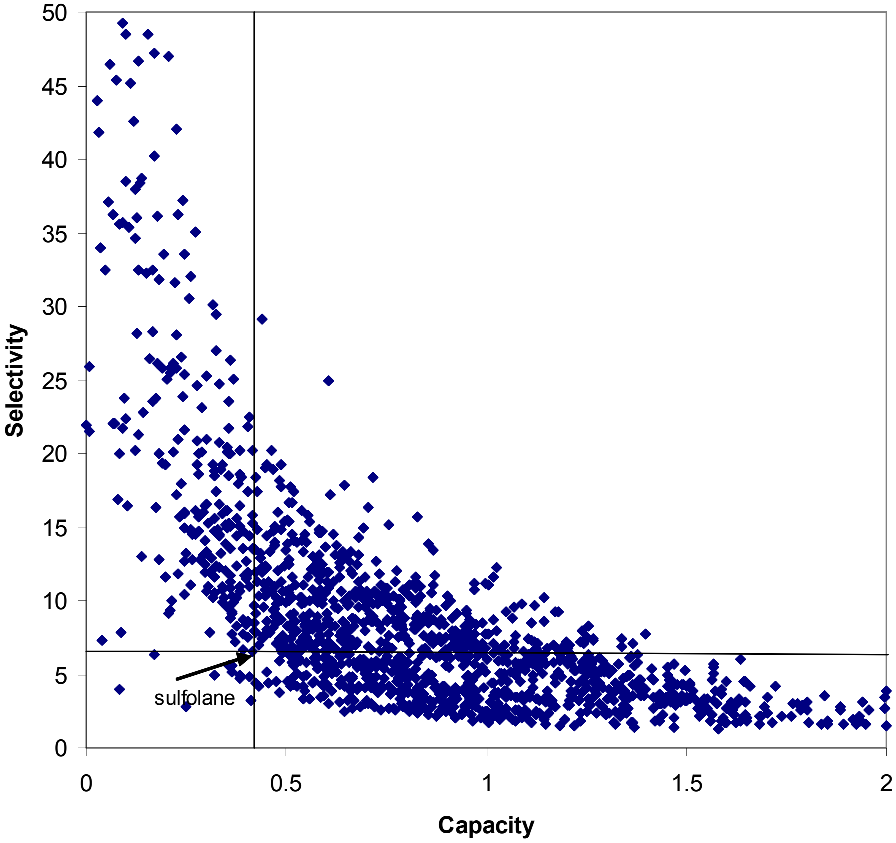

Fig 2: Selectivity vs Capacity of ILs

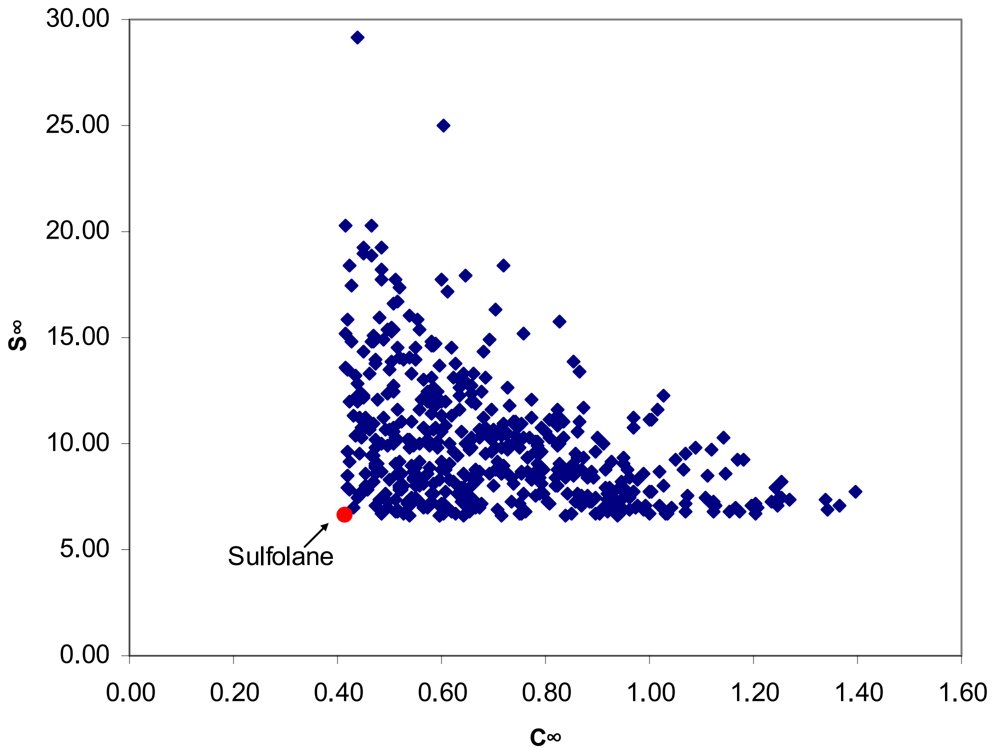

Fig-3: Solvents with Capacity & Selectivity higher than Sulfolane

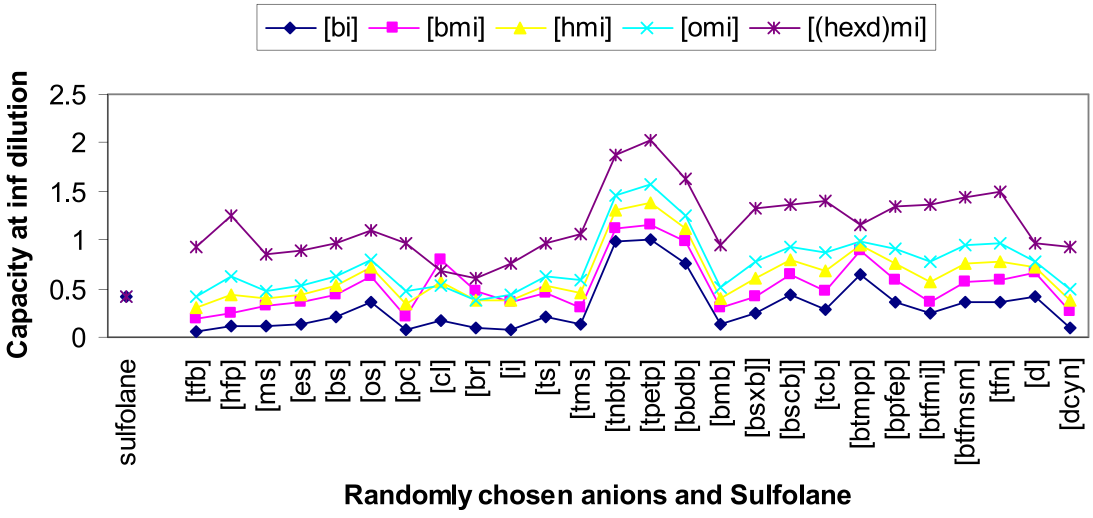

Fig 4-a: Capacity of imidazoliumium ILs consisting of cations

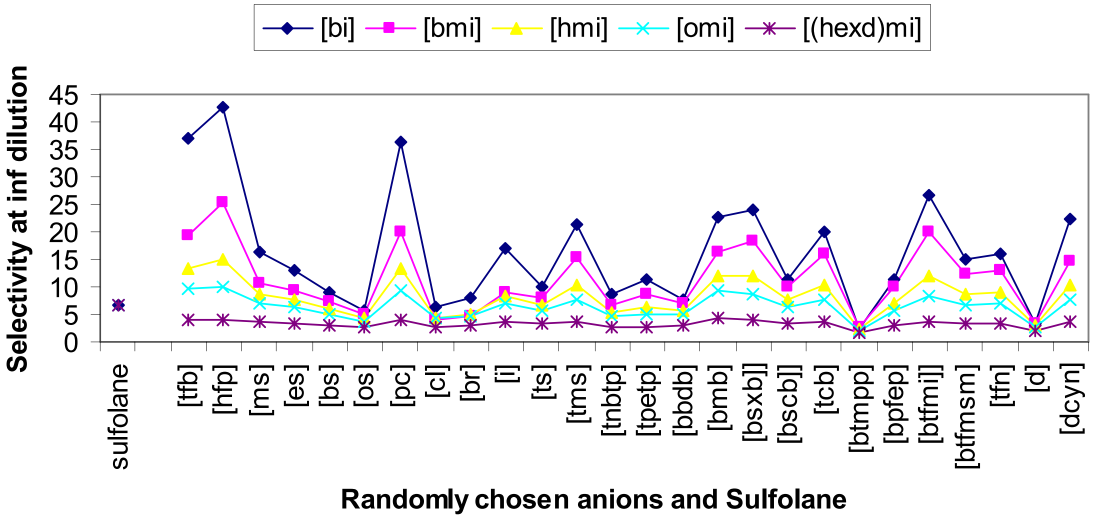

Fig 4-b: Selectivity of imidazoliumium ILs consisting of cations

In figure 4-a and 4-b selectivity and capacity of imidazolium based ILs are shown. These ILs are tailored by a cation from 1-butyl-imidazolium ([bi]), 1-butyl-3-methyl-imidazolium ([bmi]), 1-hexyl-3-methyl-imidazolium ([hmi]), 1-octyl-3-methyl-imidazolium ([omi]),and 1-hexadecyl-3-methyl-imidazolium ([(hexd)mi]) cations and an anions from the 26 anions listed in the appendix-1 with their symbols used for this study. It is observed that with the increased of chain length in the cation capacity increases whereas selectivity decreases.

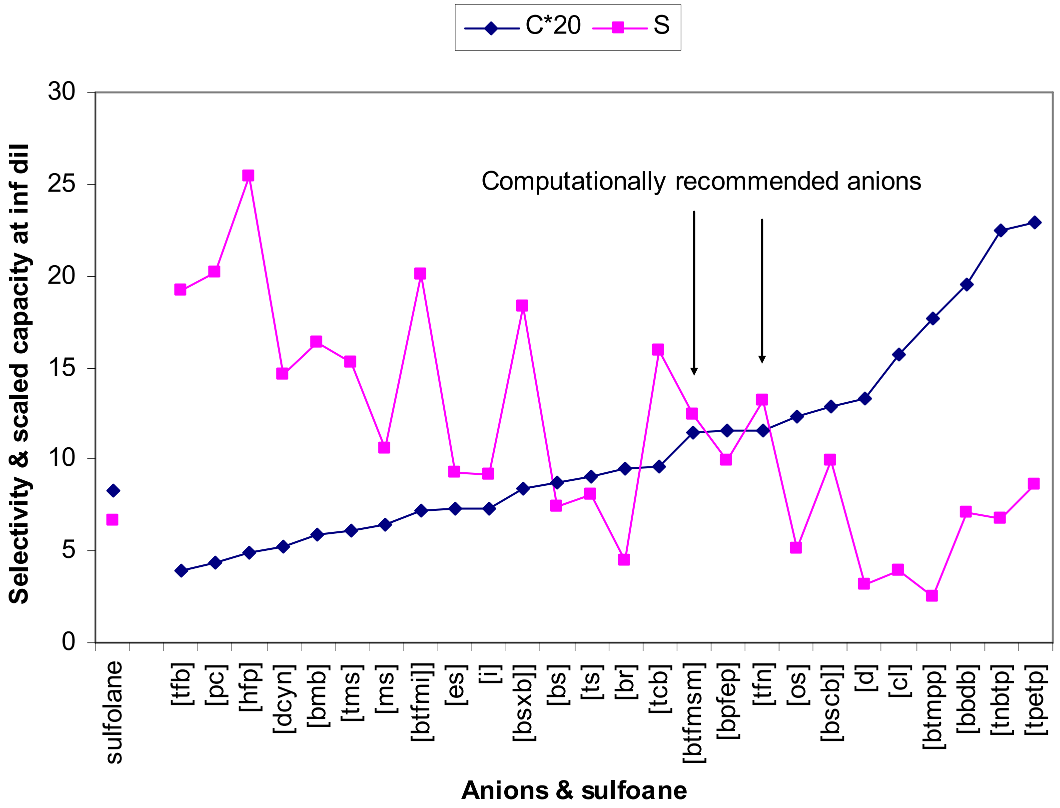

Fig 5: Trend of capacity & selectivity of a typical 1-butyl-3-methyl-imidazolium based ILs

To find suitables anions that work best with imidazolium cations, S^∞ and C^∞ of ILs based on 1-butyl-3-methyl imidazolium cations with different anions are shown in figure 5.The S^∞ and C^∞ of sulfolane are also shown for comparison. It is observed that the anions bis(trifluoromethylsulfonyl)methane([btfmsn]), bis-pentafluoroethyl-phosphinate ([bpfep]) , tf2n ([tfn]), bissalicylatoborate ([bscb]) gives higher S^∞ and C^∞ than sulfolane and are primarily recommended computationally. Anion

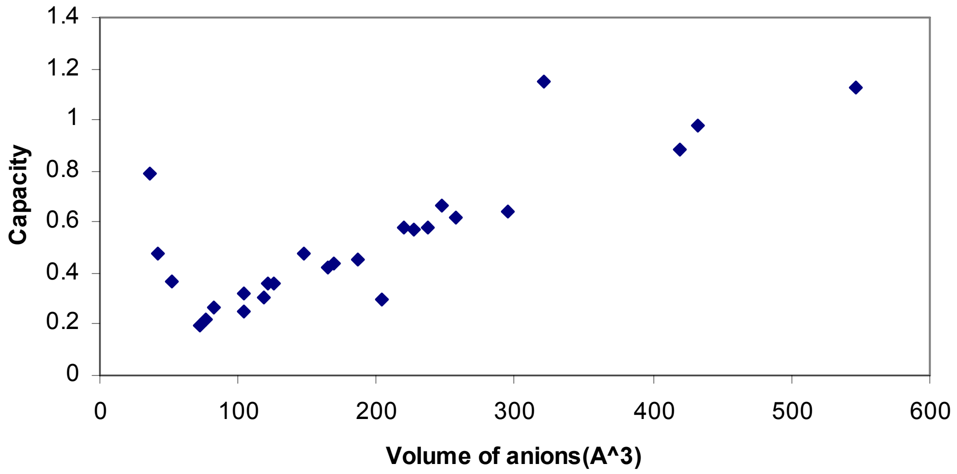

Fig 6-a: Capacity vs volume of anions with a typical imidazolium cation(1-butyl-1-methyl imidazolium)

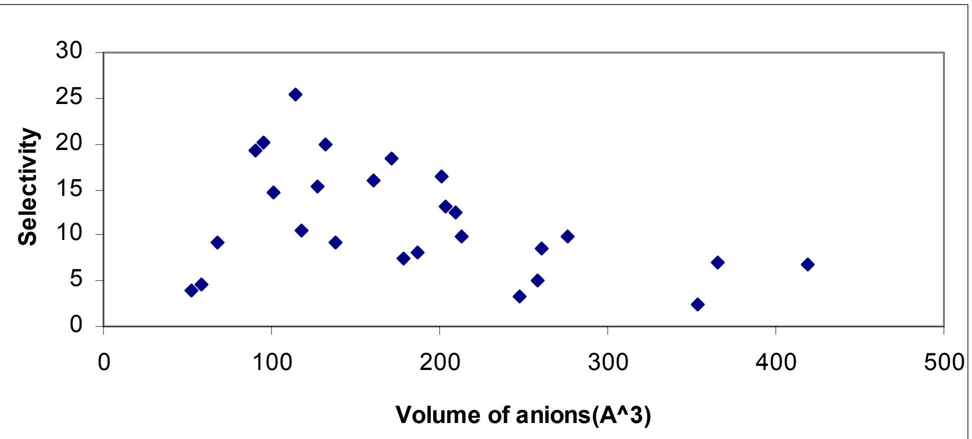

Fig 6-b Selectivity vs volume of anions with a typical imidazolium cation(1-butyl-1-methyl imidazolium)

Figure 6-a ad 6-b display the dependence of S^{∞} and C^{∞} on the volume of anions in 1-butyl-3-methyl-imidazolium based ionic liquids. Capacity increases with the increase of volume. Selectivity shows no straightforward relation with anion size.

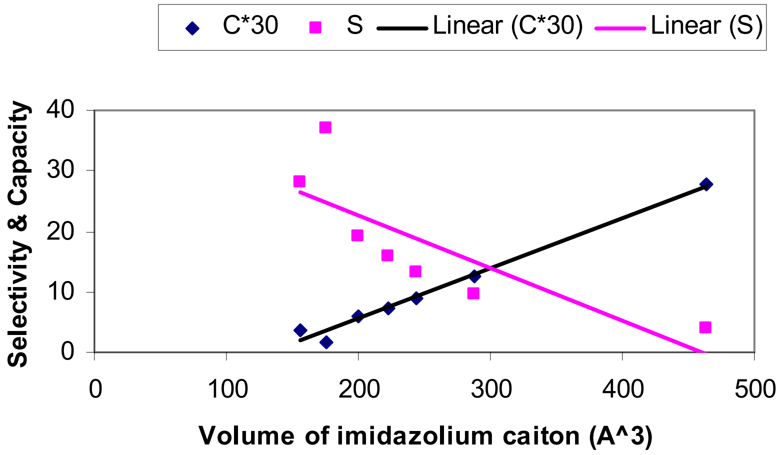

Fig 7: Effect of volume of cation on S & C of imidazolium-based ILs with tetrafluroborate as anion

Figure 7 displays the dependence of S^{∞} and C^{∞} on the volume of cations in thyl-imidazolium based ionic liquids with a typical tetrafluroborate anion. Capacity increases and selectivity decreases with the increase of volume . Since the ideal solvent has to display a good compromise between selectivity and capacity, a cation with moderate volume is considered suitable.

From figure 8, it is observed that temperature does not have any strong influence on the S^{∞} and C^{∞} values .Though with increased temperature, C^{∞} increases and S^{∞} decreases, but this change is not appreciable.

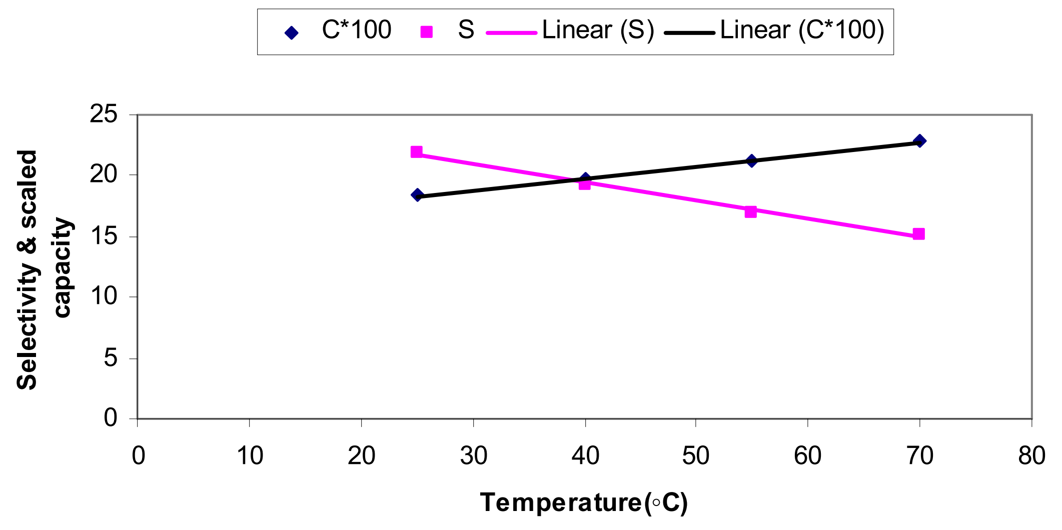

Fig 8:Effect of temperature on S & C of 1-butyl-3-methyl-imidazolium tetrafluroborate

Conclusion: There are many potential ionic liquids that display higher selectivity and capacity than sulfolane. C^{∞} increases with increase in alkyl chain length, volume of anion, volume of cation and temperature whereas S^{∞} decreases with increase in alkyl chain length, volume of cation and temperature. This behavior pattern is general for pyridinium, pyrrolidinium, phosphonium and ammonium cation based ILs. The effect of temperature is not prominent. It is observed that the anions bis(trifluoromethylsulfonyl)methane ([btfmsn]), bis-pentafluoroethyl-phosphinate([bpfep] :f2n([tfn]), bissalicylatoborate ([bscb]) with imidazolium based cations display a good compromise between S^{∞} and C^{∞} . Tetrafluroborate anion show very high selectivity and tris(pentafluoroethyl ·ifluorophosphate show very high capacity with imidazolium based cations.

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References:

[1] Michael Diedenhofen, Frank Eckert, and Andreas Klamt , Prediction of infinite dilution activity coefficients of organic compounds in ionic liquids using COSMO-RS, J. Chem. Eng. Data 2003, 48, 475-479.

[2] I. Clausen, PhD Thesis, Technische Universitat Berlin, 1999.

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[4] Eckert, F.; Klamt, A. Fast Solvent Screening via Quantum Chemistry: COSMO-RS Approach. AIChE J. 2002, 48, 369-385.

[5] F. Eckert and A. Klamt ,COSMO *therm*, Version C2.1 Release 01.04, COSMO *logic* GmbH & Co KG, Leverkusen, Germany, 2004.

[6] Eckert, F. and A. Klamt, " Fast Solvent Screening via Quantum Chemistry: COSMO-RS approach" AIChE Journal, 48,369 (2002).

Appendix-1

Symbols used in this study	Full name in cosmo database
[bi]	1-butyl-imidazolium0.cosmo
[bmi]	1-butyl-3-methyl-imidazolium0.cosmo
[hmi]	1-hexyl-3-methyl-imidazolium0.cosmo
[omi]	1-octyl-3-methyl-imidazolium0.cosmo
[(hexd)mi]	1-hexadecyl-3-methyl-imidazolium0.cosmo

Symbols used in this study	Full name in cosmo database
[tfb]	bf4.cosmo
[hfp]	pf6.cosmo
[ms]	methylsulfate.cosmo
[es]	ethylsulfate0.cosmo
[bs]	butylsulfate0.cosmo
[os]	octylsulfate0.cosmo
[pc]	clo4.cosmo
[cl]	cl.cosmo
[br]	br.cosmo
[i]	i.cosmo
[ts]	toluene-4-sulfonate.cosmo
[tms]	trifluoromethane-sulfonate.cosmo
[tnbtp]	tris(nonafluorobutyl)trifluorophosphate.cosmo
[tpetp]	tris(pentafluoroethyl)trifluorophosphate.cosmo
[bbdb]	bisbiphenyldiolatoborate.cosmo
[bmb]	bismalonatoborate.cosmo
[bsxb]]	bisoxalatoborate.cosmo
[bscb]]	bissalicylatoborate.cosmo
[tcb]	tetracyanoborate.cosmo
[btmpp]	bis(2,4,4-trimethylpentyl)phosphinate.cosmo
[bpfep]	bis-pentafluoroethyl-phosphinate.cosmo
[btfmi]]	bis(trifluoromethyl)imide.cosmo
[btfmsm]	bis(trifluoromethylsulfonyl)methane0.cosmo
[tfn]	tf2n0.cosmo
[d]	decanoate.cosmo
[dcyn]	dicyanamide.cosmo