R&D NOTES

An Apparatus for Phase Equilibria of Heavy Paraffins in Supercritical Fluids

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Phase equilibria of heavy paraffins in supercritical fluids (SCFs) have not been investigated thoroughly by conventional methods, due in part to various experimental limitations (for example, long time required to obtain a measurement and large amounts of pure solute required). This work describes an experimental technique for the rapid and accurate determination of the phase equilibrium properties of heavy saturated hydrocarbons in SCFs, utilizing a packed chromatographic column coupled with an evaporative light scattering detector (ELSD).

Chromatographic techniques have proven to provide rapid and accurate phase equilibrium information (Yonker et al., 1987; Smith et al., 1987; Brown et al., 1987; Barker et al., 1988; Bartle et al., 1990a,b; Shim and Johnston, 1991; and Ekart et al., 1993a,b). They are an attractive experimental alternative to conventional methods due to the short time required for each run, the small sample size required, and the capability to provide phase equilibrium data at high temperatures or at low pressures where other techniques fail, since the solubility is small or simply because the solute may not be in its solid state. They have not yet been applied to heavy aliphatic substances, since these are difficult to detect in SCF solvents with common detectors such as UV, TC, and FID. One could use FT-IR or MS, but a cheaper and easier alternative is the ELSD. The light scattering detector modified for SCFs proved to be highly efficient and reproducible for such heavy molecules. The chromatographic apparatus is used to determine capacity factors and from these other phase equilibrium properties such as solubilities, partial molar volumes, and partial molar enthalpies.

Theory

In chromatography, the degree of retention of a solute depends on its distribution between the mobile and stationary phases; it is characterized by a dimensionless capacity factor k_i:

$$k_i = \frac{t_i - t_0}{t_0} \tag{1}$$

where t_i is the retention time of solute i, and t_0 is the retention time of a solute that is not retained in the stationary phase. If one assumes equilibrium (van Deemter et al., 1956):

$$k_i = \frac{x_i}{y_i}\frac{V^S}{v^S}\frac{v^M}{V^M} \tag{2}$$

where x_i and y_i are the mole fractions of component i in the stationary and mobile phases, respectively. The molar volumes in the stationary and mobile phases in the chromatographic column are represented as v^S and v^M, while V^S and V^M are the volumes of the stationary and mobile phases, respectively. Phase equilibrium considerations then yield ϕ_i^∞, the fugacity coefficient of solute i in the mobile phase at infinite dilution in terms of pressure and Henry's constant between the solute and the packing material. If one assumes that $\bar{v}_i^\infty$ is the stationary phase is equal to the liquid molar volume:

$$\phi_i^\infty = \frac{k_i H_i^0}{P v^M} \exp\left(\frac{v_i (P - P^0)}{RT}\right) \left[\frac{V^M v^S}{V^S}\right] \tag{3}$$

Note that the ratio in brackets, $[V^m v^S / V^S]$, depends *only* on the column and should not vary significantly with pressure. One application of this derivation is in SCFs where it has been successfully applied to obtain solubilities (Barker et al., 1988; Bartle et al., 1990a,b). Since the solubilities of many solutes of interest in SCFs are low (<0.001 mol fraction), the fugacity coefficient at saturation is nearly equal to the fugacity coefficient at infinite dilution.

$$y_i^{\text{sat}} = \left[\frac{P_i^s V^S}{H_i^0 V^M v^S} \exp\left(\frac{v_i (P^0 - P^s)}{RT}\right)\right] \frac{v^M}{k_i} = [C_i(T)] \frac{v^M}{k_i} \tag{4}$$

The expression in brackets was called $C_i(T)$, by Barker et al. (1988); Bartle et al. (1990a,b), and Ekart et al. (1992a,b). *In a given column*, $C_i(T)$ is a function of *temperature* and of the *solute i*. To determine $C_i(T)$ for a solute i at any temperature it is necessary to measure at least one solubility data

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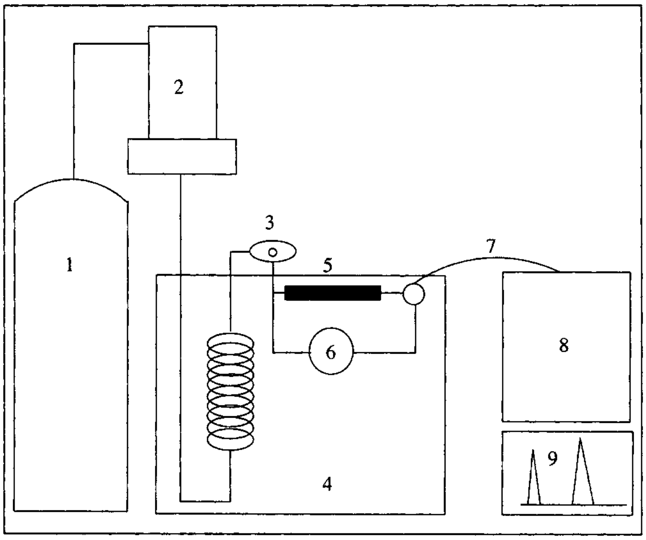

Figure 1. High-pressure chromatographic system.

1 = gas cylinder
2 = syringe pump
3 = injection valve
4 = water bath
5 = packed column
6 = pressure transducer
7 = heated restrictor
8 = light scattering detector
9 = recorder

point at that temperature with an independent technique. Once $C_i(T)$ is known, the entire solubility isotherm can be determined rapidly utilizing the chromatographic capacity factors.

Instrumentation and Equipment

The experimental apparatus used for the determination of phase equilibrium properties is shown in Figure 1. The system consists of a pulse-free liquid delivery system into a chromatographic packed column and subsequently to the ELSD. In this procedure, the fluid (carbon dioxide) is withdrawn from a cylinder as a liquid into a cooled high-pressure syringe pump (ISCO 500D). The preheated fluid then enters an injection valve (VALCO 4C16UW1), where small amounts of solid material dissolved in pentane are injected in a 10-μL injection loop. Pentane was selected as the solvent, since it dissolved the solid hydrocarbons and was not retained in the packed column, and its peak was detected each time providing a reference (t_0). The column (100 mm in length and 4.6 mm internal diameter) was packed with 10-μm particles of HYPERSIL ODS C_{18}. The small pressure drop across the column (1-3 bar) is measured using a differential pressure transducer (VALYDINE CD12), while the system pressure is monitored with a pressure transducer and indicator (HEISE 901B). The effluent flows through a deactivated silica restrictor (50 μm inside diameter and 40 cm length) where the fluid undergoes decompression and evaporation. The restrictor is heated with a heat-transfer fluid (UCON Heat Transfer Fluid 500) to compensate for the cooling effect from the expansion of the mobile phase. This procedure avoids the possible crystallization of the mobile phase (Joule-Thompson effects).

An important feature of the interface is to extend the restrictor 1-2 mm into the evaporative chamber of the ELSD to act as the nebulizer. Other studies using liquid solvents (Carraud et al., 1987; Nizeri et al., 1989) have indicated the need of an additional heating step at the tip of the nebulizer to overcome crystallization of the mobile phase upon expansion. In this investigation, however, the additional precaution was not required. Other investigators have reported that the use of such nebulizing gas might not be necessary for SCF applications (Carraud et al., 1987; Nizeri et al., 1989); however, our studies demonstrated greater stability in the response (signal to noise ratio, S/N) when using such nebulizing gas. The gas then goes through a laser light beam where the particles of nonvolatile material scatter the light, which is measured with a sensitive photodiode. The retention times used for this investigation were an average of several measurements obtained at the maxima of their response. The chromatographic column was maintained under pressure continuously to maintain constantly its performance (activity). Since all solutions studied were highly dilute, the densities used in the calculations were pure-fluid densities obtained from *The International Thermodynamic Tables for the Fluid State Carbon Dioxide* (IUPAC, Volume 3, 1976).

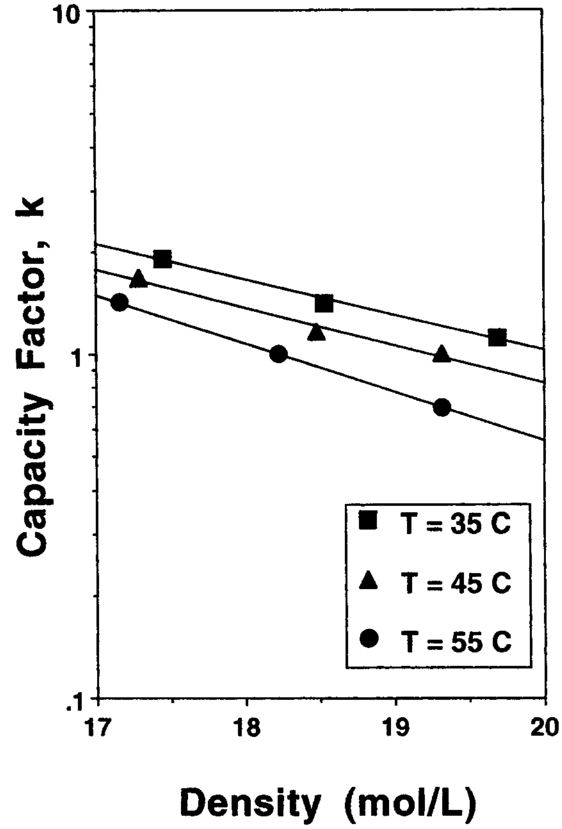

Figure 2. Capacity factors vs. density: phenanthrene in CO_2.

Chemicals

SFE-grade CO_2 (99.99 + % purity) was obtained from Scott Specialty Gases. The solutes, phenanthrene (+ 98% purity) and $C_{24}H_{50}$ (99% purity), were obtained from Aldrich Chemical Company. They were used without further purification, since the chromatographic system separated out the impurities.

Results and Discussion

The well studied CO_2-phenanthrene system was investigated

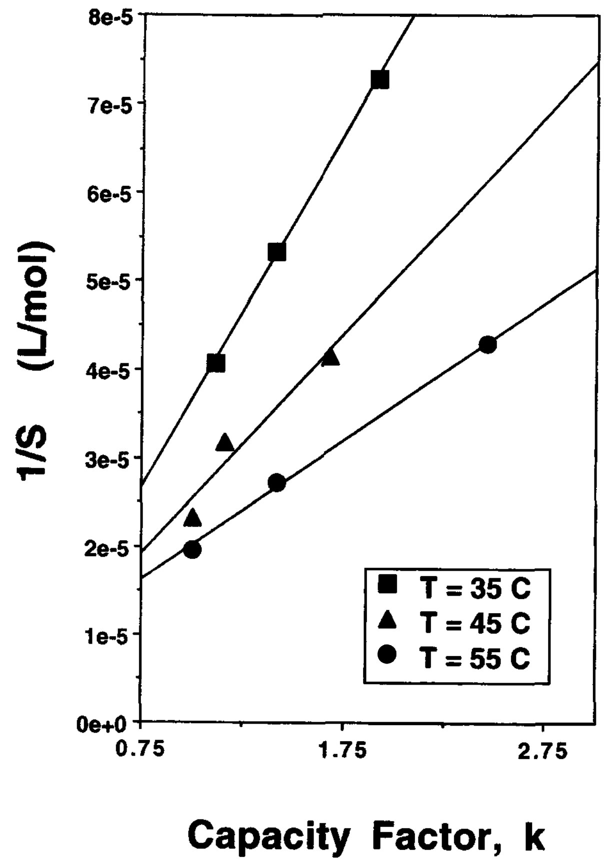

Figure 3. 1/*S* vs. *k*; phenanthrene in CO_2.

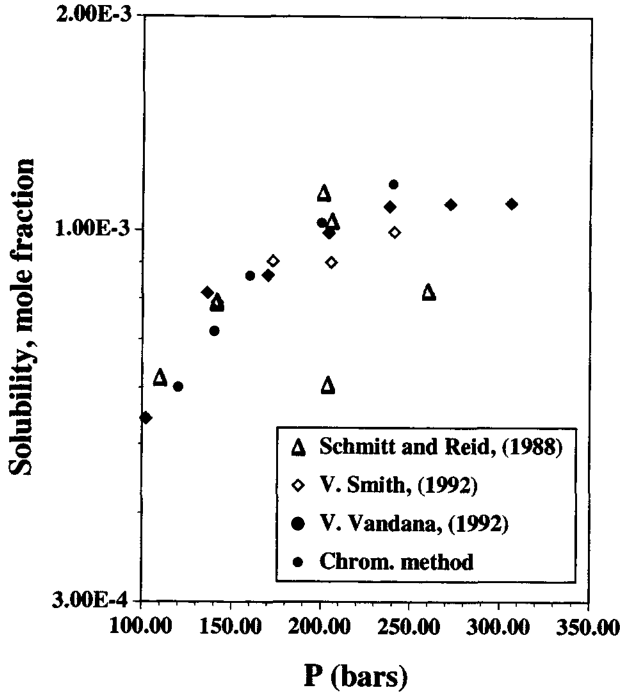

Figure 4. Solubility vs. pressure: $C_{24}H_{50}$ in CO_2 at 35°C.

first to confirm the reliability and validity of the technique. In the vicinity of the solvent's critical point the log (y_2) varies linearly with the fluid density (Kumar and Johnston, 1988); thus log (k_i) should be linear in density as well (Figure 2).

Bartle and coworkers (1990a,b) plotted inverse solubility vs. capacity factors; we show such plot (Figure 3) for phenanthrene in CO_2 at 35, 45 and 55°C. The solubility data used were obtained from Dobbs et al. (1986) at 35°C, and Kurnik et al. (1981) at 45 and 55°C. The fits are linear and accurate to within 5%. The overall estimated experimental error is probably 5-10%, with the largest contributions (about 2% each) coming from the pressure drop across the column (1-3 bar), the pressure variations from the constant flow control (±0.5 bar), and the retention times (±0.5 s).

Next, the $C_{24}H_{50}$-CO_2 system was studied and compared with various authors (Figure 4). The $C_i(T)$ needed for the chromatographic method was obtained from Smith (1992), and the results showed comparable agreement to those of other investigators (Schmitt and Reid, 1984; Vandana, 1992). The data of Schmitt and Reid were taken about ten years ago by a conventional method and exhibit more scatter. The chromatographic isotherm was obtained and replicated in less than two hours.

In short, a chromatographic method for the rapid and accurate determination of the phase equilibrium properties of heavy hydrocarbon systems has been presented. This method emphasizes the determination of fugacity coefficients for these solubilities, but the method could also be used for other thermodynamic properties, such as partial molar volumes and partial molar enthalpies (Shim and Johnston, 1991). Currently, the method is limited by the need of one additional piece of information [$C_i(T)$]. For similar systems, however, one can envision the correlation of $C_i(T)$ based on carbon number and temperature. The proposed method overcomes the limitations of conventional methods and may open doors to further understanding the phase equilibrium behavior not only of long-chain paraffins, but also of other heavy molecules, such as biological molecules which are more difficult to detect.

Acknowledgment

Financial support for this investigation from the GRI (Gas Research Institute) and GPA (Gas Processors Association) is greatly appreciated.

Notation

$C_i(T)$ = constant for a particular solute, packed column, and temperature
ELSD = evaporative light scattering detector
H_i = Henry's constant for solute *i*
H_i^0 = Henry's constant for solute *i* at the reference pressure P^0
k_i = chromatographic capacity factor
P = pressure
P^0 = reference pressure
P_i^s = saturation (vapor) pressure of solute *i*
R = universal gas constant
S = solubility (mol/volume)
SCF = supercritical fluid
t_i = retention time of the solute *i*
t_0 = retention time of the unretained solvent (pentane)
T = temperature
v_i^M = molar volume of solute *i* in the mobile phase
v_i^S = molar volume of solute *i* in the stationary phase
$\bar{v}_i^\infty$ = infinite dilution partial molar volume of solute *i*
V^M = volume of the mobile phase inside the chromatographic column

V^S = volume of the stationary phase
x_i = mole fraction of the solute in the stationary phase
y_i = mole fraction of the solute in the mobile phase

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Manuscript received Aug. 21, 1992, and revision received Nov. 5, 1992.
