

OPTIMIZED IONIC LIQUIDS FOR TOLUENE ABSORPTION

E. Ruiz, J. Bedia, V. Ferro, J. Palomar and J. J. Rodríguez.

Sección de Ingeniería Química (Departamento de Química Física Aplicada), Universidad Autónoma de Madrid, Cantoblanco, 28049 Madrid, Spain.

Corresponding author: elia.ruiz@uam.es

Keywords: Ionic liquids, Toluene, Vocs, Absorption

Introduction: Gases decontamination plays an important role in sustainable development of new industrial processes. VOCs are organic substances characterized by their high vapor pressure at ambient temperature and their low boiling point [1]. They are involved in photochemical reactions and entail the most common air pollutants emitted from chemical, petro-chemical, and allied industries, thus leading to serious environmental problems and financial losses. Room-temperature ionic liquids (ILs) have received much attention in the last few years as “green solvents”, and they are being investigated as substitutes of conventional organic solvents in industrial processes [2, 3]. The aim of this work was to introduce optimized ILs with adequate thermodynamic and kinetic properties for absorbing toluene.

Results and discussion: A computational study was first carried out to select the chemical structure of the IL for obtaining high toluene solubilities. Thus, a quantum-chemical COSMO-RS analysis was performed to analyze the solute-solvent intermolecular interactions determining the gas-liquid equilibrium data. Subsequently, a rational COSMO-RS screening of Henry’s law coefficient of toluene over 620 ionic liquids was performed to select potential high-capacity toluene solvents. The COSMO-RS screening results for Henry’s law constants of toluene in ILs are presented in Figure 1. It was observed that the ILs capacity for toluene absorption is mainly determined by the cation, while the anion plays a secondary role. On the other hand, it was found that, even when anion structure does not dominate the toluene absorption in ILs, highly fluorinated anions - such as [C6F18P-] and [NTF2-] - or chlorated anions - such as [FeCl4-] -, seem to improve the absorption capacity of toluene in ILs.

Predicted Henry’s law constants for toluene in different ILs were related to the excess enthalpy HE of the toluene-IL systems estimated by COSMO-RS, as it was shown in Figure 2. The higher solubilities of toluene in ILs are associated to the lowest endothermicity of the mixtures, where intermolecular interactions become less repulsive. Analyzing the computational screening results in Figure 2, it was able to find eight commercially available optimized ILs as potential solvents with promising features to be experimentally studied in the development of toluene absorption systems based on ILs.

The selected ILs were experimentally evaluated by thermodynamic and kinetic measurements of absorption phenomena. Toluene absorption equilibrium and kinetic experiments were carried out in a thermogravimetric analyzer at atmospheric pressure and three temperatures (293, 303 and 313 K) using around 20 mg of IL. Temperature of the sample was kept constant with a regulated external thermostat bath. Toluene inlet

concentration was set by saturation of a nitrogen flow through a saturator at controlled-temperature. Gas-liquid equilibrium data for toluene in ILs were obtained by setting the toluene partial pressure in toluene/N₂ gas flow and monitoring the sample weight increase. Gas-Liquid equilibrium was reached when no further weight changes were observed. Desorption was also carried out at the absorption temperature under dry nitrogen flow.

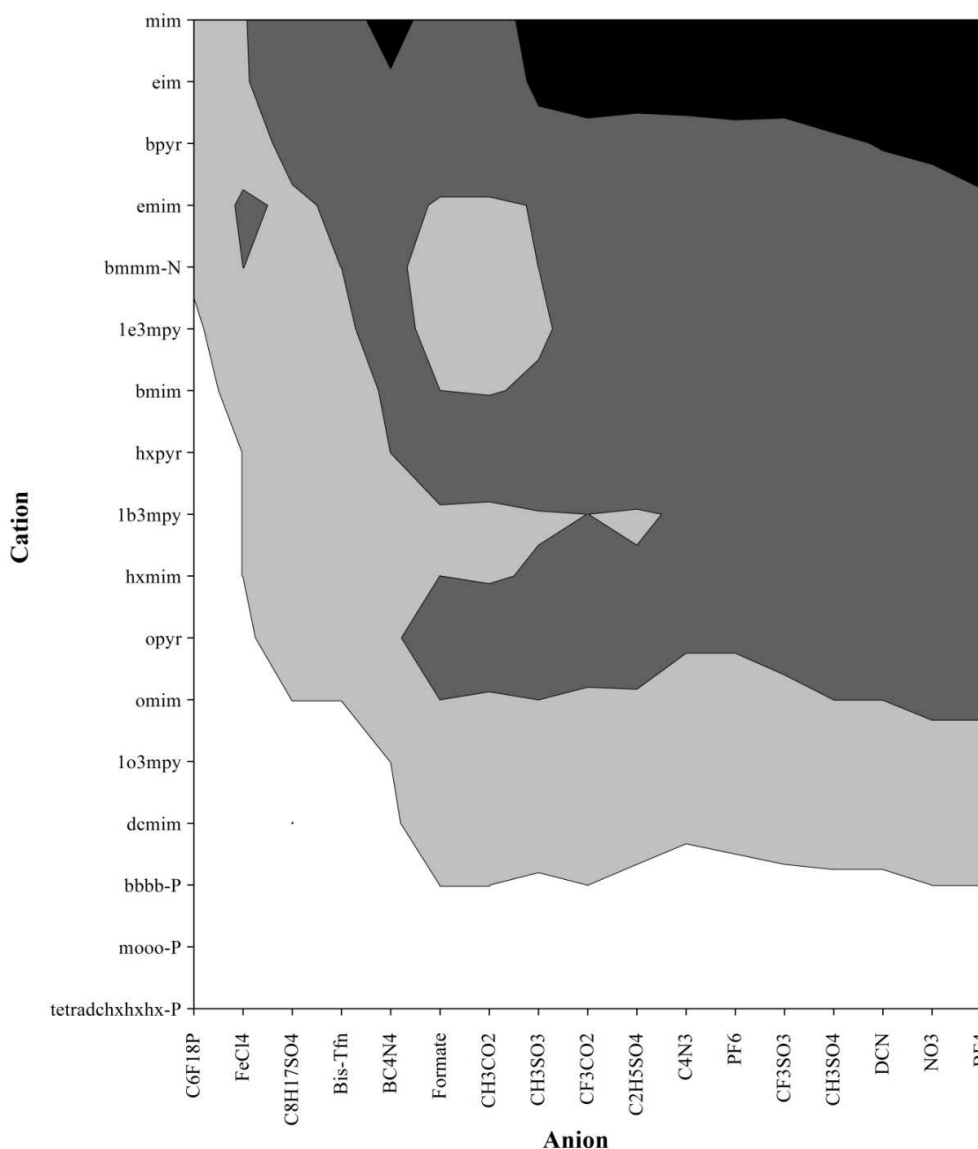


Figure 1. Screening of predicted Henry's law constants (MPa) for toluene in 272 ILs at T= 298.15 K calculated by COSMO-RS.

Table 1 summarizes the toluene effective diffusivity at different absorption temperatures. D increases with the absorption temperature, since the IL viscosity becomes lower. D values decrease with the length of the imidazolium-cations alkyl chain for ILs containing [NTf₂]. [dcmim][BF₄] shows comparable toluene effective diffusivities to the rest despite its much higher viscosity in all the analyzed temperature range.

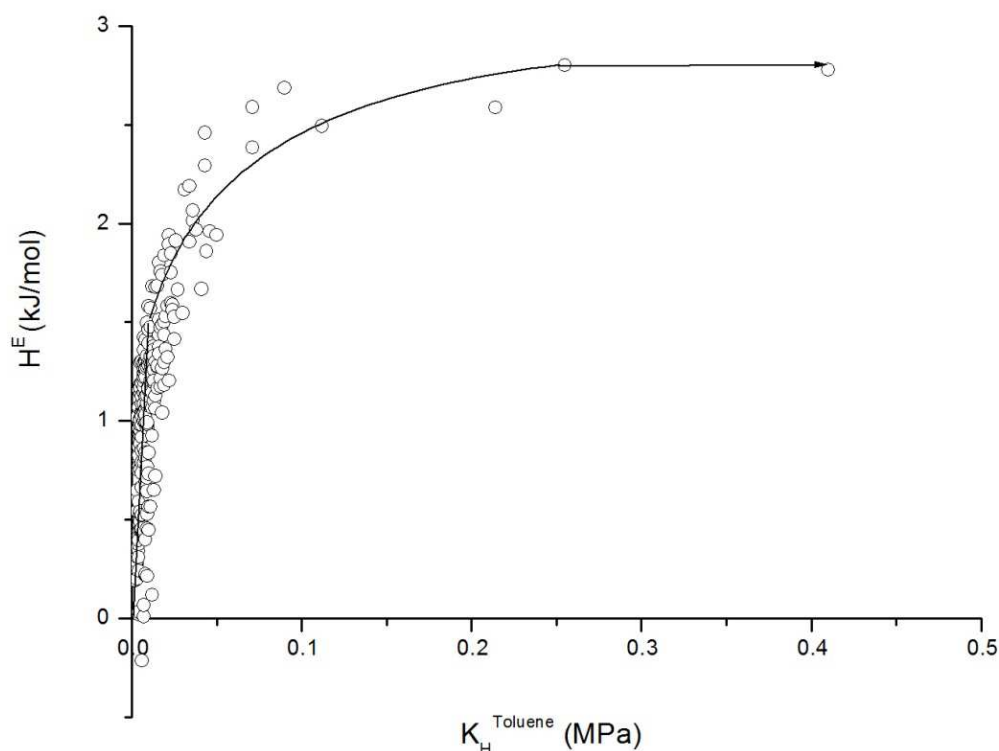


Figure 2. Henry's law constants related to the excess molar enthalpies for toluene in ILs at $T=298.15\text{K}$ computed by COSMO-RS.

An efficiency parameter was also proposed to analyze the IL behavior in the successive absorption-desorption cycles at fixed operation conditions. The efficiency parameter is defined as the real absorbed mass of toluene per time and per IL-mass.

Figure 3 shows the efficiency values of the tested task-specific ILs. Every IL shows the highest efficiency - higher absorption capacity - at the lowest test temperature (293 K). It means that a favorable thermodynamics dominates over the negative effects due to a slower kinetics (lower diffusivities).

Therefore, there exists a counterbalance effect with increasing temperature: an increase in the diffusivities and a decrease in the amount of toluene absorbed at saturation. The counterbalance effect displaces the maximum of efficiency to the lowest test temperature, while the minimum of the efficiency depends on the IL. Combining thermodynamic and kinetic effects, [dcnim][NTf2] proved to be the most suitable IL for toluene absorption at 293 and 313 K, while [emim][NTf2] was the most suitable IL at 303 K.

Table 1. Effective diffusion coefficients of Toluene in ILs at different temperatures.

IL	Temperature (K)	$D \times 10^{-11}$ (m^2/s)
----	-----------------	---

	293	3.92
[dcmim][NTf ₂]	303	6.05
	313	8.93
	293	3.84
[omim][NTf ₂]	303	6.15
	313	9.04
	293	3.91
[hxmim][NTf ₂]	303	7.12
	313	10.1
	293	4.61
[bmim][NTf ₂]	303	7.79
	313	10.6
	293	5.54
[emim][NTf ₂]	303	8.06
	313	10.7
	293	3.76
[dcmim][BF ₄]	303	6.13
	313	9.86
	293	6.50
[emim][C ₂ H ₅ SO ₄]	303	10.2
	313	11.0
	293	7.10
[bmim][BF ₄]	303	8.97
	313	10.8

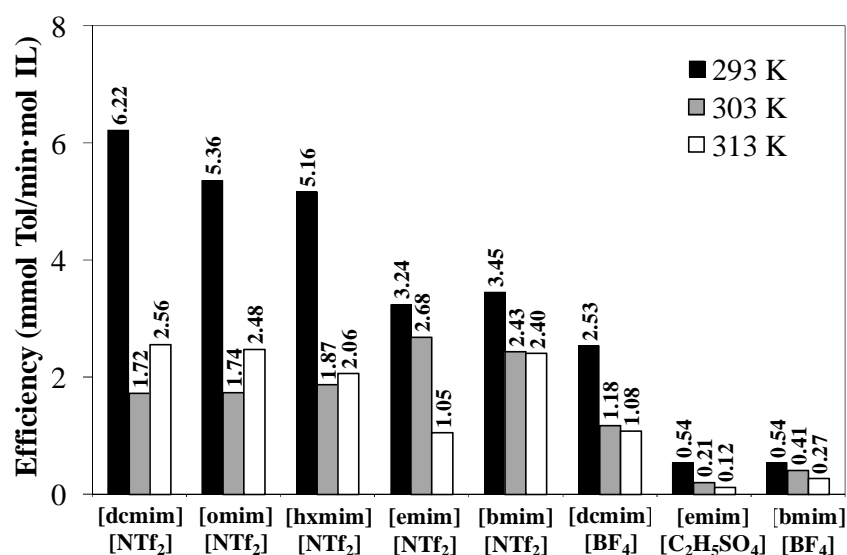


Figure 3. Efficiency of task-specific ILs for toluene absorption-desorption cycles at different temperatures (at a toluene partial pressure of 2.0 kPa for absorption).

Conclusions: A computational-experimental strategy research was developed to propose new ILs with favorable properties for toluene absorption. Considering both kinetic and thermodynamic aspects, we propose [dcmim][NTf₂] as the most suitable solvent among

the selected ILs for toluene absorption. This new toluene-[dcmim][NTf₂] absorption system would make feasible the replacement of the traditional toluene-sulfolane absorption systems at near room temperature and atmospheric pressure.

References:

1. P. Hunter, S. T. Oyama. Control of volatile organic compounds emissions, in: Conventional and Emerging Technologies. Wiley-Interscience, 2000.
2. K. R. Seddon, "Ionic liquids: A taste of the future, " Nature Mater., London, vol. 2, 2003.
3. P. Wasserscheid, T. Welton. Ionic Liquids in synthesis. Wiley-VCH Verlag GmbH & Co. KGaA, 2008.