Capillary-Column Supercritical Fluid Chromatography as a Route to Solute Partition Coefficients in Ionic Liquid–CO_2 Systems: Feasibility Study

Josef Planeta and Michal Roth*
Institute of Analytical Chemistry, Academy of Sciences of the Czech Republic, 61142 Brno, Czech Republic
(E-mail: roth@iach.cz ; fax +420 541 212 113)

Combination of a room-temperature ionic liquid (RTIL) and supercritical carbon dioxide provides a „green“ alternative to conventional reaction media/solvent systems comprising volatile organic solvents. A typical application of an RTIL–CO_2 system would involve a reaction in the RTIL environment, and a subsequent extraction of the reactants and products from the RTIL with supercritical CO_2. For both fundamental understanding and process utilisation of such a procedure, high-pressure partition coefficients are necessary of the substances concerned between both phases in the RTIL–CO_2 system. Owing to their ionic character and extremely low vapour pressures, many RTILs are effectively insoluble in supercritical CO_2. Therefore, supercritical fluid chromatography (SFC) with the RTIL as the stationary liquid phase and CO_2 as the mobile-phase fluid presents a convenient and inexpensive route to the partition coefficients, at least in low-volatility solutes. In this contribution, we report the results of a feasibility study in naphthalene–1-butyl-3-methylimidazolium hexafluorophosphate–CO_2 system, employing both micropacked and open-tubular capillary chromatographic columns.

INTRODUCTION

Molten 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 [1-4] or extraction [5]. Because of their ionic character, the RTILs usually display extremely low vapour pressures. Consequently, an increased use of RTILs instead of conventional organic solvents could result in significant reduction of emissions of volatile organic compounds. Among the many classes of RTILs, the ionic liquids containing alkylmethylimidazolium cations have received particular attention because of their stability to air and water [6].

Some applications of RTILs involve their combination with supercritical carbon dioxide ($scCO_2$), a „green“ solvent with tunable solvent strength [7]. A typical application of an 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 $scCO_2$ [8]. Therefore, increased attention has been paid to exploring the thermodynamic properties and phase behaviour of RTIL–compressed gas binary systems [9-11]. For both fundamental understanding and process utilisation of the procedure mentioned above, high-pressure partition coefficients are also needed of the prospective solutes between both phases in the RTIL–CO_2 system.

Because of an 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 a RTIL as a stationary liquid. In this contribution, we report the results of a SFC study of naphthalene partitioning in 1-butyl-3-methylimidazolium hexafluorophosphate–CO_2 system. To our knowledge, this is the first thermodynamic application of chromatography to high-pressure systems involving RTILs. Previously, gas chromatography (GC) at low pressures has been used to determine activity coefficients of numerous solutes in RTILs [12,13].

MATERIALS AND METHODS

Chemicals

Naphthalene (99 mol %), methylene chloride (HPLC grade, 99.9 mol %), and *n*-hexane (HPLC grade, >95 mol %) were purchased from Sigma-Aldrich s. r. o. (Prague, Czech Republic) and used as received. 1-Butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]) (>98 mol %) was a sample from Sachem, Inc. (Austin, Texas, USA). Carbon dioxide (purity 4.5) was supplied by Messer Griesheim GmbH, Krefeld, Germany. The silica sorbent Biospher Si-100 (spherical particles, diameter 20 μm) was purchased from Labio, a. s. (Prague, Czech Republic). The fused-silica capillary tubing used for column preparation was obtained from CACO s.r.o. (Bratislava, Slovak Republic). Sodium chloride (>99 mol %) for the tubing pre-treatment (surface roughening procedure) was purchased from Sigma-Aldrich s.r.o. (Prague, Czech Republic).

Apparatus

All measurements were carried out using a Varian 3700 gas chromatograph equipped with flame ionisation detector (FID) and modified for use in supercritical fluid chromatography. 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. The experiments were performed without flow splitting at the column inlet.

Micropacked 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 hours at 80 °C to remove the residual methylene chloride. After cooling down, the prepared packing was packed into a fused-silica capillary (150 mm × 320 μm i.d.), and the open end of the column was sealed with an in-situ formed porous silica frit. The details of the procedure have been described elsewhere [14].

Open-Tubular Capillary Columns

Fused-silica capillary tubing (4.2 m × 85 μm i.d.) was subject to surface roughening procedure similar to that described before [15]. Then the column was filled with a solution of [bmim][PF_6] in methylene chloride, and the volatile solvent was slowly evaporated under vacuum. The amount of [bmim][PF_6] in the column was calculated from the volume of the tube and the concentration of the coating solution. The column (either open-tubular or micropacked) was connected to fused silica capillary restrictor (30 cm × 10 μm i.d.) mounted into the FID.

Determination of Column Hold-up Time

The column hold-up time was determined from injections of methane. Under the operating conditions of the present study, the retention time of methane was indistinguishable from the onset of the peak of *n*-hexane. Hexane was used as the solvent for naphthalene injections, with the injection solution containing 5 mg of naphthalene per 1 ml of hexane.

Operating Conditions in Retention Measurements

The retention factors of naphthalene were measured at temperatures within 313 – 353 K and pressures within 8.1 – 23.2 MPa. The detector signal was recorded and processed with the CSW v. 1.7 data acquisition software (DataApex s.r.o., Prague, Czech Republic).

Conversion of Retention Factors to Partition Coefficients and K-Factors

The chromatographic retention factor of a solute is given by

$$k = (t_{\mathrm{R}} - t_0)/t_0 \qquad (1)$$

where t_{R} is the retention time of the solute and t_0 is the retention time of an unretained substance (= column hold-up time). In the limit of an effective infinite dilution of the solute in both the stationary (liquid) and the mobile (gaseous) phase, the relationship between k and the solute partition coefficient K_{c} may be written as

$$K_{\mathrm{c}} = c_{1\mathrm{L}} / c_{1\mathrm{G}} = kV_{\mathrm{G}} / V_{\mathrm{L}} \qquad (2)$$

where $c_{1\mathrm{L}}$ and $c_{1\mathrm{G}}$ are molar concentrations of the solute (1) in the liquid and the gaseous phase, respectively, and V_{L} and V_{G} are the geometric volumes of the two phases in the column. V_{L} and V_{G} sum up to the temperature- and pressure-independent internal volume of the column, and V_{L} is related to the mole number of RTIL (2) in the column, $n_{2\mathrm{L}}$, by

$$V_{\mathrm{L}} = n_{2\mathrm{L}} v_{\mathrm{L}} / (1 - x_{3\mathrm{L}}) \qquad (3)$$

where $x_{3\mathrm{L}}$ is the equilibrium mole-fraction (solubility) of the mobile-phase fluid (3) in the RTIL (2), and v_{L} is the molar volume of the (2+3) liquid mixture.

As an alternative to the molar-concentration-based partition coefficient K_{c}, the K-factor of the solute in the RTIL–scCO$_2$ system, i.e., the infinite-dilution limit of the equilibrium ratio of solute mole fraction in the gaseous and the liquid phase, is related to the chromatographic retention factor by

$$K = x_{1\mathrm{G}} / x_{1\mathrm{L}} = n_{2\mathrm{L}} / [kV_{\mathrm{G}}\, r_{\mathrm{G}} (1 - x_{3\mathrm{L}})] \qquad (4)$$

where r_{G} is the molar density of the mobile-phase fluid (3) at the temperature and mean pressure in the column. The molar density of CO$_2$ was calculated from the high-precision equation of state of Span and Wagner [16].

RESULTS

In micropacked capillary columns prepared with the particular brand of spherical silica support, we have observed a significant contribution of surface adsorption to the retention of naphthalene. Naphthalene was significantly retained even in a 'blank' column containing no [bmim][PF_6]. Therefore, all the results reported below refer to open-tubular capillary columns.

We prepared several open-tubular columns with [bmim][PF_6] film thickness ranging within 0.08–0.62 µm. Isothermal dependence of the retention factor on the mobile-phase density is approximately linear when plotted in logarithmic axes as shown in Figure 1. With the increasing temperature, the trend in the $(\partial \ln k / \partial \ln r_{\mathrm{G}})_T$ slopes corresponds to that found in conventional systems of open-tubular-column SFC [17,18].

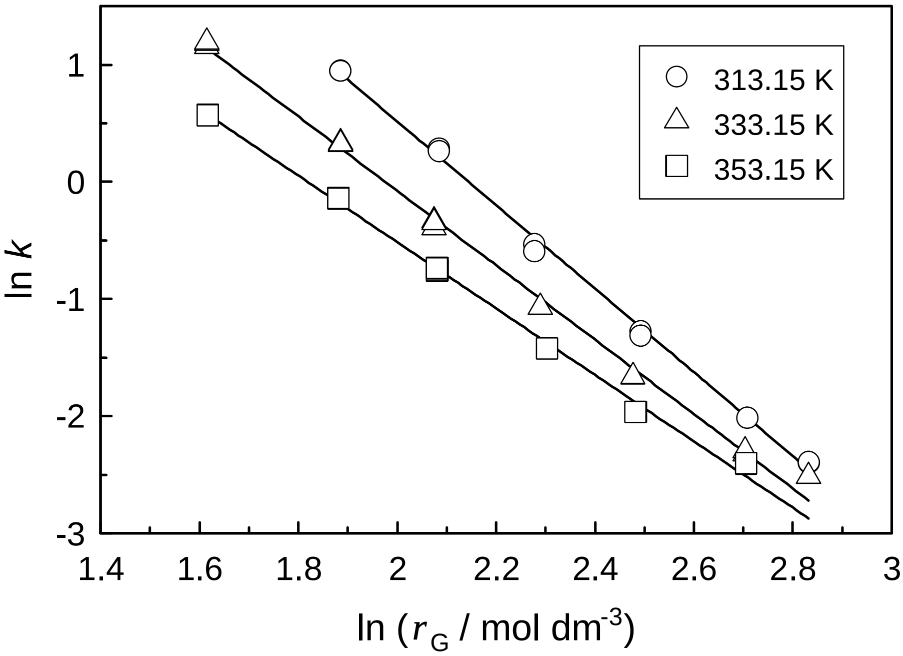

Figure 1. Retention factor of naphthalene as a function of mean molar density of CO_2. Open tubular column (4.20 m × 85 µm i.d.), [bmim][PF_6] film thickness 0.16 µm.

The retention factors of naphthalene (k) were converted to the partition coefficients (K_c) and K-factors (K) listed in Table 1. The raw values were obtained assuming no dissolution of scCO_2 in [bmim][PF_6], i.e., ignoring the volume- and composition changes in the stationary phase upon dissolution of CO_2 ($x_{3L} = 0$, $v_L \neq f(P, x_{3L})$). In a limited range of temperature and pressure, the corrected values could be obtained using the volumetric and composition data [9] for the [bmim][PF_6]–scCO_2 system. The relative difference between the raw and the corrected K-factors is much larger than that between the raw and the corrected partition coefficients. The reason is that dissolution of scCO_2 in [bmim][PF_6] is marked by high solubility of CO_2 (x_{3L}) but little volumetric expansion of the liquid phase [9].

CONCLUSION

Open-tubular capillary columns containing [bmim][PF_6] as the stationary liquid are capable to provide reproducible retention factors. In accord with the literature reports of extremely low solubility of [bmim][PF_6] in scCO_2, we have not observed any measurable loss of the RTIL from the column as the retention times have not decreased during a prolonged use of the column.

Table 1. Limiting partition coefficients (K_c) and K-values (K) of naphthalene in [bmim][PF_6]–CO_2 system (the same column as in Figure 1).

			Partition coefficient (K_c)		K-factor (K)	
T / K	P / MPa	r_G / mol dm^{-3}	raw	corrected	raw	corrected
313.15	8.1	6.585	345	275	0.00211	0.00553
	8.5	8.042	175	143	0.00340	0.00917
	8.8	9.750	74.3	62.1	0.00661	0.0182
	9.2	12.09	36.6	32.0	0.0108	0.0304
	10.5	15.00	17.8		0.0180	
	13.2	16.98	12.1		0.0232	
333.15	8.7	5.028	433	358	0.00220	0.00602
	10	6.588	185		0.00393	
	10.9	7.963	93.2		0.00646	
	12	9.871	45.7		0.0106	
	13.3	11.90	25.2		0.0159	
	16.7	14.93	13.3		0.0242	
	21.6	16.98	10.8		0.0262	
353.15	10	5.035	236		0.00402	
	11.8	6.557	116		0.00629	
	13.3	8.007	63.2		0.00946	
	15.3	9.995	32.2		0.0149	
	17.6	11.96	18.7		0.0214	
	23.2	14.96	12.1		0.0265	

In relatively nonpolar solutes such as naphthalene, the contributions to solute retention of spurious interfacial adsorption phenomena appear to be tolerable. Therefore, the solute capacity factors measured with open-tubular capillary columns can be converted into credible values of limiting partition coefficients and K-factors provided that the necessary volumetric and composition data for the [bmim][PF_6]–scCO_2 system become available.

In the micropacked capillary columns containing very thin films of [bmim][PF_6] on the surface of silica microspheres, there may be significant retention by spurious adsorption even with low-polarity solutes. This adverse conclusion has been supported by our experimental finding of a significant retention of naphthalene in a ‘blank’ column containing just barren silica microspheres without any [bmim][PF_6]. As regards the potential adverse effect of the pressure drop along the column, the micropacked capillaries would not present a problem. Calculations based on the Ergun equation [19] indicate that, under the particular experimental conditions of our measurements, the column pressure drop does not exceed 0.25 MPa. With an inactive support, therefore, even micropacked capillary columns could perhaps provide a feasible way to solute partition coefficients in RTIL–CO_2 systems.

Application of SFC retention to determine the solute partition coefficient K_c or K-factor K requires the data on molar volume (in K_c) or composition (in K) of the liquid phase in the RTIL–$scCO_2$ system. To date, such information has been scarce; as shown in Table 1, we could obtain the corrected values of K_c or K only for a small part of the (T,P)-range of the retention measurements. However, if independent values of K_c or K were known for a reference solute B (e. g., from spectroscopic measurements), the K_c or K of another solute A could readily be obtained from relative retention of A/B even without the volumetric and composition data on the RTIL–$scCO_2$ system. The relative retention route would also eliminate the uncertainty in the amount of RTIL in the column as the most important source of error in the resultant K_c and K values.

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