Partition Coefficients of Low-Volatility Solutes in the Ionic Liquid 1-*n*-Butyl-3-methylimidazolium Hexafluorophosphate–Supercritical CO_2 System from Chromatographic Retention Measurements

Josef Planeta and Michal Roth*

Institute of Analytical Chemistry, Academy of Sciences of the Czech Republic, Veveří 97, 61142 Brno, Czech Republic

Room temperature ionic liquid (RTIL) 1-*n*-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]) was employed as the stationary liquid in capillary column chromatography with supercritical carbon dioxide (scCO_2) as the mobile phase. Open tubular capillary columns were used to measure the retention factors of anisole, azulene, benzil, α-ionone, naphthalene, pyrene, and veratrole within 313–353 K and 8.1–23.2 MPa. The retention factors were converted to infinite-dilution solute partition coefficients in the [bmim][PF_6]–scCO_2 system. Analysis of the relative retention data by regular solution theory resulted in approximate values of the solubility parameter of CO_2-expanded [bmim][PF_6]. Open tubular supercritical fluid chromatography appears to provide a viable method for rapid acquisition of partitioning data on low-volatility solutes in biphasic RTIL–scCO_2 systems.

Introduction

Organic salts with melting points near the ambient temperature, or room temperature ionic liquids (RTILs), have recently attracted growing interest as environmentally benign solvents for synthesis[1–6] or extraction.[7–9] Because of their ionic character, the RTILs usually display extremely low vapor pressures. Consequently, an increased use of RTILs instead of conventional organic solvents could result in significant reduction of emissions of volatile organic compounds. Therefore, RTILs have usually been classified as "green" solvents[10–12] although certain aspects of their environmental safety have yet to be clarified.[13–15] The widespread use of RTILs has also included their application as stationary phases in analytical separations by gas–liquid chromatography (GLC)[16–18] and liquid–liquid chromatography,[19] and GLC has been used extensively to measure activity coefficients of diverse solutes in RTILs.[20–24] Among the many classes of RTILs, the ionic liquids containing alkylmethylimidazolium cations have received particular attention because of their relative stability to air and water.[25] Some applications of RTILs involve their combination with supercritical carbon dioxide (scCO_2), a "green" solvent with tunable solvent strength.[26] A typical application of a RTIL–scCO_2 system would include a reaction in the RTIL environment and a subsequent extraction of the reactants and products from the RTIL with scCO_2.[27,28] Other promising possibilities offered by RTIL–scCO_2 systems include catalytic reactions in the RTIL phase[29–34] and the use of scCO_2 as a phase-separation switch in a RTIL–organic solvent system.[35,36] Consequently, considerable effort has been spent to investigate the RTIL-compressed gas interactions using phase-equilibrium measurements,[37–40] IR spectroscopy,[41,42] and UV–vis and fluorescence spectroscopy with solvatochromic probes.[43] For both fundamental understanding and process utilization of biphasic RTIL–scCO_2 systems, partition coefficients of the prospective solutes between both phases would also be helpful.

Because of effective insolubility of imidazolium-based RTILs in scCO_2, it appears that the solute partition coefficients can conveniently be obtained by supercritical fluid chromatography (SFC) using scCO_2 as a mobile fluid and the RTIL as a stationary liquid. In this contribution, we report the results of a SFC study of solute partitioning in the 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6])–scCO_2 system. We have selected this particular RTIL because it has been relatively well characterized in terms of pure component properties and interactions with scCO_2. The test solutes were selected so as to cover a wide range of volatility while trying to avoid the danger of spurious adsorption of the solutes within the chromatographic columns.

Experimental Section

Materials. Anisole (methoxybenzene), azulene (bicyclo[5.3.0]-decapentaene), benzil (1,2-diphenylethane-1,2-dione), α-ionone [4-(2,6,6-trimethyl-2-cyclohexen-1-yl)-3-buten-2-one], naphthalene, pyrene, and veratrole (1,2-dimethoxybenzene) were purchased from Sigma-Aldrich s.r.o. (Prague, Czech Republic) in the highest purity available and used as received. 1-*n*-Butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]) (>98 mol %) was a sample from Sachem, Inc. (Austin, TX). Prior to the use for column preparation, [bmim][PF_6] was dried under vacuum at room temperature for several days. Carbon dioxide (purity 4.5) was supplied by Messer Griesheim GmbH (Krefeld, Germany). HPLC grade solvents, *n*-hexane (>99 mol %), methanol (>99.9 mol %), and methylene chloride (99.9 mol %) were purchased from Sigma-Aldrich. Silica sorbent Biospher Si-100 (spherical particles, diameter 20 μm) to prepare packed capillary columns was purchased from Labio, a.s. (Prague, Czech Republic). Fused-silica capillary tubing used for column preparation was obtained from CACO s.r.o. (Bratislava, Slovak Republic).

* Corresponding author: Tel +420-532-290-171; Fax +420-541-212-113; e-mail roth@iach.cz.
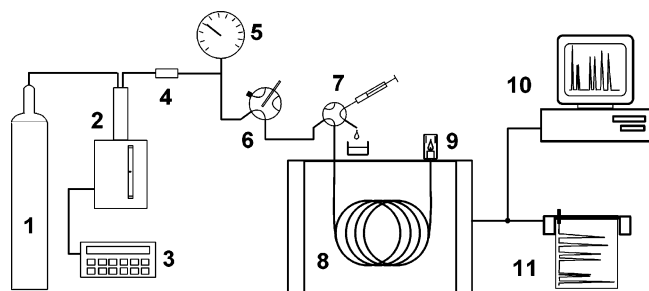
Partition Coefficients in a RTIL−CO$_2$ System

J. Phys. Chem. B, Vol. 108, No. 30, 2004 **11245**

Figure 1. Principal parts of the SFC apparatus: 1, CO$_2$ tank; 2, modified HPLC pump; 3, pressure controller; 4, filters; 5, pressure gauge; 6, main control valve/system vent; 7, injection valve; 8, column; 9, restrictor + detector (FID); 10, data acquisition system; 11, line recorder.

TABLE 1: Open Tubular Capillary Columns Employed

column no.	1	2
length/m	3.85	4.06
internal diameter/μm	85	85
amount of [bmim][PF$_6$]/mol	7.8×10^{-7}	4.1×10^{-7}
equivalent film thickness of pure [bmim][PF$_6$] at 298 K and ambient pressure/μm	0.16	0.08

Apparatus. All measurements were carried out using a Varian 3700 gas chromatograph equipped with flame ionization detector (FID) and modified for use in SFC. The modifications involved installation of a flow restrictor between the chromatographic column and the FID and replacement of the gas chromatographic sample port with a high-pressure injection valve (type CI4W, Valco, Switzerland) fitted with a 60 nL sampling loop. The delivery of SFC-grade CO$_2$ was controlled by a HPP 5001 high-pressure syringe pump (Laboratory apparatus, Prague, Czech Republic) operated in constant-pressure mode. During a chromatographic run, the column temperature was stable to within 0.5 K, and variations in the column inlet pressure did not exceed 0.02 MPa. The experiments were performed without flow splitting at the column inlet. Figure 1 shows a schematic diagram of the apparatus.

Packed Capillary Columns. With the purpose to secure a thorough control of the amount of [bmim][PF$_6$] in the column, the initial experiments were carried out with packed capillary columns. The column packings were prepared by dissolving a weighed amount of [bmim][PF$_6$] in methylene chloride, transferring the solution to a weighed amount of silica sorbent, and evaporating the solvent. The packing was then purged with a gentle stream of helium for 2 h at 80 °C to remove the residual methylene chloride. After cooling, the prepared material was packed into a fused-silica capillary (150 mm × 320 μm i.d.) with an in-situ formed porous silica frit at one end, and the open end of the column was closed with an analogous frit. The details of the packing procedure were the same as those described elsewhere[44] for conventional packed capillary columns. However, when using [bmim][PF$_6$] with the particular brand of spherical silica support, we observed a significant contribution of surface adsorption to solute retention. Therefore, all results reported below were obtained with open tubular columns.

Open Tubular Capillary Columns. A suitable loading of the capillary with [bmim][PF$_6$] has to be a compromise among several requirements, including suppression of spurious adsorption of the solutes on the column wall, satisfactory stability of the [bmim][PF$_6$] film to provide sufficient efficiency of the column, and reasonable retention times of the solutes at the particular temperature, pressure, and flow rate of scCO$_2$. Preparation of open tubular columns with [bmim][PF$_6$] is complicated because of poor wettability of untreated silica with [bmim][PF$_6$] and because of very low viscosity of [bmim][PF$_6$] as compared to more conventional materials (siloxane polymers) used to prepare open tubular columns for SFC. Moreover, as the pressure of CO$_2$ increases, the viscosity of CO$_2$-expanded [bmim][PF$_6$] decreases significantly below the viscosity of pure [bmim][PF$_6$] at the same temperature.[40,43,45] Therefore, to improve adhesion of [bmim][PF$_6$] to the capillary wall, the capillary was first treated by a surface modification procedure similar to that described by Dhanesar et al.[46] The treated capillary was filled with solution of [bmim][PF$_6$] in methylene chloride and sealed at one end. Methylene chloride was slowly evaporated under vacuum applied to the other end, and the amount of [bmim][PF$_6$] in the resultant column was calculated from the internal volume of the capillary and the concentration of the coating solution. The procedure was employed to prepare several columns containing different amounts of [bmim][PF$_6$], and two of the columns were used to measure all data reported below. The parameters of the two columns are specified in Table 1. Retention factors of anisole, azulene, α-ionone, and veratrole were measured with column 1 whereas column 2 was employed for benzil and pyrene. With either column, the respective injection solution also contained naphthalene as a reference solute.

Procedure. Solute retention factors were measured along three isotherms (313, 333, and 353 K) at mean column pressures within 8.1−23.2 MPa. At a particular isotherm, at least three injections were carried out at each pressure setting, with the retention factors being reproducible to within 1% of the mean value. The measurements were performed in the sequence of increasing pressure. After completing each isotherm, solute retention factors at the lower pressure limit were measured again to check for any possible loss of [bmim][PF$_6$] from the column during the run. We did not observe any measurable loss of [bmim][PF$_6$] from either column employed. The concentration of injection solutions was 2.5 mg/mL of each solute in *n*-hexane. Hexane was used as the injection solvent because, unlike more polar solvents, it was shown[47] to exhibit almost no cosolvent effect on solubility of [bmim][PF$_6$] in scCO$_2$. It was possible to use methane as a marker of the column holdup time because the columns were efficient enough to separate the methane peak from the solvent peak of hexane. To secure coherent values of the solute retention time and the column holdup time, it is advisable to obtain both from a single injection. Prior to an injection, therefore, the sampling loop in the injection valve was first flushed with methane and then partly filled with the injection solution. The pressure drop along the open tubular columns was calculated from the Hagen−Poiseuille equation using the correlation for viscosity of CO$_2$ described by Vesovic et al.,[48] and it did not exceed 0.02 MPa.

Data Reduction

In what follows, the solute will be identified by subscript 1, the principal component of the stationary phase (= [bmim][PF$_6$]) by subscript 2, and the mobile-phase fluid (= CO$_2$) by subscript 3. The quantities pertaining to the stationary and the mobile phases will be identified by subscripts s and m, respectively.

Conversion of Retention Factors to Partition Coefficients. Under conditions of linear chromatography at an effective infinite dilution of the solute, the solute retention factor

$$k_1 = (t_R - t_0)/t_0 \qquad (1)$$

11246 *J. Phys. Chem. B, Vol. 108, No. 30, 2004*

Planeta and Roth

where t_R is the solute retention time and t_0 the column holdup time, is related to column-independent characteristics of solute partitioning between the stationary and the mobile phase by

$$K_c = k_1 V_m (1 - x_{3s})/(n_{2s} v_s) \quad (2)$$

and

$$K = M_3 n_{2s}/[k_1 V_m \rho_m (1 - x_{3s})] \quad (3)$$

In eqs 2 and 3, M_3 is the molar mass of CO_2, n_{2s} is the number of moles of [bmim][PF$_6$] in the column, ρ_m is the density (mass/volume) of CO_2, V_m is the geometric volume of the mobile phase in the column (= void volume of the column), v_s is the molar volume of CO_2-expanded [bmim][PF$_6$], and x_{3s} is the solubility (mole fraction) of CO_2 in [bmim][PF$_6$]. The quantities ρ_m, v_s, and x_{3s} refer to the temperature and mean pressure in the column. The partition coefficient, K_c, of the solute is defined by

$$K_c = c_{1s}/c_{1m} \quad (4)$$

where c_{1s} and c_{1m} are the molar concentrations of the solute in the two phases. The K factor of the solute is defined by

$$K = x_{1m}/x_{1s} \quad (5)$$

where x_{1s} and x_{1m} are the mole fractions of the solute in the two phases. The partition coefficient K_c has often been used in physical and/or analytical chemistry, whereas the K factor has been a preferred characteristics of partitioning processes in chemical engineering. Note that the positions of stationary- and mobile-phase-related quantities in the fraction differ between eqs 4 and 5.

It is apparent from eqs 2 and 3 that both composition data (x_{3s}) and volumetric data (v_s) on CO_2-expanded [bmim][PF$_6$] are needed to convert the retention factors to true values of K_c and K. High-pressure composition data on CO_2-expanded [bmim][PF$_6$] were reported by several groups[37−40] while somewhat less information has been available on volumetric properties.[37,42,43] Therefore, to ensure consistency in k_1-to-K_c and k_1-to-K conversions, we used the composition and volumetric data from a single source[37] although the data only covered a relatively small part of the pressure range of our SFC measurements. The density of pure CO_2 was calculated from the equation of state (EOS) of Span and Wagner.[49]

Solubility Parameter of CO_2-Expanded [bmim][PF$_6$]. Employing the condition of equal fugacities of the solute in both phases at equilibrium, the solute partition coefficient may be written as

$$K_c = \gamma_{1m}^\infty v_m/(\gamma_{1s}^\infty v_s) \quad (6)$$

where the γ_1^∞'s are the Raoult law-based activity coefficients of the solute at infinite dilution in the two phases and v_m is the molar volume of the mobile phase. Within the frame of the regular solution theory[50]

$$\ln \gamma_{1s}^\infty = \frac{v_{1L}^0}{RT}(\delta_1 - \delta_s)^2 \quad (7)$$

where δ_1 is the solubility parameter of the liquid solute (or subcooled liquid solute if the melting point exceeds the column temperature), δ_s is the solubility parameter of CO_2-expanded [bmim][PF$_6$], R is the molar gas constant, T is the temperature, and v_{1L}^0 is the molar volume of (subcooled) liquid solute. Substituting from eq 7 and from the corresponding expression

TABLE 2: Relative Values of Solute Partition Coefficients with Respect to Naphthalene

			$\alpha_{AB}{}^a$					
T/K	P/MPa	ρ_m/kg m^{-3}	anisole	α-ionone	veratrole	azulene	benzil	pyrene
313	8.1	289.8	0.236	0.398	1.66	2.49		
	8.5	353.9	0.262	0.321	1.56	2.35		
	8.8	429.1		0.291	1.47	2.24		
	9.2	532.0		0.304	1.41	2.13		
	10.5	660.1		0.298	1.35	2.01	5.82	16.2
	13.2	747.4			1.26	1.83	2.95	7.76
333	8.7	221.3	0.223	0.570	1.70	2.52		
	10	290.0	0.257	0.418	1.56	2.38		
	10.9	350.4	0.284	0.315	1.49	2.29	13.6	
	12.1	442.0		0.296	1.40	2.15	8.48	21.9
	13.3	523.8		0.275	1.35	2.04	6.08	16.0
	16.7	657.0			1.20	1.78	3.38	8.62
353	10	221.6	0.245	0.550	1.55	2.41		
	11.8	288.6	0.280	0.428	1.45	2.28	16.2	
	13.3	352.4		0.360	1.38	2.18	11.3	26.4
	15.3	439.9		0.326	1.31	2.05	6.90	16.8
	17.6	526.3		0.301	1.24	1.89	4.75	11.5
	23.2	658.3					3.05	7.06

^{a} For solutes A and B, $\alpha_{AB} = k_A/k_B = K_{cA}/K_{cB} = K_B/K_A$ (B = naphthalene).

for γ_{1m}^∞ into eq 6, one obtains

$$\ln K_c = \frac{v_{1L}^0}{RT}(\delta_m - \delta_s)(\delta_s + \delta_m - 2\delta_1) + \ln v_m - \ln v_s \quad (8)$$

where δ_m is the solubility parameter of pure CO_2.

Relative retention of two solutes A and B, $\alpha_{AB} = k_A/k_B$, is also equal to the ratio of the two partition coefficients

$$\alpha_{AB} = K_{cA}/K_{cB} \quad (9)$$

Substitution for the partition coefficients from eq 8 into eq 9 and rearrangement yields a quadratic equation in δ_s

$$(v_{BL}^0 - v_{AL}^0)\delta_s{}^2 + 2(v_{AL}^0\delta_A - v_{BL}^0\delta_B)\delta_s + (v_{AL}^0 - v_{BL}^0)\delta_m{}^2 + 2(v_{BL}^0\delta_B - v_{AL}^0\delta_A)\delta_m - RT \ln \alpha_{AB} = 0 \quad (10)$$

From eq 10, δ_s can be obtained using only pure-component properties and α_{AB}. To calculate the molar volumes of (subcooled) liquid solutes, one can use a modified form[51] of the Rackett equation employing a reference density[52] and the critical properties estimated from the Joback correlation.[53] The solubility parameters of the (subcooled) liquid solutes[54] then result from combining the molar volumes with the cohesive energies obtained from vaporization enthalpy data[55] or from vapor pressure equations.[56] At a particular temperature and pressure, the pertinent value of δ_m can be derived from the EOS of Span and Wagner.[49]

There are two principal reasons to use relative rather than absolute partition coefficients in the estimation of δ_s. First, provided that bulk partitioning is the dominant mechanism of retention of both solutes, the relative retention data are invariant with respect to uncertainty in the amount of [bmim][PF$_6$] in the column. Second, the composition and volumetric data on CO_2-expanded [bmim][PF$_6$] are not needed in eq 10.

Results and Discussion

Partition Coefficients. Table 2 shows the relative values, α_{AB}, of solute partition coefficients with respect to naphthalene at the particular conditions. The retention factors, partition coefficients, and K factors of naphthalene are listed in Table 3. In Table 3, the data labeled "RTIL w/CO_2" were calculated from

Partition Coefficients in a RTIL−CO$_2$ System

J. Phys. Chem. B, Vol. 108, No. 30, 2004 **11247**

TABLE 3: Retention Factors, Partition Coefficients, and *K* Factors of Naphthalene

|				K_c		K	
	$P/$	$\rho_m/$		RTIL	RTIL	RTIL	RTIL
T/K	MPa	kg m^{-3}	k_1	w/CO$_2$	w/o CO$_2$	w/CO$_2$	w/o CO$_2$
313	8.1	289.8	2.32	238	307	0.00731	0.00235
	8.5	353.9	1.10	114	145	0.0132	0.00407
	8.8	429.1	0.471	49.8	62.3	0.0262	0.00782
	9.2	532.0	0.218	24.0	28.9	0.0473	0.0136
	10.5	660.1	0.121		15.9		0.0199
	13.2	747.4	0.0796		10.5		0.0266
333	8.7	221.3	3.25	342	425	0.00729	0.00219
	10	290.0	1.33		174		0.00409
	10.9	350.4	0.737		96.3		0.00612
	12.1	442.0	0.340		44.4		0.0105
	13.3	523.8	0.187		24.4		0.0161
	16.7	657.0	0.0917		12.0		0.0262
353	10	221.6	1.74		224		0.00411
	11.8	288.6	0.833		107		0.00658
	13.3	352.4	0.457		59.0		0.00980
	15.3	439.9	0.222		28.6		0.0162
	17.6	526.3	0.133		17.1		0.0226
	23.2	658.3	0.0417^a		10.8^a		0.0288^a

^{a} From column 2; all other data from column 1.

eqs 2 and 3 employing the x_{3s} and ν_s values interpolated from the results of Blanchard et al.[37] The data labeled "RTIL w/o CO$_2$" contain no correction for dissolution of CO$_2$ in [bmim]- [PF$_6$]. They were calculated assuming $x_{3s} = 0$ and $\nu_s \neq f(P,x_{3s})$ and were only corrected for the effect of temperature on the geometric volumes of both phases in the column using thermal expansivity values[57] for pure [bmim][PF$_6$].

The correction for dissolution of CO$_2$ in [bmim][PF$_6$] is important because of high solubility of scCO$_2$ in [bmim][PF$_6$][37−40] and, to a lesser extent, because of variation of ν_s with composition of CO$_2$-expanded [bmim][PF$_6$].[37] In the K factors, the relative effect of the correction is larger than in the partition coefficients, K_c. The reason is that, in K_c, there is a partial cancellation between the effects of CO$_2$ dissolution on $(1 - x_{3s})$ and ν_s (see eq 2). In K, on the contrary, the effect of dissolving CO$_2$ on $(1 - x_{3s})$ is manifested nearly to its full extent. Because of very small volumes of ionic liquid in the columns (see Table 1), the decrease in V_m brought about by CO$_2$-induced expansion of [bmim][PF$_6$] is not significant.

Phase equilibrium in the [bmim][PF$_6$]−scCO$_2$ system has been known to be affected by the presence of a small amount of water in the system.[37] In principle, therefore, the presence of moisture could also affect the solute partitioning in the [bmim][PF$_6$]−scCO$_2$ system. In the present experimental arrangement, a small amount of [bmim][PF$_6$] in the column was exposed to a continuous flow of scCO$_2$. Therefore, after the system reached a steady state at a particular temperature and pressure, the equilibrium concentration of water in [bmim][PF$_6$] was determined by the partition coefficient of water between [bmim][PF$_6$] and scCO$_2$ and by the concentration of water in the incoming stream of scCO$_2$. According to the supplier's specification, the mole fraction of residual water in the particular grade of CO$_2$ employed was as low as 5×10^{-6} or less. Therefore, we conclude that the results listed in Tables 2 and 3 are not likely to be influenced by the presence of moisture.

The accuracy of the resultant partition coefficients has been difficult to assess because no comparable data have yet been available. The primary source of error in the partition coefficients is the uncertainty in the calculated amount of RTIL in the column. This is also why the data for naphthalene in Table 3 differ from our preliminary results reported elsewhere.[58] The values of the partition coefficients relative to a reference solute
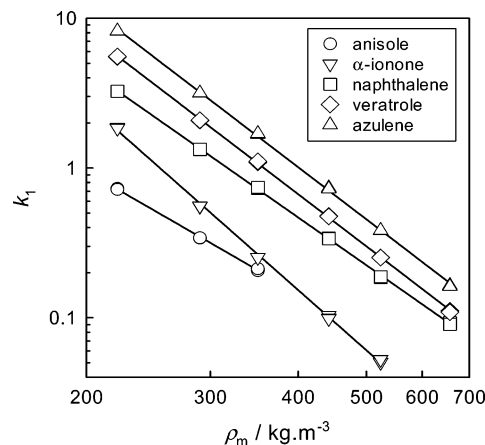
Figure 2. Retention factors of several solutes at 333 K as functions of CO$_2$ density. Column 1.

are significantly more robust with respect to this error source (provided that bulk partitioning is the dominant mechanism of retention). With the column preparation procedure described above, the partition coefficients obtained at a particular temperature and pressure from columns with different amounts of [bmim][PF$_6$] are reproducible to within 20% of the mean value. The relative values, however, can be reproduced to within 3%.

Retention Factor vs Density Plots. At a constant temperature of the column, the variation of solute retention factor with density of CO$_2$ may be written as[59,60]

$$\left(\frac{\partial \ln k_1}{\partial \ln \rho_m}\right)_T = \frac{1}{RT\beta_{mT}}\left[\bar{v}_{1m}^\infty - \bar{v}_{1s}^\infty - \left(\frac{\partial \mu_{1s}^\infty}{\partial x_{3s}}\right)_{T,P,n_{2s}}\left(\frac{\partial x_{3s}}{\partial P}\right)_{T,\sigma}\right] - \frac{V_s}{V_m}\frac{\beta_{sT\sigma}}{\beta_{mT}} \quad (11)$$

where P is the pressure, V_s is the geometric volume of the CO$_2$-expanded [bmim][PF$_6$] in the column, μ_{1s}^∞ is the infinite-dilution chemical potential of the solute in CO$_2$-expanded [bmim][PF$_6$], β_{mT} is the isothermal compressibility of CO$_2$, $\beta_{sT\sigma}$ is the isothermal compressibility of CO$_2$-expanded [bmim][PF$_6$] at saturation with CO$_2$, and $\bar{v}_{1m}^\infty$ and $\bar{v}_{1s}^\infty$ are the infinite-dilution partial molar volumes of the solute in CO$_2$ and in CO$_2$-expanded [bmim][PF$_6$], respectively. Figure 2 shows a few examples of the isothermal decrease in solute retention factor with raising density of CO$_2$. Within the temperature and density range of the measurements, the isothermal plots of $\ln k_1$ vs $\ln \rho_m$ were linear in all solutes. The variation of the slopes in a single solute with temperature is illustrated in Figure 3, and the numerical values of the slopes $(\partial \ln k_1/\partial \ln \rho_m)_T$ are included in the Supporting Information. In azulene and naphthalene, the data differ markedly from the slopes observed in previous measurements of the two solutes in conventional open tubular SFC systems with poly(dimethylsiloxane) (PDMS) stationary polymer.[61,62] Compared to the results with the PDMS stationary polymer, the slopes $(\partial \ln k_1/\partial \ln \rho_m)_T$ in the present measurements are more negative (larger in magnitude) by up to 50%, indicating a steeper decrease of solute retention in the [bmim]- [PF$_6$] columns with increasing density of CO$_2$. The different behaviors of the PDMS and the [bmim][PF$_6$] systems most probably come from different responses of the solute chemical potential (μ_{1s}^∞) to the changing molecular environment in the stationary phase as the mole fraction of dissolved CO$_2$ (x_{3s}) increases with raising pressure. Accordingly, in the SFC systems with [bmim][PF$_6$], the product of x_{3s}-containing terms in eq 11

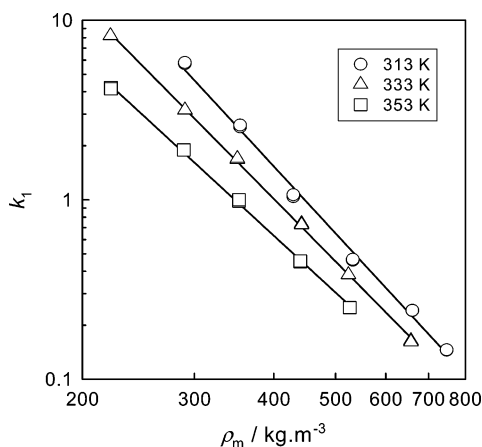**11248** *J. Phys. Chem. B, Vol. 108, No. 30, 2004*

Planeta and Roth

Figure 3. Effect of temperature on the density variation of the retention factor of azulene. Column 1.
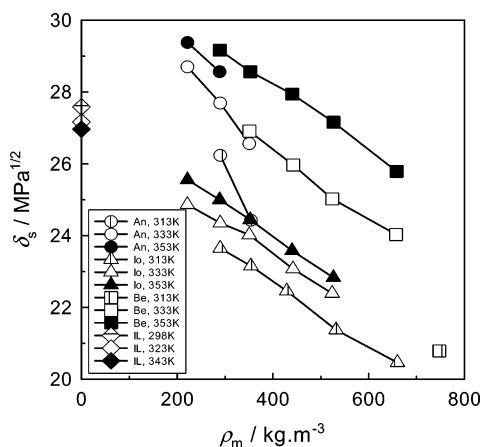

Figure 4. Solubility parameter of CO_2-expanded [bmim][PF_6] calculated from relative retention factors of anisole (An), α-ionone (Io), and benzil (Be) with respect to naphthalene. The values at zero density of CO_2 (IL) are square roots of the cohesive energy densities obtained by Morrow and Maginn[63] from molecular simulation of pure [bmim][PF_6].

appears to be more important than in the systems with PDMS. This notion, however, can only be validated after a reliable thermodynamic model for RTIL−scCO₂ systems becomes available.

Solubility Parameter of CO_2-Expanded [bmim][PF_6]. The calculation of δ_s via eq 10 was based on the retention data of anisole, benzil, and α-ionone, with naphthalene serving as the reference solute. Pyrene and azulene were not used because they belong to the same family (polycyclic aromatic hydrocarbons) as the reference solute, and veratrole was not used because of lack of reliable thermal data to calculate δ_1. The resultant values of δ_s are shown in Figure 4, and the numerical data are available in the Supporting Information (only the physically meaningful roots of eq 10 are shown, $\delta_s > \delta_m$). The scattering among the δ_s values from the three solutes reflects a limited validity of the regular solution theory in the RTIL-containing systems as well as possible inconsistencies in the literature data used to calculate the solubility parameters and molar volumes of the solutes. Some trends, however, are clearly apparent from Figure 4. First, along each isotherm, the δ_s values decrease with increasing density of CO_2. This finding certainly accords with one's expectation because of concomitant increase in solubility of CO_2 in [bmim][PF_6]. One could certainly argue that the decrease might partly result from the neglect of the pressure effect on the solute activity coefficients γ_{1m}^{∞} and γ_{1s}^{∞} in the simple analysis leading to eq 10. In such a case, however, the

rate of decrease would be temperature dependent because, near the critical temperature of CO_2, the temperature variation of $\bar{v}_{1m}^{\infty}$ is much more important than the temperature variation of $\bar{v}_{1s}^{\infty}$. Figure 4 shows that there is some effect of temperature on the rate of δ_s decrease in the data from anisole but not in the data from the other solutes. It is also apparent from Figure 4 that, at a constant density of CO_2, δ_s increases with raising temperature. Most probably, this feature again reflects a composition shift to lower solubility of CO_2, x_{3s}. Finally, there appears to be a relatively fair degree of consistency between the δ_s values and the solubility parameters of pure [bmim][PF_6] given by square roots of the cohesive energy densities obtained from molecular simulation of pure [bmim][PF_6].[63]

Conclusion

The results of this study indicate that SFC in open tubular columns provides a self-contained method to measure relative values of solute partition coefficients in biphasic RTIL−scCO₂ systems. Application of columns with different amounts of RTIL makes it possible to cover a range of solutes of different volatility and molecular size. However, the experience obtained with [bmim][PF_6] indicates that care should be taken to avoid overloading of the fused-silica capillary with RTIL and to secure sufficient stability of the ionic liquid film in the column. The uncertainty in the amount of RTIL in the column is the major factor determining the accuracy of absolute values of solute partition coefficients. To exploit the full potential of SFC to study solute partitioning in RTIL−scCO₂ systems, a thermodynamic model will be needed to correlate and/or predict the composition and density of the CO_2-expanded RTILs involved.

Supporting Information Available: Mean values of the slopes ($\partial \ln k_1 / \partial \ln \rho_m)_T$ in all solutes and estimated values of the solubility parameter of CO_2-expanded [bmim][PF_6]. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Welton, T. *Chem. Rev.* **1999**, *99*, 2071−2083.
(2) Holbrey, J. D.; Seddon, K. R. *Clean Prod. Process.* **1999**, *1*, 223−236.
(3) Earle, M. J.; Seddon, K. R. *Pure Appl. Chem.* **2000**, *72*, 1391−1398.
(4) Marsh, K. N.; Deev, A.; Wu, A.-C. T.; Tran, E.; Klamt, A. *Korean J. Chem. Eng.* **2002**, *19*, 357−362.
(5) Dupont, J.; de Souza, R. F.; Suarez, P. A. Z. *Chem. Rev.* **2002**, *102*, 3667−3692.
(6) Branco, L. C.; Afonso, C. A. M. *Chem. Commun.* **2002**, 3036−3037.
(7) Huddleston, J. G.; Willauer, H. J.; Swatloski, R. P.; Visser, A. E.; Rogers, R. D. *Chem. Commun.* **1998**, 1765−1766.
(8) Carda-Broch, S.; Berthod, A.; Armstrong, D. W. *Anal. Bioanal. Chem.* **2003**, *375*, 191−199.

Partition Coefficients in a RTIL−CO$_2$ System

J. Phys. Chem. B, Vol. 108, No. 30, 2004 **11249**

(9) Liu, J. F.; Jiang, G. B.; Chi, Y. G.; Cai, Y. Q.; Zhou, Q. X.; Hu, J. T. *Anal. Chem.* **2003**, *75*, 5870−5876.

(10) Wheeler, C.; West, K. N.; Liotta, C. L.; Eckert, C. A. *Chem. Commun.* **2001**, 887−888.

(11) *Ionic Liquids. Industrial Applications for Green Chemistry*; Rogers, R. D., Seddon, K. R., Eds.; ACS Symposium Series Vol. 818; American Chemical Society: Washington, DC, 2002.

(12) *Ionic Liquids As Green Solvents. Progress and Prospects*; Rogers, R. D., Seddon, K. R., Eds.; ACS Symposium Series Vol. 856; American Chemical Society: Washington, DC, 2003.

(13) Wasserscheid, P.; van Hal, R.; Bösmann, A. *Green Chem.* **2002**, *4*, 400−404.

(14) Jastorff, B.; Störmann, R.; Ranke, J.; Mölter, K.; Stock, F.; Oberheitmann, B.; Hoffmann, W.; Hoffmann, J.; Nüchter, M.; Ondruschka, B.; Filser, J. *Green Chem.* **2003**, *5*, 136−142.

(15) Swatloski, R. P.; Holbrey, J. D.; Rogers, R. D. *Green Chem.* **2003**, *5*, 361−363.

(16) Armstrong, D. W.; He, L. F.; Liu, Y.-S. *Anal. Chem.* **1999**, *71*, 3873−3876.

(17) Berthod, A.; He, L.; Armstrong, D. W. *Chromatographia* **2001**, *53*, 63−68.

(18) Anderson, J. L.; Armstrong, D. W. *Anal. Chem.* **2003**, *75*, 4851−4858.

(19) Shetty, P. H.; Poole, S. K.; Poole, C. F. *Anal. Chim. Acta* **1990**, *236*, 51−61.

(20) Heintz, A.; Kulikov, D. V.; Verevkin, S. P. *J. Chem. Eng. Data* **2001**, *46*, 1526−1529.

(21) Heintz, A.; Kulikov, D. V.; Verevkin, S. P. *J. Chem. Eng. Data* **2002**, *47*, 894−899.

(22) Heintz, A.; Kulikov, D. V.; Verevkin, S. P. *J. Chem. Thermodyn.* **2002**, *34*, 1341−1347.

(23) Letcher, T. M.; Soko, B.; Ramjugernath, D.; Deenadayalu, N.; Nevines, A.; Naicker, P. K. *J. Chem. Eng. Data* **2003**, *48*, 708−711.

(24) Letcher, T. M.; Soko, B.; Reddy, P.; Deenadayalu, N. *J. Chem. Eng. Data* **2003**, *48*, 1587−1590.

(25) Wilkes, J. S.; Zaworotko, M. J. *J. Chem. Soc., Chem. Commun.* **1992**, 965−967.

(26) Eckert, C. A.; Knutson, B. L.; Debenedetti, P. G. *Nature (London)* **1996**, *383*, 313−318.

(27) Blanchard, L. A.; Brennecke, J. F. *Ind. Eng. Chem. Res.* **2001**, *40*, 287−292.

(28) Dzyuba, S. V.; Bartsch, R. A. *Angew. Chem., Int. Ed.* **2003**, *42*, 148−150.

(29) Liu, F.; Abrams, M. B.; Baker, R. T.; Tumas, W. *Chem. Commun.* **2001**, 433−434.

(30) Sellin, M. F.; Webb, P. B.; Cole-Hamilton, D. J. *Chem. Commun.* **2001**, 781−782.

(31) Brown, R. A.; Pollet, P.; McKoon, E.; Eckert, C. A.; Liotta, C. L.; Jessop, P. G. *J. Am. Chem. Soc.* **2001**, *123*, 1254−1255.

(32) Jessop, P. G.; Stanley, R. R.; Brown, R. A.; Eckert, C. A.; Liotta, C. L.; Ngo, T. T.; Pollet, P. *Green Chem.* **2003**, *5*, 123−128.

(33) Ballivet-Tkatchenko, D.; Picquet, M.; Solinas, M.; Francio, G.; Wasserscheid, P.; Leitner, W. *Green Chem.* **2003**, *5*, 232−235.

(34) Webb, P. B.; Sellin, M. F.; Kunene, T. E.; Williamson, S.; Slawin, A. M. Z.; Cole-Hamilton, D. J. *J. Am. Chem. Soc.* **2003**, *125*, 15577−15588.

(35) Scurto, A. M.; Aki, S. N. V. K.; Brennecke, J. F. *J. Am. Chem. Soc.* **2002**, *124*, 10276−10277.

(36) Najdanovic-Visak, V.; Serbanovic, A.; Esperança, J. M. S. S.; Guedes, H. J. R.; Rebelo, L. P. N.; Nunes da Ponte, M. *ChemPhysChem* **2003**, *4*, 520−522.

(37) Blanchard, L. A.; Gu, Z.; Brennecke, J. F. *J. Phys. Chem. B* **2001**, *105*, 2437−2444.

(38) Kamps, A. P.-S.; Tuma, D.; Xia, J. Z.; Maurer, G. *J. Chem. Eng. Data* **2003**, *48*, 746−749.

(39) Shariati, A.; Peters, C. J. High-Pressure Phase Behavior of Binary Systems of Carbon Dioxide and Certain Ionic Liquids. In *Proceedings of the 6th International Symposium on Supercritical Fluids*, Versailles, France, April 28−30, 2003; Brunner, G., Kikic, I., Perrut, M., Eds.; International Society for Advancement of Supercritical Fluids and Institut National Polytechnique de Lorraine: Vandoeuvre, France, 2003; Vol. 2, pp 687−691.

(40) Liu, Z. M.; Wu, W. Z.; Han, B. X.; Dong, Z. X.; Zhao, G. Y.; Wang, J. Q.; Jiang, T.; Yang, G. Y. *Chem.−Eur. J.* **2003**, *9*, 3897−3903.

(41) Kazarian, S. G.; Briscoe, B. J.; Welton, T. *Chem. Commun.* **2000**, 2047−2048.

(42) Sakellarios, N. I.; Kazarian, S. G. High-Pressure CO$_2$-Induced Swelling of Ionic Liquids. In *Proceedings of the 6th International Symposium on Supercritical Fluids*; Versailles, France, April 28−30, 2003; Brunner, G., Kikic, I., Perrut, M., Eds.; International Society for Advancement of Supercritical Fluids and Institut National Polytechnique de Lorraine: Vandoeuvre, France, 2003; Vol. 2, pp 925−928.

(43) Lu, J.; Liotta, C. L.; Eckert, C. A. *J. Phys. Chem. A* **2003**, *107*, 3995−4000.

(44) Planeta, J.; Karásek, P.; Vejrosta, J. *J. Sep. Sci.* **2003**, *26*, 525−530.

(45) Baker, S. N.; Baker, G. A.; Kane, M. A.; Bright, F. V. *J. Phys. Chem. B* **2001**, *105*, 9663−9668.

(46) Dhanesar, S. C.; Coddens, M. E.; Poole, C. F. *J. Chromatogr. Sci.* **1985**, *23*, 320−324.

(47) Wu, W. Z.; Zhang, J. M.; Han, B. X.; Chen, J. W.; Liu, Z. M.; Jiang, T.; He, J.; Li, W. J. *Chem. Commun.* **2003**, 1412−1413.

(48) Vesovic, V.; Wakeham, W. A.; Olchowy, G. A.; Sengers, J. V.; Watson, J. T. R.; Millat, J. *J. Phys. Chem. Ref. Data* **1990**, *19*, 763−808.

(49) Span, R.; Wagner, W. *J. Phys. Chem. Ref. Data* **1996**, *25*, 1509−1596.

(50) Prausnitz, J. M.; Lichtenthaler, R. N.; Gomes de Azevedo, E. *Molecular Thermodynamics of Fluid-Phase Equilibria*; Prentice Hall: Upper Saddle River, NJ, 1999; pp 313−326.

(51) Poling, B. E.; Prausnitz, J. M.; O'Connell, J. P. *The Properties of Gases and Liquids*, 5th ed.; McGraw-Hill: New York, 2001; p 4.35, eq 4-11.4.

(52) *CRC Handbook of Chemistry and Physics on CD ROM, Version 2004*; Lide, D. R., Ed.; CRC Press: Boca Raton, FL, 2004.

(53) Reference 51, p 2.3.

(54) Reference 50, pp 646−647.

(55) *NIST Chemistry WebBook. NIST Standard Reference Database Number 69*; Linstrom, P. J., Mallard, W. G., Eds.; National Institute of Standards and Technology: Gaithersburg, MD, 2003; http://webbook.nist-.gov/chemistry.

(56) Dykyj, J.; Repáš, M. *Tlak nasýtenej pary organických zlúčenín (Saturation Vapor Pressure of Organic Compounds)*; Veda: Bratislava, Slovak Republic, 1979.

(57) Gu, Z.; Brennecke, J. F. *J. Chem. Eng. Data* **2002**, *47*, 339−345.

(58) Planeta, J.; Roth, M. Capillary-Column Supercritical Fluid Chromatography as a Route to Solute Partition Coefficients in Ionic Liquid-CO$_2$ Systems: Feasibility Study. In *Proceedings of the 6th International Symposium on Supercritical Fluids*, Versailles, France, April 28−30, 2003; Brunner, G., Kikic, I., Perrut, M., Eds.; International Society for Advancement of Supercritical Fluids and Institut National Polytechnique de Lorraine: Vandoeuvre, France, 2003; Vol. 2, pp 711−716.

(59) Roth, M. *J. Chromatogr.* **1991**, *543*, 262−265.

(60) Roth, M. *Fluid Phase Equilib.* **1998**, *148*, 189−199.

(61) Jeon, Y.-P.; Roth, M.; Kwon, Y. J. *J. Phys. Chem. B* **1999**, *103*, 8132−8136.

(62) Jeon, Y.-P.; Roth, M.; Kwon, Y. J. *J. Phys. Chem. A* **2000**, *104*, 5396−5400.

(63) Morrow, T. I.; Maginn, E. J. *J. Phys. Chem. B* **2002**, *106*, 12807−12813.