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LFER correlations for room temperature ionic liquids: Separation of equation coefficients into individual cation-specific and anion-specific contributions

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Abstract

Linear free energy relationship (LFER) correlations have been obtained for describing the gas-to-RTIL (room-temperature ionic liquid) and water-to-RTIL partition coefficients based on both the Abraham solvation parameter model and the Abraham model as modified by Goss. Each derived correlation contains six cation-specific and six anion-specific equation coefficients that were determined through regression analyses. The derived equations correlated the observed gas-to-RTIL and water-to-RTIL partition coefficient data to within 0.10 and 0.14 log units, respectively. Both models were found to have identical predictive/descriptive abilities. The 8 sets of cation-specific and 4 sets of anion-specific equation coefficients can be combined to yield equations capable of predicting the partition coefficients of solutes in 32 different RTILs. Two computational methods are proposed for determining additional ion-specific coefficients once more experimental data become available.

Keywords: Room-temperature ionic liquids; Partition coefficient; Solubility; Activity coefficient; Linear free energy relationship; Predictive method

1. Introduction

Room temperature ionic liquids (RTILs) have generated considerable interest in recent years because of their unique physical and chemical properties. New generation RTILs have become an increasingly popular solvent choice for the manufacture of nanomaterials and new pharmaceutical drug molecules, as resources for the controlled release of drug molecules in pharmaceutical formulations, as gas absorption agents, and as an extraction solvent system for the removal of organic contaminants from soil samples. RTILs are usually prepared by combining a poorly coordinating cation and anion to give a highly polar ionic liquid. Immiscibility of ionic liquids with supercritical carbon dioxide, linear hydrocarbons and several acyclic organic solvents makes RTILs ideally suited for synthetic preparations involving biphasic catalysis. Most (if not all) of the classic synthetic methods have been performed in RTILs. Much higher product yields were reported for RTILs than for the more conventional organic solvents. Moreover, ionic liquids have negligible vapor pressures, and their nonvolatility allows them to be used as solvent media in manufacturing processes requiring high vacuum.

Currently, synthetic procedures are known for making more than 200 different RTILs. Considerable time and effort is devoted to developing ionic liquids having specific solvent characteristics. The overall physical and solubilizing properties of ionic liquids result from the composite properties of the cation and anion. The anion usually controls the extent to which the RTIL is miscible with water. The cation of an ionic liquid is generally a bulky organic structure (alkylimidazolium, alkylpyridinium, alkylphosphonium, quaternary ammonium) with low symmetry. Cation type and size/symmetry affect the ionic liquid's melting point temperature. The melting point temperature is important because it represents the lower limit of liquidity, and when combined with thermal stability, it defines the temperature interval that the RTIL can be used as a solvent. Our understanding of the properties of ionic liquids has improved considerably in recent years; however, we are not yet to the point where we can "tailor make" ionic liquids having specific physical and chemical properties.

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The present study continues our systematic search for methods to estimate the activity coefficients of organic solutes in RTILs, and the partition for the transfer of solutes from both water-to-RTILs and from gas-to-RTILs. Previously, Acree, Abraham and co-workers reported mathematical correlations based on the Abraham general solvation parameter model for the gas-to-solvent, *K*, and water-to-solvent partition coefficients, *P*, for ten different anhydrous RTILs [1–3] and for two practical water-to-RTIL partition systems [4]. The ten anhydrous water-to-RTIL correlations describe "hypothetical" partitions, and the partition coefficient is calculated as the molar solubility ratio for the solute dissolved in both neat solvents. Practical partitions, on the other hand, represent true equilibrium partitioning between the water-saturated organic phase and an aqueous phase that is saturated with the organic solvent. Correlations derived from the Abraham model described the log *K* and log *P* data for 10 RTILs to within average standard deviations of ±0.086 log units and ±0.129 log units, respectively. The quoted values represent the average value of the standard deviations of the individual log *K* and log *P* correlations of the 10 RTILs.

In a follow-up study, Sprunger et al. [5] modified the Abraham solvation parameter model

$$\log P = c + (e_{\text{cation}} + e_{\text{anion}})E + (s_{\text{cation}} + s_{\text{anion}})S + (a_{\text{cation}} + a_{\text{anion}})A + (b_{\text{cation}} + b_{\text{anion}})B + (v_{\text{cation}} + v_{\text{anion}})V \quad (1)$$

$$\log K = c + (e_{\text{cation}} + e_{\text{anion}})E + (s_{\text{cation}} + s_{\text{anion}})S + (a_{\text{cation}} + a_{\text{anion}})A + (b_{\text{cation}} + b_{\text{anion}})B + (l_{\text{cation}} + l_{\text{anion}})L \quad (2)$$

by rewriting each of the six solvent equation coefficients as a summation of their respective cation and anion contribution. The dependent variables in Eqs. (1) and (2) are solute descriptors as follows: *E* and *S* refer to the excess molar refraction in units of $(\text{cm}^3\,\text{mol}^{-1})/10$ and dipolarity/-polarizability descriptors of the solute, respectively, *A* and *B* are measures of the solute hydrogen-bond acidity and basicity, *V* is the McGowan volume in units of $(\text{cm}^3\,\text{mol}^{-1})/100$ and *L* is the logarithm of the gas-to-hexadecane partition coefficient at 298 K. As part of the study the authors calculated equation coefficients for 8 cations and 4 anions using a database that contained 584 experimental log *K* and 571 experimental log *P* data points. No loss in predictive accuracy was observed by separating the equation coefficients into individual cation-specific and anion-specific values. The calculated coefficients described the 584 experimental log *K* and 571 experimental log *P* values to within a standard deviation of S.D. = 0.102 and 0.135 log units, respectively.

The major advantage of splitting the equation coefficients into individual cation-specific and anion-specific contributions is that one can make predictions for more RTILs. Normally one needs partition coefficient data for 40–50 solutes dissolved in a given RTIL to develop an Abraham model correlation. By combining all of the experimental data for an RTIL containing lets say either a 3-methyl-1-ethylimidazolium cation, $[\text{MEIm}]^+$, and tetrafluoroborate, $[\text{BF}_4]^-$, it may be possible to calculate $[\text{MEIm}]^+$-specific and $[\text{BF}_4]^-$-specific equations when there was too few data points for the $[\text{MEIm}]^+[\text{BF}_4]^-$ ionic liquid to develop a meaningful correlation. The computational methodology that we proposed permits us to calculate more ion-specific equation coefficients as more experimental data becomes available in the future, and the basic computational methodology can be applied to LFERs that employ different kinds/types of solute descriptors.

Since the publication of our last paper on RTILs, experimental Henry's law constant data have been reported for hydrogen, nitrogen, methane and ethane dissolved in several of the RTILs for which we had calculated both cation-specific and anion-specific equation coefficients [6–14]. The new experimental data, when compared against predicted values based on our cation-specific and anion-specific equation coefficients, differed by as much as 0.3 log units. The calculated differences between these predicted and experimental values prompted us in this communication to re-evaluate how the *c*-constant should be treated. The *c*-constant normally relates to the value of log *P* (Eq. (1)) and log *K* (Eq. (2)) for a solute with zero values for all descriptors. It also contains a contribution for the particular standard state used in the definition of the partition coefficient as discussed elsewhere [15,16]. For very small gaseous solutes, like H_2 and N_2, the *c*-constant can be the dominant term. In the present communication we explore the effect of separating the *c*-constant into a cation-specific and anion-specific contribution, and apply our basic computational methodology to a second linear free energy relationship (LFER) model, namely the Abraham model as modified by Goss [17–21]. The latter LFER model uses the five Abraham solute descriptors of *S*, *A*, *B*, *V* and *L* in both the log *P* and log *K* correlations. The Abraham *E* solute descriptor is eliminated.

2. Data set and computational methodology

The majority of the experimental log *P* and log *K* values were reported in the Supporting information that accompanied our last paper on RTILs [5]. The database contained log *K* and log *P* values for solutes dissolved in 4-methyl-*N*-butylpyridinium tetrafluoroborate ($[\text{BMPy}]^+[\text{BF}_4]^-$), 1-methyl-3-ethylimidazolium *bis*(trifluoromethylsulfonyl)imide ($[\text{MEIm}]^+[(\text{Tf})_2\text{N}]^-$), 1,2-dimethyl-3-ethylimidazolum *bis* (trifluoromethylsulfony)imide ($[\text{M}_2\text{EIm}]^+[(\text{Tf})_2\text{N}]^-$), 1-methyl-3-butylimidazolium *bis*(trifluoromethylsulfony)imide ($[\text{MBIm}]^+[(\text{Tf})_2\text{N}]^-$), 1-methyl-3-hexylimidazolium *bis*(trifluoromethylsulfony)imide ($[\text{MHIm}]^+[(\text{Tf})_2\text{N}]^-$), trimethylbutylammonium *bis*(trifluoromethylsulfony)imide ($[\text{M}_3\text{BAm}]^+[(\text{Tf})_2\text{N}]^-$), 1-methyl-3-octylimidazolium tetrafluoroborate ($[\text{MOIm}]^+[\text{BF}_4]^-$), 1-methyl-3-butylimidazolium hexafluorophosphate ($[\text{MBIm}]^+[\text{PF}_6]^-$), 1-methyl-3-ethylimidazolium ethylsulfate ($[\text{MEIm}]^+[\text{EtSO}_4]^-$), 1-butyl-3-methylimidazolium tetrafluoroborate ($[\text{BMIm}]^+[\text{BF}_4]^-$), *N*-ethylpyridinium *bis*(trifluoromethylsulfony)imide ($[\text{NEPy}]^+[(\text{Tf})_2\text{N}]^-$), 1-methyl-3-hexylimidazolium tetrafluoroborate ($[\text{MHIm}]^+[\text{BF}_4]^-$), 1-methyl-3-ethylimidazolium tetrafluoroborate ($[\text{MEIm}]^+$