

SOLVENT PROPERTIES OF IONIC LIQUID/LIQUID BIPHASE SYSTEMS BASED ON ABRAHAM'S LINEAR SOLVATION ENERGY RELATIONSHIPS

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Ionic liquids (ILs) as alternative solvents are a promising area of research in new 'green' technologies.¹ In contrast to traditional salts, ILs are composed of organic cations and inorganic or organic anions and possess melting points below 100 °C. Room temperature ionic liquids (RTIL) are a subset of ILs that have melting points below or at room temperature and have garnered the most attention as potential green solvents. Their potential "greenness" is due to the observation of no vapor pressure above the liquid surface caused by their ionic nature. ILs exist which are immiscible with organic solvents or with water and provide novel biphasic systems for liquid/liquid separations.

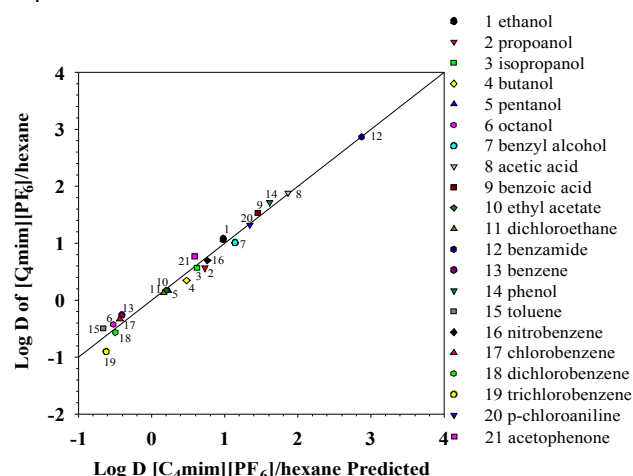
The physical properties of these ILs can be fine tuned to suit any particular set of parameters needed for a process. By changing the anion, the bulk properties of the ILs are affected with fine tuning of the properties controlled by changes in the cation. In order to choose the proper solvent for a particular application both the physical properties and solvent properties must be understood. Understanding the solvent interactions with solutes is vital to predicting solubilities and reaction mechanisms. These interactions between solvents and solutes have been studied by solvatochromatic methods using UV-vis spectra of a set of different reporter dye molecules to study polarity, hydrogen bond donor ability, and hydrogen bond acceptor ability of solvents.^{2,3} In order for a solute to be dissolved in a solvent, several different interaction modes can take place; such as cavity formation, hydrogen bonding, and polarity. One measure of solvent properties which accounts for multiple interactions uses linear solvation energy relationships (LSER) based on Abraham's generalized solvation equation.⁴

$$\text{Log } D = c + s\pi_2^H + a\Sigma\alpha_2 + b\Sigma\beta_2 + vV_x + rR_2$$

Log D is the distribution ratio of a solute between two phases and π_2^H , $\Sigma\alpha_2$, $\Sigma\beta_2$, V_x , R_2 are the solute parameters that correspond to polarity, hydrogen bond donor (HBD), hydrogen bond acceptor (HBA), volume, and molar refractivity, respectively. LSERs have been used to describe solute-solvent interactions in several solvent/water systems and liquid/gas systems.⁵⁻⁸

The LSER studies using IL/water systems illustrated that the solvent properties of the water phase dominate the results,⁹ therefore a substitute solvent with different solvent parameters should change the resulting properties of the system. A system comprising of hexane and IL should show different properties than those systems containing water. Hexane was chosen because of its negligible solubility in the ionic liquids and because the polarity and hydrogen bonding character of hexane are defined as zero; the results of the LSER should reflect the solvent properties of the ionic liquid. The results of this study show that the ionic liquids interact differently with solutes than IL/water systems. In the IL/water systems the volume parameter is the most important, meaning a cavity must first form in the phase for the solute to partition. In the IL/hexane systems,

the HBA parameter is the most important, meaning solutes with high HBD character will prefer the ionic liquid phase. The figure below is a plot of the theoretical Log of the distribution ratio versus the experiment data for a series of solutes in a [C₄mim][PF₆]/hexane biphasic system. The regression illustrates the fit of the experiment data with that obtained from Abraham's equation ($r^2=0.98$). A comparison of solvent properties between the IL/water system and new data using IL/hexane system, and with literature values from gas-liquid chromatography (GLC) and HPLC studies will be discussed.^{10,11} This comparison highlights the changes in the properties of the system by changing the comparator solvent, i.e. water and hexane, in the system, and leads to a better comprehension of the solvent properties and interactions present in different ionic liquids.



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