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ARTICLE

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Limiting Partition Coefficients of Sulfur-Containing Aromatics in a Biphasic [bmim][$MeSO_4$]−Supercritical CO_2 System

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Supporting Information

ABSTRACT: Infinite dilution (limiting) partition coefficients of several sulfur-containing aromatics (benzo[*b*]thiophene, benzothiazole, dibenzothiophene, 4,6-dimethyldibenzothiophene, phenoxathiin, and thianthrene) in a biphasic (1-*n*-butyl-3-methylimidazolium methyl sulfate ([bmim][$MeSO_4$]) + carbon dioxide) system were measured at temperatures of (313 to 353) K and pressures of (8.5 to 23.2) MPa. The measurement method was capillary column supercritical fluid chromatography (SFC) with [bmim][$MeSO_4$] serving as the stationary liquid and supercritical CO_2 as the carrier fluid. Partition coefficients of sulfur-containing aromatics are discussed as functions of temperature and CO_2 density. In addition, other solute partition coefficient data obtained from previous SFC measurements in the systems with ionic liquids [bmim][PF_6], [bmim][BF_4], [bmim][$MeSO_4$], [hmim][Tf_2N], and [thtdp][Cl] are reported in the Supporting Information.

INTRODUCTION

An important part of the growing applications of ionic liquids (ILs)[1] involves biphasic systems composed of an IL and a supercritical fluid, mostly carbon dioxide ($scCO_2$).[2−4] Biphasic IL + $scCO_2$ solvent systems can be tuned and tailored by varying the IL cation or anion as well as by varying the operating pressure or temperature to control the density and solvent power of $scCO_2$. The ensuing flexibility together with the effective insolubility of most ILs in $scCO_2$[5,6] makes the IL + $scCO_2$ solvent systems suitable for diverse applications in synthesis[7,8] and extractions.[9−12] The use of IL + $scCO_2$ systems in phase transfer catalysis and extractions always involves partitioning of the target organic(s) between both phases. Therefore, quantitative data on the pertinent phase equilibria are needed in the design of the respective processes as well as in the development of predictive thermodynamic models.

In the past few years, it has been shown that the classical techniques of phase equilibrium measurements in ternary IL + $scCO_2$ + organic systems[13−17] can be complemented with supercritical fluid chromatography (SFC) employing the IL as the stationary liquid and $scCO_2$ as the carrier fluid. Both open tubular capillary columns[18−22] and packed columns[23,24] were used to measure the retention times of organic solutes and convert them into the limiting (infinite dilution) partition coefficients of the solutes between both phases. The interplay among the solute volatility, the solute−IL interactions, and the solvent power of $scCO_2$ defines the region of operating temperature and pressure where reasonable retention times of the particular solute can be obtained.

The present contribution is concerned with the limiting partition coefficients of several sulfur-containing aromatic heterocycles in 1-*n*-butyl-3-methylimidazolium methyl sulfate ([bmim][$MeSO_4$])−$scCO_2$ system. The solutes employed here are the same as those used in an earlier study with 1-*n*-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([hmim][Tf_2N]).[20] The purpose of the present study was to compare the magnitude of the partition coefficients of the sulfur compounds in the [bmim][$MeSO_4$]−$scCO_2$ system with those obtained before in the [hmim][Tf_2N]−$scCO_2$ system. From the comparison, a more general assessment can be obtained regarding the feasibility of re-extraction of sulfur heterocycles with $scCO_2$ after the IL had been used for extractive desulfurization of transportation fuels.[25−27]

In most of our previous SFC studies of solute partitioning in IL−$scCO_2$ systems,[18,19,21,22] the partition coefficient of a solute was expressed relative to that of naphthalene at the particular temperature and pressure. The principal advantage of the relative partition coefficients is a significant reduction of the experimental error caused by the uncertainty in the amount of IL in the capillary column. However, although the relative partitioning data are very useful for selectivity considerations, they are less so as regards the development of thermodynamic models; the parametrization of thermodynamic models[23,24,28] for the ternary solute−IL−$scCO_2$ systems certainly requires absolute values of the partition coefficients. Therefore, to provide a consistent set of additional data for prospective use in thermodynamic model development, the Supporting Information of the present article contains a compilation of the absolute partition coefficient values obtained from previous SFC retention measurements with several ILs.[18−22]

EXPERIMENTAL SECTION

Materials. Benzo[*b*]thiophene (thianaphthene) (mole fraction purity $x = 0.99$, CAS No. 95-15-8), benzothiazole ($x = 0.96$, CAS No. 95-16-9), dibenzothiophene (DBT) ($x > 0.99$, CAS No. 132-65-0), 4,6-dimethyldibenzothiophene (4,6-DMDBT)

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($x = 0.97$, CAS No. 1207-12-1), thianthrene ($x = 0.97$, CAS No. 92-85-3), phenoxathiin ($x = 0.97$, CAS No. 262-20-4), and naphthalene ($x > 0.99$, CAS No. 91-20-3) were supplied by Sigma-Aldrich (Prague, Czech Republic) and used as received. The ionic liquid [bmim][$MeSO_4$] was originally supplied by Solvent Innovation (Cologne, Germany) and purified and provided to us by Dr. Dirk Tuma (Department of Applied Thermodynamics, University of Kaiserslautern, Germany). To remove residual moisture from the IL before preparation of the coating solution (see below), a 2 cm^3 sample of [bmim][$MeSO_4$] was purged with a gentle stream of nitrogen in a gas chromatographic oven at a programmed temperature, with the final period of 12 h at 403 K. SFC-grade carbon dioxide (mole fraction of residual water $< 5 \cdot 10^{-6}$) was obtained from SIAD (Branany u Mostu, Czech Republic). Hexane ($x > 0.95$), methanol ($x > 0.999$), and methylene chloride ($x = 0.999$) were purchased from Sigma-Aldrich. Fused-silica capillary tubing for preparation of the column and the outlet restrictor was purchased from Agilent (Waldbronn, Germany). The agents for surface treatment of fused silica, namely, ammonium hydrogen difluoride and 2-chloro-1,1,2-trifluoroethylmethylether, were supplied by Sigma-Aldrich and Apollo Scientific Ltd. (Stockport, Cheshire, UK), respectively.

Column Preparation. Prior to the use for column preparation, the inner surface of fused-silica tubing had to be treated to improve adhesion of [bmim][$MeSO_4$]. As the first step, one-third of the tubing length was filled with liquid 2-chloro-1,1,2-trifluoroethylmethylether; both ends of the tubing were sealed by melting with a methane−oxygen microflame torch, and the tubing was kept at 593 K for 12 h. After cooling to room temperature, cutting the ends, and flushing with methanol, the tubing was filled with saturated solution of ammonium hydrogen difluoride in methanol, sealed with silicone rubber, and etched at 313 K for 12 h. Subsequently, the tubing was filled with a coating solution (75.47 mg of [bmim][$MeSO_4$] in 10 cm^3 of CH_2Cl_2); one end of the column was tightly sealed, and methylene chloride was carefully evaporated by applying vacuum to the open end. The resultant column was 3.30 m long, had a 100 μm inner diameter (i.d.), and contained $7.81 \cdot 10^{-7}$ mol of [bmim][$MeSO_4$]. The equivalent film thickness of [bmim][$MeSO_4$] in the column at 298 K and at ambient pressure was 0.16 μm.

Apparatus and Procedure. The apparatus was based on a modified Varian 3700 gas chromatograph and described before,[18] and the procedure was similar to that used in our previous SFC studies with other ILs.[20,21] Solute retention factors were measured along three isotherms at (313, 333, and 353) K at mean column pressures within (8.5 to 23.2) MPa. The pressure drop along the open tubular column was calculated from the Hagen−Poiseuille equation using the correlation for viscosity of CO_2 developed by Vesovic et al.,[29] and it did not exceed 0.016 MPa. The density of CO_2 was obtained from the Span−Wagner equation of state,[30] and the calculations were accomplished with the interactive software by Wagner and Overhoff.[31] To maximize the usable lifetime of the column, retention measurements were performed in the sequence of increasing density of CO_2. The six solutes were divided among several injection solutions so that well-resolved peaks could be obtained from every injection. The injection solutions were prepared in n-hexane, and the concentrations of individual solutes ranged within (1.6 to 3.2) $mg \cdot cm^{-3}$, with each injection solution also containing naphthalene as a reference. Throughout the measurement procedure, the current amount of [bmim][$MeSO_4$] in the column was frequently determined from regular checks of the retention factor of naphthalene at 333 K and 10 MPa as described before.[20] All retention factors reported below were corrected to the initial amount of [bmim][$MeSO_4$] in the column so that consistent results could be obtained. At the end of the whole series of measurements, the column only contained 72.6 % of the initial amount of [bmim][$MeSO_4$]. The retention factors used to obtain the partition coefficients were averages of triplicate determinations, with the relative standard deviation ranging within 2 % of the mean value. The standard uncertainties[32] in the measurements of the column temperature and the column inlet pressure were ± 0.15 K and ± 0.05 MPa, respectively. Considering also the uncertainty in the amount of [bmim][$MeSO_4$] in the column, we conclude that the total relative expanded uncertainty[32] in the resultant partition coefficients was ± 15 % (confidence level of 95 %).

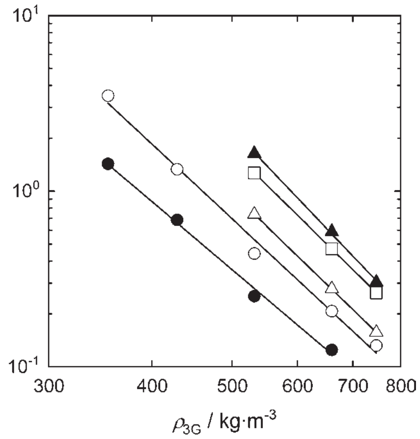

Figure 1. Retention factors of sulfur-containing aromatics against the CO_2 density at 313.2 K: ○, benzothiazole; ●, benzo[b]thiophene; □, dibenzothiophene; △, phenoxathiin; ▲, thianthrene. The lines serve just to guide the eye.

RESULTS AND DISCUSSION

Variations of SFC Retention Factors with Operating Parameters. At a constant temperature, the retention factor of a solute in SFC decreases with increasing pressure P. To a first approximation, neglecting the effects of varying solubility of CO_2 in the stationary phase,[33−35] the isothermal pressure slope of $\ln k_1$ is given by

$$(\partial \ln k_1 / \partial \ln P)_T \approx (\overline{V}_{1G}^{\infty} - \overline{V}_{1L}^{\infty})/(RT) - \beta_{3T} \qquad (1)$$

where $\overline{V}_{1G}^{\infty}$ and $\overline{V}_{1L}^{\infty}$ are the infinite-dilution partial molar volumes in the gas (mobile) and liquid (stationary) phases, respectively, and β_{3T} is the isothermal compressibility of pure CO_2. At the critical point of CO_2, β_{3T} diverges, and near the critical point, $\overline{V}_{1G}^{\infty}$ scales as β_{3T}.[36] Therefore, the dependence of $\ln k_1$ on pressure is strongly curved.[34] Dividing eq 1 with β_{3T}, one obtains the isothermal derivative of $\ln k_1$ with respect to the density of CO_2, ρ_{3G},

$$(\partial \ln k_1 / \partial \ln \rho_{3G})_T \approx (\overline{V}_{1G}^{\infty} - \overline{V}_{1L}^{\infty})/(RT\beta_{3T}) - 1 \qquad (2)$$

Because of the form of eq 2, the effects of near-critical anomalies in β_{3T} and $\overline{V}_{1G}^{\infty}$ are eliminated from $(\partial \ln k_1 / \partial \ln \rho_{3G})_T$, and the isothermal plots of $\ln k_1$ against $\ln \rho_{3G}$ are often nearly linear.[37] A sample plot of solute retention factors against the CO_2 density at 313.2 K is shown in Figure 1, illustrating the typical decrease of the retention factor with increasing density of CO_2.

Table 1. Infinite-Dilution Solute Partition Coefficients in [bmim][$MeSO_4$]−$scCO_2$ System as Functions of Temperature T, Pressure P, CO_2 Density ρ_{3G}, CO_2 Solubility in [bmim][$MeSO_4$] x_{3L}, and the Mass Ratio m_{2L}/m_{3G}

T	P	ρ_{3G}			K_N						
K	MPa	$kg \cdot m^{-3}$	x_{3L}	m_{2L}/m_{3G}	benzothiazole	benzo[*b*]thiophene	DBT	4,6-DMDBT	phenoxathiin	thianthrene	naphthalene
313.2	8.5	353.9	0.1229	0.0215	0.00614	0.0150					0.0245
313.2	8.8	429.1	0.1245	0.0177	0.0133	0.0258					0.0423
313.2	9.2	532.0	0.1263	0.0143	0.0323	0.0564	0.0113		0.0194	0.00872	0.0870
313.2	10.5	660.1		0.0115	0.0554	0.0921	0.0244		0.0413	0.0195	0.140
313.2	13.2	747.4		0.0102	0.0768		0.0385		0.0647	0.0335	0.180
333.2	8.7	221.3	0.0927	0.0343	0.00420	0.00990					0.0158
333.2	10.0	290.0		0.0262	0.00824	0.0222					0.0279
333.2	10.9	350.4		0.0217	0.0149	0.0299		0.00833	0.00680		0.0480
333.2	12.1	442.0		0.0172	0.0242	0.0471	0.00846	0.0172	0.0132	0.00595	0.0732
333.2	13.3	523.8		0.0145	0.0412	0.0722	0.0171	0.0361	0.0269	0.0130	0.112
333.2	16.7	657.0		0.0116	0.0763	0.123	0.0379	0.0835	0.0619	0.0323	0.181
353.2	10.0	221.6		0.0343	0.00817	0.0191					0.0296
353.2	11.8	288.6		0.0263	0.0136	0.0296			0.00576		0.0462
353.2	13.3	352.4		0.0216	0.0215	0.0447	0.00719		0.0109	0.00473	0.0697
353.2	15.3	439.9		0.0173	0.0378	0.0738	0.0159		0.0244	0.0116	0.111
353.2	17.6	526.3		0.0144	0.0580	0.105	0.0279		0.0438	0.0216	0.156
353.2	23.2	658.3		0.0115	0.102	0.173	0.0608		0.0955	0.0524	0.228

Neglecting again the effects of varying solubility of CO_2 in the stationary phase, variation of the solute retention factor with temperature at a constant pressure can be expressed by[34,35,38]

$$(\partial \ln k_1/\partial T)_P \approx (\bar{H}_{1L}^{\infty} - \bar{H}_{1G}^{\infty})/(RT^2) + \alpha_{3P} \qquad (3)$$

where $\bar{H}_{1L}^{\infty}$ and $\bar{H}_{1G}^{\infty}$ are the infinite-dilution partial molar enthalpies in the liquid (stationary) and gas (mobile) phases, respectively, and α_{3P} is the isobaric expansivity of pure CO_2. At the temperatures and pressures near the critical point of CO_2, the quantities α_{3P} and $\bar{H}_{1G}^{\infty}$ also display anomalous behavior,[36] and consequently, the isobaric dependence of $\ln k_1$ on temperature is strongly curved.[34]

Partition Coefficients. For practical purposes, the distribution of a trace amount of solute between the liquid phase containing the m_{2L} mass of the IL and the gas phase containing the m_{3G} mass of CO_2 has previously been described by a partition coefficient defined as[20]

$$K_N = \frac{m_{1G}}{m_{1L}} \frac{m_{2L}}{m_{3G}} \qquad (4)$$

where m_{1G} and m_{1L} are the masses of the solute in the gas and the liquid phases, respectively, at equilibrium. Under the conditions of linear chromatography,[39] K_N is related to the solute retention factor k_1 by

$$K_N = \frac{m_{2L}}{k_1 m_{3G}} \qquad (5)$$

with the solute retention factor given by

$$k_1 = (t_R - t_0)/t_0 \qquad (6)$$

where t_R is the solute retention time and t_0 is the column holdup time.

The partition coefficient K_N can be useful for initial design of the processes employing IL−$scCO_2$ biphasic systems. It should be noted, however, that K_N is an application-oriented quantity rather than a rigorous thermodynamic parameter. The equilibrium distribution of a trace amount of solute between both phases is better described in terms of mole fractions, that is, by the K-factor defined as

$$K = x_{1G}/x_{1L} \qquad (7)$$

where x_{1G} and x_{1L} are the equilibrium mole fractions of the solute in the gas and the liquid phases, respectively. Provided that the IL−$scCO_2$ equilibrium is not disturbed by the presence of a trace amount of the solute, an alternative expression of the K-factor in terms of the quantities introduced above is

$$K = \frac{M_3 m_{2L}}{M_2 k_1 m_{3G}(1 - x_{3L})} \qquad (8)$$

where M_2 and M_3 are the molar masses of the IL and CO_2, respectively, and x_{3L} is the solubility (mole fraction) of CO_2 in the IL at the particular temperature and pressure. Therefore, the partition coefficient K_N and the K-factor are related by

$$K = \frac{M_3}{M_2} \frac{K_N}{1 - x_{3L}} \qquad (9)$$

Tables 1 and 2 list the values of K_N and K, respectively, as obtained in the present work. The solubilities (x_{3L}) of CO_2 in [bmim][$MeSO_4$] were interpolated from the data reported by Kumełan et al.[40] Because of limited overlap between the temperature and pressure ranges of the data by Kumełan et al. and the present study, only a few values of the K-factors could be obtained (Table 2). At a constant temperature, the partition coefficients K_N increase with the rising pressure in all solutes (Table 1). While the isothermal pressure dependence of K_N of a particular solute would be curved, largely for the same reasons as those mentioned below eq 1 above, the isothermal log−log plots of K_N against the density of CO_2 are nearly linear as illustrated by Figure 2.

Table 2. **Infinite-Dilution Solute *K*-Factors in [bmim][MeSO$_4$]−scCO$_2$ System as Functions of Temperature *T*, Pressure *P*, CO$_2$ Density ρ_{3G}, CO$_2$ Solubility in [bmim][MeSO$_4$] x_{3L}, and the Mass Ratio m_{2L}/m_{3G}**

T	P	ρ_{3G}			K					
K	MPa	kg·m^{-3}	x_{3L}	m_{2L}/m_{3G}	benzothiazole	benzo[*b*]thiophene	DBT	phenoxathiin	thianthrene	naphthalene
313.2	8.5	353.9	0.1229	0.0215	0.00123	0.00301				0.00491
313.2	8.8	429.1	0.1245	0.0177	0.00267	0.00519				0.00850
313.2	9.2	532.0	0.1263	0.0143	0.00649	0.0114	0.00226	0.00390	0.00176	0.0175
333.2	8.7	221.3	0.0927	0.0343	0.000814	0.00192				0.00306

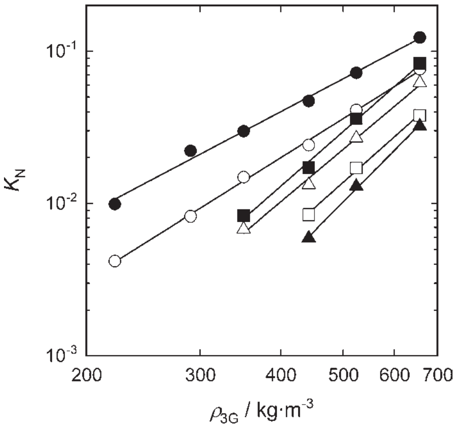

Figure 2. Partition coefficients K_N of sulfur-containing aromatics against the CO$_2$ density at 333.2 K: ○, benzothiazole; ●, benzo[*b*]thiophene; □, DBT; ■, 4,6-DMDBT; △, phenoxathiin; ▲, thianthrene. The lines serve just to guide the eye.

The value of K_N results primarily from the interplay of intermolecular forces as measured by the infinite−dilution solute fugacity coefficients in the gas (CO$_2$) phase and the liquid (IL + CO$_2$) phase. The fugacity coefficient of the solute in CO$_2$ depends on pressure. The fugacity coefficient of the solute in the liquid phase is also pressure-dependent because the solubility of CO$_2$ in the IL varies with pressure, and the solute fugacity coefficient reflects the ensuing changes in the molecular environment in the liquid phase. Therefore, the slopes of the linear fits in Figure 2, $(\partial \ln K_N/\partial \ln \rho_{3G})_T$, differ from one solute to another, and intersections (crossovers) of two solutes can occur such as that between benzothiazole and 4,6-DMDBT. In fact, a marked difference is apparent in Figure 2 between the slopes of two-ring solutes (benzo[b]thiophene and benzothiazole) and three-ring solutes (the rest).

The operating pressures in Table 1 were selected so as to produce matching densities of CO$_2$ among the individual isothermal runs. Although the densities match only approximately, the data in Table 1 indicate that, in a particular solute, the K_N values increase with the rising temperature at a constant density of CO$_2$. The temperature dependence of K_N at a constant pressure would be more complex, mainly for the same reasons as those mentioned at eq 3 above.

Additional values of K_N and K-factors as calculated from our previous measurements with other ILs and/or other solutes[18−22] are compiled in the Supporting Information file.

■ CONCLUSION

We have measured the limiting partition coefficients of several sulfur-containing aromatics in a biphasic system composed of [bmim][MeSO$_4$] and scCO$_2$. At a constant temperature, the values of K_N defined by eq 4 decrease with increasing pressure and with increasing density of CO$_2$. For a particular solute, the isothermal log−log plot of K_N against the density of CO$_2$ is nearly linear. With regard to the temperature dependence, the K_N values increase with the rising temperature at a constant density of CO$_2$. The isothermal dependence of K_N on pressure and the isobaric dependence of K_N on temperature would be strongly curved because of anomalies in the constituent quantities near the critical point of CO$_2$. The K_N values in the present system are of the same magnitude as those reported before in a similar study with [hmim][Tf$_2$N].[20] Therefore, the present results on K_N support our earlier finding[20] that extraction of sulfur-containing aromatics from ILs with scCO$_2$ would hardly be feasible.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Tables showing solute partition coefficients K_N and K-factors as obtained from previous SFC measurements of solute retention data in biphasic IL−scCO$_2$ systems with 1-*n*-butyl-3-methylimidazolium hexafluorophosphate,[18] 1-*n*-butyl-3-methylimidazolium tetrafluoroborate,[19] [bmim][MeSO$_4$],[22] [hmim][Tf$_2$N],[20] and trihexyltetradecylphosphonium chloride.[21] This material is available free of charge via the Internet at http://pubs.acs.org.

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