



Activity coefficients at infinite dilution for organic solutes dissolved in two 1-alkylquinuclidinium bis(trifluoromethylsulfonyl)imides bearing alkyl side chains of six and eight carbons



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ABSTRACT

Infinite dilution activity coefficients and gas-to-liquid partition coefficients are reported for 47 and 45 organic probe molecules dissolved in 1-hexylquinuclidinium bis(trifluoromethylsulfonyl)imide ([Quin6]⁺[Tf₂N]⁻) and 1-octylquinuclidinium bis(trifluoromethylsulfonyl)imide ([Quin8]⁺[Tf₂N]⁻), respectively, as determined by inverse gas chromatography in the temperature range of 313 K to 353 K. The measured partition coefficient data were converted to water-to-liquid partition coefficients using standard thermodynamic relationships and published gas-to-water partition coefficient data. Both sets of calculated partition coefficient data for each ionic liquid solvent were analyzed in terms of the Abraham general solvation model. Mathematical correlations derived from the Abraham model described the measured partition coefficient data to within 0.14 or fewer log units.

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1. Introduction

Increased utilization of organic solvents in chemical separations and synthetic processes, coupled with the more stringent governmental regulations regarding chemical wastes, has prompted the manufacturing sector to seek chemical replacements for the more toxic and harmful solvents. Of the replacements studied to date, ionic liquids (ILs) have shown considerable promise as media for preparing many different classes of organic compounds, as dissolving media for lignocellulosic biomass, as an entrainer in extractive distillations, as an extractant for single-drop micro-extractions, as a sorbent for gas capture and sequestration, and as a stationary phase for gas-liquid chromatographic separations. Key features such as low melting temperatures, negligible vapor pressures, high thermal and chemical stabilities, wide liquid temperature ranges, and immiscibility with many organic solvents facilitate the use of ILs in many industrial applications. These properties can be fine-tuned through the judicious combination of cation-anion pairs and by installation of functional groups onto the cation or anion. For example, the miscibility of ILs with organic solvents or water can be modified by modifying the alkyl chain length on the cation and by changing the nature of the counter anion. Considerable attention has

been given in recent years towards developing mathematical expressions for estimating the physical properties and solubilizing characteristics of IL solvents based on both group contribution methods and quantitative structure-property relationships.

Our contributions in the area of IL research have been to publish experimental physical property measurements and thermodynamic data for both neat ILs [1–3] and for solutes dissolved in IL solvents [4–21]. The latter measurements have led to the development of IL-specific Abraham model correlations [4–12,22–24]:

$$\log P = c_{p,il} + e_{p,il} \cdot E + s_{p,il} \cdot S + a_{p,il} \cdot A + b_{p,il} \cdot B + v_{p,il} \cdot V \quad (1)$$

$$\log K = c_{k,il} + e_{k,il} \cdot E + s_{k,il} \cdot S + a_{k,il} \cdot A + b_{k,il} \cdot B + l_{k,il} \cdot L \quad (2)$$

Abraham model correlations containing ion-specific equation coefficients [24–28]:

$$\log P = c_{p,cation} + c_{p,anion} + (e_{p,cation} + e_{p,anion})E + (s_{p,cation} + s_{p,anion})S + (a_{p,cation} + a_{p,anion})A + (b_{p,cation} + b_{p,anion})B + (v_{p,cation} + v_{p,anion})V \quad (3)$$

$$\log K = c_{k,cation} + c_{k,anion} + (e_{k,cation} + e_{k,anion})E + (s_{k,cation} + s_{k,anion})S + (a_{k,cation} + a_{k,anion})A + (b_{k,cation} + b_{k,anion})B + (l_{k,cation} + l_{k,anion})L \quad (4)$$

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and Abraham model correlations containing fragment-group values [29]

$$\log P = \sum_{\text{group}} n_i c_{p,i} + \sum_{\text{group}} e_{p,i} n_i E + \sum_{\text{group}} s_{p,i} n_i S + \sum_{\text{group}} a_{p,i} n_i A + \sum_{\text{group}} b_{p,i} n_i B + \sum_{\text{group}} v_{p,i} n_i V + (c_{p,\text{anion}} + e_{p,\text{anion}} E + s_{p,\text{anion}} S + a_{p,\text{anion}} A + b_{p,\text{anion}} B + v_{p,\text{anion}} V) \quad (5)$$

$$\log K = \sum_{\text{group}} n_i c_{k,i} + \sum_{\text{group}} e_{k,i} n_i E + \sum_{\text{group}} s_{k,i} n_i S + \sum_{\text{group}} a_{k,i} n_i A + \sum_{\text{group}} b_{k,i} n_i B + \sum_{\text{group}} l_{k,i} n_i L + (c_{k,\text{anion}} + e_{k,\text{anion}} E + s_{k,\text{anion}} S + a_{k,\text{anion}} A + b_{k,\text{anion}} B + l_{k,\text{anion}} L) \quad (6)$$

for predicting the logarithms of solute partition coefficients into anhydrous IL solvents from both water ($\log P$) and from the gas phase ($\log K$). In Eqs. (5) and (6), n_i denotes the number of times that the given fragment group appears in the cation and the summations extend over all fragment groups.

Predictions based on Eqs. (1)–(6) require knowledge of the solute descriptors (upper case letters) and equation coefficients/fragment group values (lower case letters) for the solutes and ILs of interest. Solute descriptors are available for more than 5000 different organic and inorganic compounds, and are defined as follows: the solute excess molar refractivity in units of ($\text{cm}^3 \text{mol}^{-1}$)/10 (**E**), the solute dipolarity/polarizability (**S**), the overall or summation hydrogen-bond acidity and basicity (**A** and **B**, respectively), the McGowan volume in units of ($\text{cm}^3 \text{mol}^{-1}$)/100 (**V**), and the logarithm of the gas-to-hexadecane partition coefficient at 298 K (**L**). To date, we have reported IL-specific equation coefficients for more than 35 different ILs (Eqs. (1) and (2)), ion-specific equation coefficients for 41 different cations and 16 different anions (Eqs. (3) and (4)), and numerical group values for 12 cation fragments (CH_3- , $-\text{CH}_2-$, $-\text{O}-$, $-\text{O}-\text{N}_{\text{cyclic}}$, $-\text{OH}$, $\text{CH}_{2\text{cyclic}}$, $\text{CH}_{\text{cyclic}}$, C_{cyclic} , N_{cyclic} , $>\text{N}<^+$, $>\text{P}<^+$, and $>\text{S}<^+$) and 9 individual anions (TF_2N^- , PF_6^- , BF_4^- , EtSO_4^- , OCSO_4^- , SCN^- , CF_3SO_3^- , AcF_3^- , and $(\text{CN})_2\text{N}^-$) (Eqs. (5) and (6)). The 41 different cation-specific and 16 different anion-specific equation coefficients can be combined to permit the estimation of $\log P$ and $\log K$ values for solutes in a total of 656 different ILs (i.e., 41×16). The number of ion-specific equation coefficients and fragment group values is expected to increase as additional experimental data become available for functionalized IL solvents.

In the present investigation, we report the infinite dilution activity coefficients and gas-to-IL partition coefficients for 47 and 45 organic probe molecules dissolved in 1-hexylquinuclidinium bis(trifluoromethylsulfonyl)imide ($[\text{Quin6}]^+[\text{TF}_2\text{N}]^-$) and 1-octylquinuclidinium bis(trifluoromethylsulfonyl)imide ($[\text{Quin8}]^+[\text{TF}_2\text{N}]^-$), respectively. See Fig. 1 for the molecular structures of the $[\text{Quin6}]^+$ and $[\text{Quin8}]^+$ cations. The experimental partition coefficient data obtained from these measurements are used to derive IL-specific Abraham model correlations, and to calculate ion-specific Abraham model equation coefficients for the $[\text{Quin6}]^+$ and $[\text{Quin8}]^+$ cations. The derived Abraham model correlations should enable the prediction of gas-to-liquid partition coefficients and infinite dilution activity coefficients for additional solute molecules not directly studied herein.

2. Experimental methods

2.1. Preparation of 1-alkylquinuclidinium ionic liquids

2.1.1. ($[\text{Quin6}]^+[\text{Br}]^-$)

Freshly-sublimed quinuclidine (9.01 g, 81.0 mmol) and 1-bromohexane (14.08 g, 85.3 mmol, 1.0₅ eq) were combined in 80 mL of ethyl acetate and stirred at room temperature for 4 days. The resulting off-white precipitate was filtered, washed with ethyl acetate on a ceramic frit (5×25 mL), and dried under vacuum to yield the corresponding bromide salt in 87% yield. To initiate ion exchange, the bromide salt ($[\text{Quin6}]^+[\text{Br}]^-$) was dissolved in 100 mL of deionized water

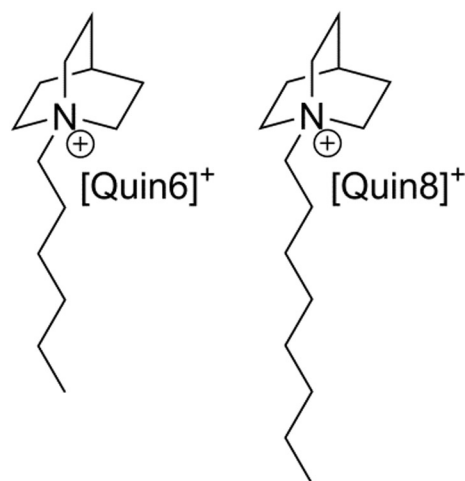


Fig. 1. Molecular structures of the 1-hexylquinuclidinium $[\text{Quin6}]^+$ and 1-octylquinuclidinium $[\text{Quin8}]^+$ cations.

followed by the addition of lithium bis(trifluoromethylsulfonyl)imide (1.02 equivalents, pre-dissolved in a minimal amount of water). The dense lower phase that resulted was extracted with deionized water several times (5×100 mL) to exhaustively remove LiBr residues. The resulting fluid was dried under vacuum at 70°C for 12 h to yield ($[\text{Quin6}][\text{TF}_2\text{N}]^-$) as a colorless free-flowing fluid: $^1\text{H NMR}$ (CDCl_3 , 300 MHz): δ 0.88 (t, 3H), 1.34 (m, 6H), 1.66 (m, 2H), 2.02 (m, 6H), 2.21 (m, 1H), 3.09 (m, 2H), 3.39 (m, 6H).

2.1.2. ($[\text{Quin8}]^+[\text{Br}]^-$)

Freshly-sublimed quinuclidine (5.16 g, 46.4 mmol) and 1-bromooctane (8.96 g, 46.4 mmol, 1.0 Eq) were combined in 80 mL of ethyl acetate and stirred at room temperature for 4 days. The resulting precipitate was filtered, washed with ethyl acetate on a ceramic frit (5×20 mL), and dried under vacuum to yield the bromide salt in 93% yield. Metathesis was performed in the same manner as for the $[\text{Quin6}]^+$ salt described above to yield ($[\text{Quin8}]^+[\text{TF}_2\text{N}]^-$): $^1\text{H NMR}$ (CDCl_3 , 300 MHz): δ 0.87 (t, 3H), 1.26–1.31 (m, 10H), 1.66 (m, 2H), 2.02 (m, 6H), 2.21 (m, 1H), 3.08 (m, 2H), 3.39 (m, 6H).

The 47 organic solutes used in the present study were purchased from commercial sources and their chemical purities are tabulated in several earlier publications [5,6,13,14]. The presence of trace impurities in the chemical samples will not affect the measured activity coefficients and gas-to-IL partition coefficient data. The retention times of

Table 1
Densities (ρ) for the 1-alkylquinuclidinium ILs as a function of temperature at $P = 101.33$ kPa.

T/K	$\rho/(\text{kg m}^{-3})$
$([\text{Quin6}]^+[\text{TF}_2\text{N}]^-)$	
293.15	1361.9
303.15	1353.8
313.15	1345.6
323.15	1337.0
333.15	1329.0
343.15	1320.5
$([\text{Quin8}]^+[\text{TF}_2\text{N}]^-)$	
293.15	1298.8
303.15	1290.8
313.15	1282.7
323.15	1274.0
333.15	1266.0
343.15	1257.7

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

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