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Activity coefficients at infinite dilution for organic solutes dissolved in two 1,2,3-tris(diethylamino)cyclopenylium based room temperature ionic liquids

Abdelaziz Chikh Baelhadj [a], Fabrice Mutelet [b], Bihan Jiang [c], William E. Acree Jr. [c,*]

[a] Laboratoire de Thermodynamique et de Modélisation Moléculaire, Faculté de Chimie, USTHB, BP 32 El-Alia, 16111, Bab-Ezzouar, Alger, Algeria
[b] Université de Lorraine, Laboratoire de Réactions et Génie des Procédés (UPR CNRS 3349), 1 rue Grandville, BP 20451, 54001 Nancy, France
[c] Department of Chemistry, 1155 Union Circle #305070, University of North Texas, Denton, Texas 76203-5017, USA

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ABSTRACT

Infinite dilution activity coefficients and gas-to-liquid partition coefficients have been determined for at least 45 different organic solutes of varying polarity and hydrogen-bonding character dissolved in anhydrous 1,2,3-tris(diethylamino)cyclopropenylium dicyanamide, ($[TDC]^+[DCA]^-$), and 1,2,3-tris(diethylamino)cyclopropenylium bis(trifluoromethylsulfonyl)imide, ($[TDC]^+[Tf_2N]^-$). The measured infinite dilution activity coefficients were used to calculation selectivity values for various practical separation problems. Computations showed ($[TDC]^+[DCA]^-$) should afford better performance in hexane/benzene and hexane/pyridine separation problems than sulfolane and *N*-methyl-2-pyrrolidone. Abraham model correlations were derived for predicting solute transfer into both ($[TDC]^+[DCA]^-$) and ($[TDC]^+[Tf_2N]^-$) from water and from the gas phase. The derived correlations describe the observed solute transfer partition coefficients to within 0.13 (or fewer) log units.

1. Introduction

Room temperature ionic liquids (RTILs) are becoming increasingly utilized as stationary phase liquids in gas-liquid chromatographic separations because of their low volatility, high thermal stability and wide liquid phase temperature range. Ionic liquid solvents afford excel selectivity towards specific classes of organic compounds. Numerous publications have reported selectivity values regarding the separation of hexane and 1-hexene [1–4], of hexane and benzene [3,5–7], of hexane and pyridine [6], of hexane from thiophene [6], of cyclohexane from benzene [7,8], cyclohexane from thiophene [8], and of ethylbenzene from styrene [1,4], just to name a few.

Most of the published studies have involved mono-cation RTIL solvents [1–15]; however, there have been a few studies documenting the applicability and characterization of dication RTILs [16–22] and trication RTILs [22–24] as gas-liquid chromatographic stationary phases. As representative examples Ragonese and coworkers [16] successfully demonstrated the separation of fatty acid methyl esters in diesel blends using a dicationic 1,9-di(3-vinylimidazoium)nonane di(bis(trifluoromethylsulfonyl)imide) RTIL stationary phase. The large polarity of the RTIL stationary phase facilitated the separation of the fatty acid methyl esters from the less-retained hydrocarbons present in the different diesel blends, and thus eliminating the time-consuming pre-analysis sample preparation treatment that otherwise would have been required in the analysis of the complex sample matrices. Zhang et al. [17] evaluated a series of dicationic RTIL-based stationary phases as secondary columns for the separation of nonpolar aliphatic hydrocarbons in kerosene using two-dimensional gas-liquid chromatography. For the RTILs studied the authors found that the dispersive interactions played an important role in the resolution of nonpolar aliphatic hydrocarbons by the RTIL-based stationary phases. In both studies the Abraham solvation parameter model was employed to characterize the solubilizing properties of the RTIL solvents.

The Abraham solvation parameter model [25,26] enables one to quantify the dipolarity/polarizability, hydrogen-bonding character (both H-bond acidity and basicity) and dispersion forces exhibited by solvent molecules in regards to their molecular interactions with dissolved solute probe molecules. The model has been used extensively in the development of linear free energy relationships that describe solute transfer into traditional organic solvents and into RTIL solvents from both the gas phase and from water. Determination of a mathematical Abraham model equation requires experimental activity coefficient or partition coefficient data for 40 or so different solutes dissolved in a given solvent. Once derived the mathematical correlations can be used to predict gas-to-liquid partition coefficients, water-to-liquid partition coefficients and infinite dilution activity coefficients for >5000 different organic and inorganic solute molecules in the given solvent. The model's predictive capability allows one to select solvents capable of achieving a desired chemical separation; however, one must needs Abraham model

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[*] Corresponding author.
E-mail address: acree@unt.edu (W.E. Acree).

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correlations for a large number of chemically diverse liquid solvents. This includes both traditional organic solvents and RTIL solvents. Abraham model correlations are available for >100 traditional organic solvents [26–28] and for >70 different mono-cationic RTIL solvents [9–15,21,22]. Correlations are available for relatively few multifunctional monocationic RTIL [22], dicationic [21,22] and tricationic [22,23] RTIL solvents.

To address the scarcity of infinite dilution activity coefficients, $\gamma^{\infty}_{\text{solute,RTIL}}$, and gas-to-liquid partition coefficients, *K*, for solutes dissolved in multifunctional monocationic RTIL solvents, we have measured values of both of these thermodynamic quantities for at least 45 organic solutes dissolved in 1,2,3-tris(diethylamino)cyclopropenylium dicyanamide ($[\text{TDC}]^+[\text{DCA}]^-$) and 1,2,3-tris(diethylamino)cyclopropenylium bis(trifluoromethylsulfonyl)imide ($[\text{TDC}]^+[\text{Tf}_2\text{N}]^-$) in the temperature range from 323.15 K to 373.15 K. Results of these experimental measurements are used to derive Abraham model predictive correlations for solutes dissolved in the two fore-mentioned RTIL solvents.

2. Apparatus and experimental procedure

2.1. Materials and reagents

The ionic liquids 1,2,3-tris(diethylamino) cyclopropenylium dicyanamide ($[\text{TDC}]^+[\text{DCA}]^-$) and 1,2,3-tris(diethylamino)cyclopropenylium bis(trifluoromethylsulfonyl)imide ($[\text{TDC}]^+[\text{Tf}_2\text{N}]^-$) were purchased from SigmaAldrich with a purity of 97% by mass. The structures of investigated ionic liquids are presented in Fig. 1. The ionic liquids were dried for >24 h at 323.15 K under reduced pressure to remove volatile impurities and trace water. Most of the solutes were purchased from Sigma Aldrich and Fluka and the purities were >99.5% in mass percent, and were used without further purification because the GLC technique separated any impurities on the column.

2.2. Vibrating-tube densimeter and density measurement

Densities of ILs were measured using an Anton Paar DMA 60 digital vibrating-tube densimeter, with a DMA 512P measuring cell in the temperature range from 293.15 to 343.15 K at atmospheric pressure. The detailed procedure was given in our previous work [29]. All experimental data are given in Table 1.

2.3. Chromatographic instrumentation and experimental procedures

The experimental procedures used for the determination of activity coefficients were described in previous works [23,29]. A Bruker 450 gas chromatograph equipped with a heated on-column injector and a thermal conductivity detector (TCD) detector was used for the measurements. The GC operating conditions are given in Table 2. The dead time of the packed column was determined using air. Helium carrier gas flow rate was measured using an Alltech Digital Flow Check Mass Flowmeter. The temperature of the oven was measured with a Pt 100 probe and controlled within 0.1 K. Data were collected and treated with Galaxie software (Varian).

Table 1
Densities (ρ) for the ($[\text{TCD}]^+$ $[\text{Tf}_2\text{N}]^-$) and ($[\text{TCD}]^+$ $[\text{DCA}]^-$) as a function of temperature at $P = 101.33$ kPa.[a]

T/K	$\rho/(\text{kg}\cdot\text{m}^{-3})$
($[\text{TCD}]^+[\text{DCA}]^-$)	
293.15	1008.1
303.15	1000.8
313.15	995.7
323.15	988.8
333.15	983.1
343.15	977.1
($[\text{TCD}]^+$ $[\text{Tf}_2\text{N}]^-$)	
293.15	1266.5
303.15	1270.2
313.15	1260.2
323.15	1252.2
333.15	1243.9
343.15	1235.2

[a] Standard uncertainties are $u(\rho) = 0.0001$ $\text{g}\cdot\text{cm}^{-3}$, $u(T) = 0.1$ K, $u(P) = \pm 0.1$ kPa.

The preparation of columns was described in detail in our previous publications [23,29]. Packed columns of 1-m length containing between 30 and 40% RTIL stationary phase coated onto a 60–80 mesh Chromosorb WHP support material were prepared by a rotary evaporation method. Briefly, the desired RTIL was dissolved in ethanol in the presence of a precise mass of Chromosorb WHP. Ethanol was then removed from the mixture using rotary evaporation. The support was equilibrated at 343 K under vacuum during 6 h. Then, the conditioning of the packed columns was performed at 373 K over 12 h using a gas flow rate of 20 cm^3 min^{-1}.

3. Theoretical basis for thermodynamic quantities

The activity coefficient at infinite dilution of solute 1 in RTIL 2 ($\gamma^{\infty}_{1,2}$) is calculated from the following expression [30]:

$$\ln\gamma^{\infty}_{1,RTIL} = \ln\left(\frac{n_{RTIL}\,RT}{V_N P^o_1}\right) - P^o_1\cdot\frac{B_{11}-V^o_1}{RT} + \frac{2B_{13}-V^{\infty}_1}{RT}\cdot J\cdot P_o \quad (1)$$

where n_{RTIL} is the mole number of the RTIL stationary phase component inside the column, *R* is the ideal gas constant, *T* denotes the temperature of the oven, V_N is the net retention volume, B_{11} refers to the second virial coefficient of the solute in the gaseous state at temperature T, B_{13} represents the mutual virial coefficient between the solute 1 and the carrier gas helium (denoted 3), and P^0_1 is the probe vapor pressure at temperature *T*.

The retention data were used to calculate partition coefficients of the gas-to-RTIL partition coefficients, *K*, used in the LSER approach were calculated using the expression:

$$K = \frac{RT}{\gamma^{\infty}_{solute,RTIL}\,p_{solute}{}^{o}\,V_{RTIL}} \quad (2)$$

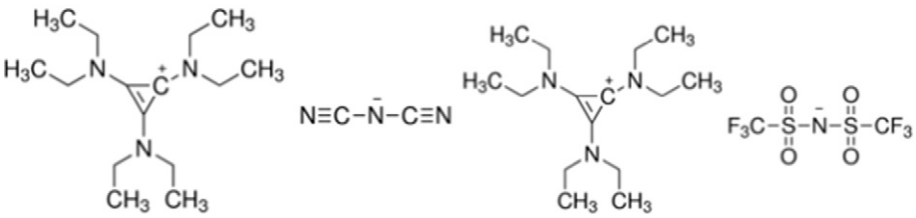

Fig. 1. Molecular structures of cations in the IL.