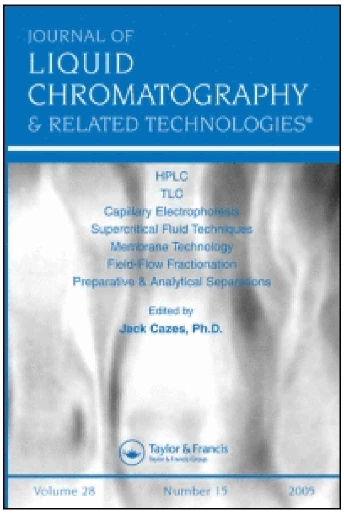

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FUNDAMENTAL INVESTIGATIONS AND TRENDS IN CCC

MEASUREMENTS OF PARTITION COEFFICIENTS IN WATER-1,1,1,2-TETRAFLUOROETHANE BY COUNTERCURRENT CHROMATOGRAPHY

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ABSTRACT

Recently, refrigerant 1,1,1,2-tetrafluoroethane (R134a) was considered as an extraction solvent alternative to supercritical fluid CO_2. We measured water-liquid R134a partition coefficients of some organic compounds using a high-speed countercurrent chromatography (HSCCC). The experiment could be operated by moderate modification of the commercial instrument. The partition coefficient data were obtained under 15°, 25°, and 45°C.

INTRODUCTION

In addition to solid-sample preparations, supercritical fluid extraction (SFE) also finds applications for liquids, especially for aqueous samples. Extractions of analytes, such as polychlorinated biphenys,[1] pesticides and herbicides,[2,3] and polyaromatic hydrocarbons[4] from aqueous samples are some examples. In addition to applications for analytical prospects, extraction for recover-

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ing low-concentration organic substances or removing pollutants from aqueous solutions using supercritical fluids, have also drawn scientific attention. Extractions to recover ethanol, 1-butanol, and pyridine from aqueous solutions directly using supercritical fluid carbon dioxide (SF CO_2), were reported recently.[5-7] Removal of furfural from aqueous effluents of a paper mill and agricultural chemicals from aqueous solutions using SFE, may provide an alternative way for waste-water treatment.[8,9] One of the major advantages of using SFE lies in the fact that supercritical fluids evaporate at atmospheric pressures, thereby separating from solutes of interest directly after extraction.

In addition to CO_2, some supercritical fluorinated ethanes also find potential applications as extraction solvents. For example, 1,1,1,2-tetrafluoroethane (R134a), an environmental benign refrigerant, possesses a dipole moment of 2.06 D that may enable it to dissolve compounds more polar than SF CO_2. A number of researches were involved in using R134a as the mobile phase in supercritical fluid chromatography (SFC)[10], or using R134a as a modifier to SF CO_2.[11-15] It was found, that R134a demonstrated different solvation power and selectivities[10,11] than SF CO_2. We recently employed liquid R134a as the mobile phase in countercurrent chromatography (CCC) to separate components of *Angelicae radix*.[16]

In addition, supercritical or liquid R134a was proven to be able to solubilize polar components in the presence of surfactants.[17,18] Formation of micelle demonstrated in our laboratory was proven responsible for the solubilization.[18] Lagalante et al.[19] measured water-R134a partition coefficients of eleven organic compounds using high-pressure spectroscopy, and applied a linear solvation energy relationship model to predict the data.

When used as an extraction solvent, liquid R134a turns into a gas like SF CO_2 after extraction, therefore it also separates from the analytes of interest easily. The extraction pressure for liquid R134a, however, is much lower than that of either supercritical or liquid CO_2. Practically, it may be more useful than CO_2 as an extraction solvent. We measured R134a partition coefficients of some organic solutes using high-speed CCC (HSCCC) in this study.

CCC is known as a pure liquid-liquid chromatography. A liquid, the mobile phase, flows through another liquid, the stationary phase; while these two phases are immiscible to each other. Compounds in a mixture are separated due to their different partition between these two phases. In addition to being a separation tool, CCC has also proven very useful for determining solute partition coefficients. For example, Berthod et al. used CCC to determine partition coefficients of the homologous of n-alkylbenzene in methanol-water-heptane solvent systems, and partition coefficients of a number of aromatic compounds in waterless biphasic liquid systems.[20,21] The same research group also recently studied the hydrophobic property of ionizable compounds by measuring the octanol-water partition coefficients of the compounds of interest.[22] Wang-Fan et al. determined partition coefficients of a series of macrolide antibiotics in order to develop purification precesses.[23] A number of other related works can be found in the literature.[24-29] The major advantages of CCC technique over the so-called shake-flask technique include speed and precision. As indicated by several CCC practitioners, the basic retention equation is:[20-22,30]

$$V_R = V_M + KV_s \tag{1}$$

where V_R, V_M and V_S are the solute retention volume, the dead volume (the mobile phase volume,) and the stationary phase volume, respectively, while *K* stands for the partition coefficient which can be expressed as:

$$K = C_s / C_m \tag{2}$$

where C_S is the solute concentration in the stationary phase, and C_M the solute concentration in the mobile phase. Since $V_S = V_T – V_M$, substituting in equation 1 gives:

$$K = \frac{V_R - V_M}{V_T - V_M} \tag{3}$$

where V_T is the total volume of the column. Parameters V_R and V_M can be obtained by chromatographic data while V_T is a fixed value.

EXPERIMENTAL

Chemicals and Sample Preparation

Naphthalene was purchased from Sigma (St. Louis, MO); 2-naphthol and m-cresol from Riedel-de Haen (Seelze, Germany); acetylacetone, benzaldehydes, and cyclohexanone from Aldrich (Milwaukee, WI). All the above chemicals were reagent grade. HPLC-grade methanol was obtained from Mallinckrodt (Paris, KY), and deionized water from Milli-Q (Millipore, St Quentin-en-Yvelines, France), while R134a (99.9%) from Ausimont (Milan, Italy).

All samples were prepared by dissolving the solutes in (50:50 v/v) methanol:water solvent and the concentrations for naphthalene, benzaldehyde, cyclohexanone, acetylacetone, 2-naphthol, and m-cresol were 1000, 5000, 50000, 2000, 5000, and 5000 µg/mL, respectively.

Experimental Set-Up and Procedures

The CCC rotor assembly for the measurement system was a Pharma-Tech Model CCC-1000 HSCCC. Three column modules were wound from three 29.5-

m long polytetrafluoroethylene (PTFE) tubing (2.54 mm O.D. × 1.59 mm I.D.), that granted a total volume of 172 mL. Two six-port-valves (Rheodyne 7010) were installed in the system, one for sample injection and the other for flow path switching. An ISCO (Lincoln, NE) Model V^4 UV/Vis detector was set at 275 nm to monitor analytes. A 0.70-mL phase separator was placed before the detector to remove solvent droplets, which were carried out occasionally by the mobile phase in order to reduce the detection interference. Usually, only very little water was observed in the phase separator after the experiment. Two 4 cm long (361 μm O.D. × 50 μm I.D.) fused-silica tubes (so-called restrictors) were connected to two metering valves V2 and V3, respectively, to maintain the desired pressures in the system.

The CCC column was first filled with water via path 1 while the oven was set to the desired temperature. The water flowed to the outlet of Valve V2 without passing the phase separator and the detector. The syringe pump (ISCO Model 260) was then filled with R134a and pressurized to the desired pressure. The centrifuge was started and the rotation speed was set at 800 rpm. R134a was pumped into the column via path 1 with Valve V1 closed. Metering valve V2 was adjusted to control the flow rate to 1.0 mL/min. The stationary phase (water) was displaced gradually until a sudden burst of R134a gas was observed at the graduate cylinder. The R134a was allowed to flow another 10 min to establish mobile phase/stationary phase equilibrium. The R134a pressure also became stabilized

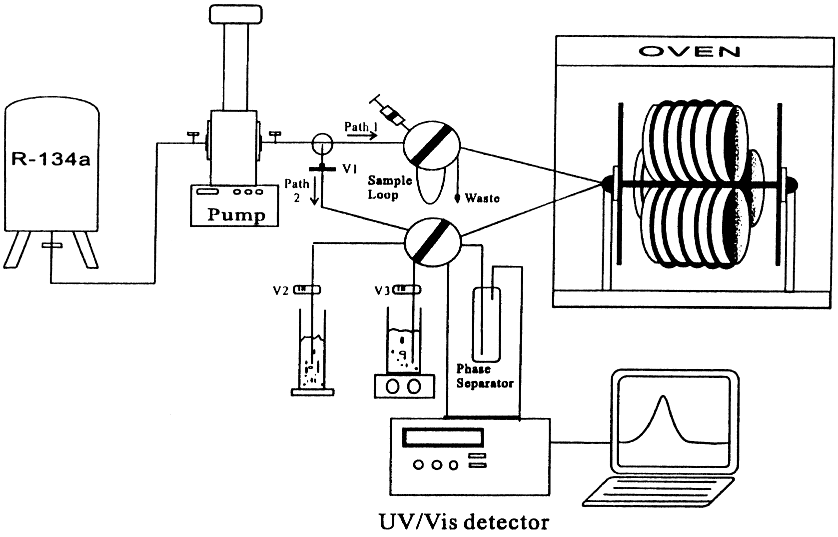

Figure 1. Schematic diagram of the experimental set-up.

in the same period. If the stationary phase retention ratio Sf was to be determined at this stage, the pump was turned off and the remaining stationary phase was pushed out and collected by a pressurized nitrogen flow. If a chromatographic experiment was to be performed, the successive procedures were followed. The R134a flow via path 1 was interrupted by adjusting the sample injection valve.

In the meantime, Valve 1 was opened to allow the R134a fluid, via path 2, pass the phase separator, and to fill the UV/Vis detector cell. Once the monitor baseline was stabilized, Valve V1 was closed and the R134a fluid was switched back to path 1 by adjusting the sample injection valve. At this moment, the path-switching six-port-valve was adjusted to allow the fluid flow via the column outlet to the phase separator, the monitor, and finally, to metering valve V3 and the restrictor outlet.

We found that the above operation, through path 2, helped acquire an adequate monitor baseline before elution started. The flow rate was finely adjusted by the metering valve V3. Since the rapidly vaporizing R134a might cause the freezing of water, so as to stop the flow at the restrictor, which was immersed in a water bath, the water bath was warmed up by a hot plate. Samples were injected through a 100-μL sample loop.

RESULTS AND DISCUSSION

Parameters, V_R and V_M in equation 3 are needed to compute the partition coefficient of a substance. While V_R, the retention volume, can be obtained directly in a chromatographic run, V_M can be obtained by the phase-retention experiment. Alternatively, V_M can also be obtained by performing a chromatographic experiment with a solvent front marker, a compound unretained by the stationary phase. The peak volume of the marker represents the unretained volume, i.e., V_M. Naphthalene was used as the solvent front marker due to its high hydrophobic property. The V_M values obtained using the naphthalene marker, matched those using the nitrogen-pushing technique within 3% for several test runs.

Solid-state matrix extraction above the critical temperature should promote the extraction speed due to the higher diffusivity and lower viscosity that help the fluid penetrate the matrix. For liquid-sample extraction, such as aqueous solutions, mechanical mixing should prevail over the diffusion factor in mass transfer. Considering higher operational temperatures to keep R134a (critical temperature = 101.5°C) under supercritical state, liquid-phase R134a would be preferable as an extraction solvent. The R134a pressure had to be high enough to remain as a liquid, and low enough not to exceed the upper pressure limit of the PTFE column. The pressure should be better kept as low as possible below the rated maximum pressure 21 bar (300 psi), because the anti-twisting operation would possibly reduce the pressure-resistance of the connecting tubing. All the experiments were performed under three different temperatures, i.e., 15, 25, and 45°C, and the same pressure of 15 bar. A typical chromatogram is shown in Fig. 2, and all the measured data are listed in Table 1. Three chromatograms were obtained for each temperature to calculate the coefficient. The relative standard deviation all fell within10%.

Since the operational conditions in this study were all far below the critical temperatures (101.5°C) and pressure (40.4 bar), the R134a should essentially possess physical properties as a liquid. The density changes corresponding to the pressure changes would be expected to be very small, and thus, the solvation power. Indeed, we found the solute retention time showed negligible change when the R134a pressure went up from 10 to 20 bar in our previous study.[30] In other words, the experimental data at 15 bar should well represent the partitioning of these compounds between water and liquid R134a. As for the temperature effect, the coefficients almost remain unchanged at this temperature range, as can be seen in Table 1. Due to the low extinction coefficient of cyclohexane, a rather high-concentration sample was injected. The partition coefficient thus obtained,

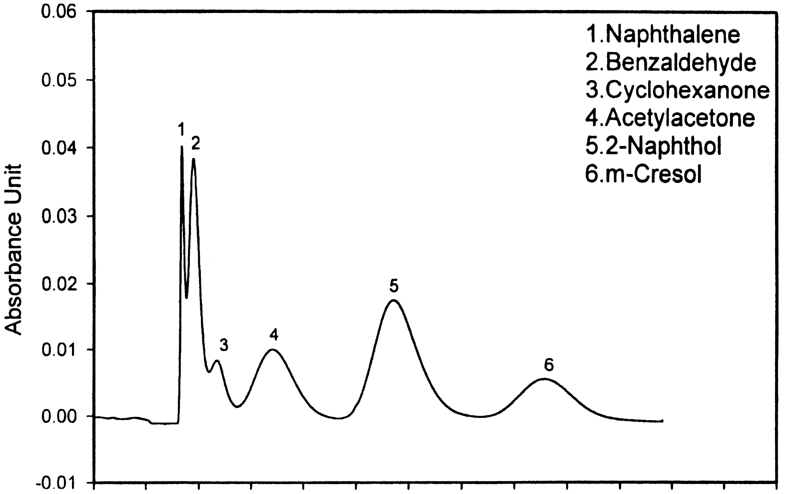

Figure 2. A typical chromatogram for the R134a/water system. Experimental conditions: 15 bar and 45°C; wavelength at 275 nm; rotation speed at 800 rpm; flow rate at 1 mL/min; injection volume 100 μL (0.1, 0.5, 5, 0.2, 0.5, and 0.5 mg for naphthalene, benzaldehyde, cyclohexanone, acetylacetone, 2-naphthol, and m-cresol, respectively).

Table 1. The Experimental Retention Data and R134a/Water Partition Coefficients for the Aromatic Compounds Studied

R134a Temp. (ºC)	Solute Retention Volume (V_R, mL) BA[a]	CH	AA	NT	MC	Dead Volume (V_M, mL) V_M
	36	48	63	116	206	32
15	35	46	62	114	200	31
	36	48	63	116	202	32
	33	44	61	111	192	29
25	35	46	62	114	193	31
	34	45	62	113	192	30
	56	64	82	122	173	52
45	36	45	66	114	173	31
	38	47	68	114	172	34

Temp. (ºC)	Partition Coefficient (K) BA	CH	AA	NT	MC
15	0.028[b]	0.11	0.22	0.60	1.2
	(3.6 %)[c]	(5.1 %)	(4.5 %)	(3.5 %)	(4.7 %)
25	0.028	0.11	0.22	0.58	1.1
	(2.1 %)	(5.2 %)	(2.6 %)	(1.7 %)	(5.2 %)
45	0.032	0.098	0.25	0.59	1.0
	(9.5 %)	(1.8 %)	——[d]	(0.98 %)	——[d]

[a] BA= Benzaldehyde, CH= Cyclohexanone, AA= Acetylacetone, NT= 2-Naphthol, MC= m-Cresol.

[b] Average of three trials.

[c] Relative standard deviation of three trials.

[d] Three numbers are same due to the round-off.

probably should just represent the saturation concentration of cyclohexane in water (for example, 0.0052% in water at 23.5°C, w/w), and should not be used as low-concentration data.

One major experimental error source was to be considered. The phase separator added 0.70 mL to the extra-column volume. The first term on the right-hand side of equation 2 was related to the retention volume. The error, possibly caused by the extra-column volume, could be cancelled out for the nominator of the term. However, V_M on the denominator would be affected by the introduction of the phase separator. Signal improvement without using a phase separator is needed to eliminate this error.

CONCLUSIONS

We measured R134a-water partition coefficients of organic compounds by HSCCC. This technique has shown more convenient than that reported in the literature. The experiments could be operated essentially using the conventional HSCCC techniques, as long as the R134a was kept under mild pressure. Although not remarked on in this study, the chromatographic data would also provide other useful physico-chemical information involving the solute mass transfer between the two phases.[21,22,30]

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