

Review

Determination of thermodynamic properties by supercritical fluid chromatography

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Abstract

This survey attempts to summarise thermodynamic applications of supercritical fluid chromatography (SFC) with an emphasis on the results published during the last 10 years. In addition to a review of thermodynamic measurements by SFC, it contains brief sections on instrumental considerations and on the sources of auxiliary information needed when processing the retention data.

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Abbreviations: ATR, attenuated total reflectance; [bmim][PF₆], 1-butyl-3-methylimidazolium hexafluorophosphate; CFC, chlorofluorocarbon; EOS, equation of state; FID, flame ionisation detection; GC, gas chromatography; GLC, gas–liquid chromatography; HHPCO₂, helium head pressure carbon dioxide; HPLC, high-performance liquid chromatography; LSER, linear solvation energy relationships; MSTPC, mass spectrometric tracer pulse chromatography; P–V, Panayiotou–Vera (lattice fluid model); PAH, polycyclic aromatic hydrocarbon; PCPMS, poly(cyanopropyl methyl siloxane); PDMS, poly(dimethyl siloxane); PMMA, poly(methyl methacrylate); PPO, poly(2,6-dimethylphenylene oxide); PVA, poly(vinyl acetate); PVP, polyvinylpyrrolidone; S–L, Sanchez–Lacombe (lattice fluid model); scCO₂, supercritical carbon dioxide; SFC, supercritical fluid chromatography; SFE, supercritical fluid extraction

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1. Introduction

Measurements of thermodynamic data by supercritical fluid chromatography (SFC) constitute an important, varied, and intriguing application of this technique. Although much of the relevant work has been covered elsewhere, e.g., in the respective sections of comprehensive reviews of analytical SFC [1–3] or unified chromatography [4–6], the field probably deserves stand-alone, periodical accounts [7] including also some specific experimental features and auxiliary thermophysical properties needed to process the chromatographic retention data. The present survey is a sequel to a short account [8] that appeared in 1991, and it largely retains the overall structure of its predecessor, comprising three major sections on thermodynamic measurements, instrumental considerations, and sources of auxiliary thermophysical data and theoretical models, respectively. Most of the results covered here appeared after 1990 although references to earlier work have been included when necessary.

2. Thermodynamic measurements

In one way or another, all thermodynamic measurements employing solute retention make use of the Gibbs energy of solute transfer between the stationary and the mobile phase. However, as the solute transfer properties in typical SFC systems are of limited use outside chromatography itself, a proper utilisation of SFC as a tool for thermodynamic measurements usually involves separation of a transfer property into contributions of the two phases. In SFC, the separation is invariably more difficult than in GC because, in SFC, uptake of the mobile phase fluid by the stationary phase is no

longer negligible. For the purpose of this review, thermodynamic properties obtainable by SFC may be classified into

- (i) the properties derived directly from solute retention (Section 2.1), and
- (ii) the properties derived from *changes* in solute retention with pressure, temperature, or composition of the (binary) mobile phase fluid (Section 2.2).

In order to reduce chromatographic retention data into either (i)- or (ii)-class of properties, one needs reliable information on uptake of the mobile phase fluid by the stationary phase (Section 2.3). There are also some thermodynamic measurements that employ chromatographic instrumentation rather than chromatographic process itself (Section 2.4).

Throughout this paper, the quantities pertaining to the individual components of the chromatographic system will be identified by numerical subscripts, with 1 identifying the solute, 2 the principal component of the stationary phase, 3 the mobile phase fluid, and 4 the cosolvent (modifier), if used. Subscripts *s* and *m* will identify the quantities pertaining to the stationary and the mobile phase, respectively. The determination of both (i)- and (ii)-classes of properties have been based on several important preconditions:

- (a) the retention time is measured to the first temporal moment of the chromatographic band so that the retention factor reflects the equilibrium distribution of the solute (1) in an analogous system under static conditions,
- (b) the principal component of the stationary phase (2) is non-volatile and insoluble in the mobile phase fluid (3),
- (c) bulk adsorption in the stationary phase is the only and exclusive mechanism of solute retention (i.e., interfacial adsorption of the solute is absent), and

- (d) the solute is effectively at infinite-dilution in both phases so that the equilibrium distribution of component 3 (or 3 and 4, if a cosolvent is used) between the mobile and the stationary phase is not affected by the presence of the solute.

2.1. Properties derived from solute retention

These applications of SFC have been focused on the determination of the relative values of solute solubilities in supercritical fluids (Section 2.1.1), and on the determination of solute partition coefficients between supercritical CO₂ (scCO₂) and the stationary phase (Section 2.1.2). The former has received more attention than the latter because of somewhat specific character of the chromatographic system (solute–stationary phase–supercritical fluid). Determination of both solute solubility and solute partition coefficient requires the knowledge of the amount of stationary phase in the column; the amount may be ascertained either directly when preparing the column or indirectly through the use of independent data.

2.1.1. Solubilities in supercritical fluids

Assuming that retention of a solute reflects the equilibrium distribution of the solute between the mobile and the stationary phase, the solute retention factor:

$$k_1 = \frac{t_R - t_0}{t_0} \quad (1)$$

may also be written as

$$k_1 = \frac{x_{1s}n_s}{x_{1m}n_m} = \frac{x_{1s}V_s v_m}{x_{1m}v_s V_m} \quad (2)$$

where x_{1s} and x_{1m} are the mole-fractions of the solute in the stationary and the mobile phase, n_s and n_m are the total amounts of substance (mole numbers) in the two phases in the column, V_s and V_m are the volumes of the two phases in the column, and v_s and v_m are the molar volumes of the two phases, respectively. Phase equilibrium considerations [9] then yield φ_{1m}^∞ , the fugacity coefficient of the solute (1) at infinite-dilution in the mobile phase fluid,

$$\varphi_{1m}^\infty = \frac{k_1 V_m v_s}{P v_m V_s} H_{1s}^r \exp \left\{ \frac{\bar{v}_{1s}^\infty (P - P^r)}{RT} \right\} \quad (3)$$

where P is the mean pressure in the column, H_{1s}^r the Henry's constant of the solute in the stationary phase at a reference pressure P^r , \bar{v}_{1s}^∞ the infinite-dilution partial molar volume of the solute in the stationary phase, R the molar gas constant, and T is the column temperature. Since the mole-fraction solubilities, y_1^σ , of non-volatile solutes in supercritical fluids are usually low ($y_1^\sigma < 10^{-3}$), the solute fugacity coefficient at saturation is nearly equal to the fugacity coefficient at infinite-dilution. Further, \bar{v}_{1s}^∞ may be approximated by the molar volume of the pure solute, v_1^0 . With these provisions, the expression for solute solubility

becomes [9–12]:

$$y_1^\sigma = \left\{ \frac{P_1^0 V_s}{H_{1s}^r V_m v_s} \exp \left[\frac{v_1^0 (P^r - P_1^0)}{RT} \right] \right\} \frac{v_m}{k_1} \\ = [C_1(T)] \frac{v_m}{k_1} \quad (4)$$

where P_1^0 is the vapour pressure of the pure solute at the column temperature. In a particular column, the bracketed term in Eq. (4) is a function of the solute and the temperature, and, to a first approximation, it does not vary with pressure. Therefore, if a single independent value of solute solubility at a particular pressure is available to fix the $C_1(T)$ term in Eq. (4), the retention factors at other pressures may rapidly yield the whole solubility isotherm, with v_m calculated from an equation of state for the pure mobile phase fluid (Section 4.1.3).

This approximate approach, introduced by Bartle and co-workers [10–13], can be used to convert the relative changes in solute retention factor into the relative changes in solute solubility in the mobile phase fluid. It has been used to extend the data bases of solubilities of diverse solutes in supercritical methane [14], ethane [15], and CO₂ [10–13,16,17]. The selection of solutes included polycyclic aromatic hydrocarbons (PAHs) [10–13,16], long-chain *n*-alkanes [14,15,17], and metal–ligand complexes [16]. Generally, the resultant solubilities are in satisfactory agreement with those obtained by other techniques. In addition to solute solubilities, Suleiman and Eckert also obtained the second cross-virial coefficients for higher *n*-alkanes with methane [14] and ethane [15].

Yang and Griffiths [18] attempted to make the above method predictive, i.e., applicable to the solutes for which no solubility data were available. To this end, they established a connection between $C_1(T)$, the solubility parameter of scCO₂, and a “threshold density” dependent of the solute, the column and the temperature. The accuracy of their method was limited to $\pm 30\%$. Mishima et al. used a related approach to measure the solubilities in scCO₂ of flavones [19] and lactones [20].

2.1.2. Partition coefficients

In analytical chromatography, the distribution of the solute between the stationary and the mobile phase is conventionally described through the partition coefficient (distribution constant) defined in terms of equilibrium molar concentration of the solute in both phases,

$$K_c = \frac{c_{1s}}{c_{1m}} = k_1 \frac{V_m}{V_s} \quad (5)$$

where c_{1s} and c_{1m} denote the molar concentrations of the solute in the stationary and the mobile phase, respectively, and the quotient V_m/V_s is sometimes called phase ratio.

Johnston and co-workers measured the partition coefficients of several aromatic hydrocarbons between C₁₈-bonded silica and CO₂ [21] and siloxane rubber and

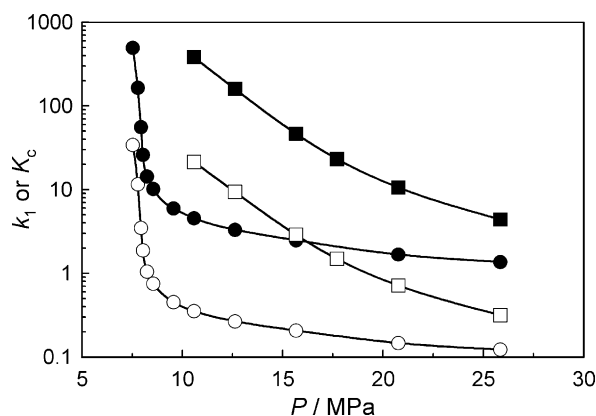


Fig. 1. SFC data on phenanthrene partitioning between swollen PDMS rubber and supercritical CO₂ [22]. Empty symbols, retention factor (k_1); full symbols, partition coefficient (K_c); circles, 34.2 °C; squares, 99.0 °C.

CO₂ [22,23] employing both packed [21,22] and open tubular [23] columns. Fig. 1 shows the retention factor and partition coefficient of phenanthrene between poly(dimethyl siloxane) (PDMS) rubber and scCO₂ at 34.2 and 99.0 °C [22]. The near-critical isotherms display the characteristic “sigmoid” shape. At a particular temperature, the k_1 and K_c isotherms would not exactly superimpose on one another because the polymer swells with the absorbed CO₂, and therefore, the phase ratio (cf. Eq. (5)) decreases with the raising pressure. Wang et al. [24] used a combination of SFC and sorption measurements with a piezoelectric sensor to study infinite-dilution partition coefficients (K factors) of benzene and toluene between scCO₂ and CO₂-swollen poly(vinyl acetate) at 40 and 60 °C and at pressures up to 8 MPa. Shim [25] compared the partition coefficients determined by elution SFC with those obtained by frontal SFC. The behaviour of the solute in the polymer phase was explained on the basis of the solute vapour pressure and the solute fugacity coefficient in scCO₂. The measured retention factors were corrected for spurious adsorption of the solute on the surface of the silica support.

Apart from the determinations of solute partition coefficients in conventional SFC systems comprising crosslinked polymers [22,23–25] or bonded phases [21], a few applications were devised involving more special systems.

Yan and Martire developed a lattice-model-based molecular theory of SFC retention of block-like solutes in anisotropic [26] and isotropic [27] stationary phases, and applied it to a successful explanation of the retention factors of PAHs in a smectic stationary polymer (biphenyl carboxylate ester polysiloxane) [28] as well as to the selectivity enhancement [29] for PAHs in the smectic polymer as compared to an isotropic stationary polymer (octyl methyl polysiloxane).

Planeta and Roth [30] used open tubular columns with a room-temperature ionic liquid (RTIL) stationary phase, 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF₆]), for preliminary measurements of naphthalene partition coefficients in the two-phase system formed

by scCO₂ and CO₂-expanded [bmim][PF₆]. In the opinion of a practising chromatographer, such an application of SFC would certainly suffer from very low viscosity of [bmim][PF₆] and poor wettability of silica by [bmim][PF₆]. Nevertheless, SFC appears to be a feasible tool for rapid acquisition of solute partition coefficients in biphasic, “green”, emission-free solvent systems comprising scCO₂ and RTILs [31].

2.1.3. Correlation of solute retention with solvatochromic parameters

Within the widely used concept of the linear solvation energy relationships (LSERs), many properties of dilute solutions such as rate constants, partition coefficients, and chromatographic retention factors [32] may be expressed as linear combinations of a cavity-formation term and several terms describing the contributions of individual types of intermolecular forces to the overall solute–solvent interaction. Since the first applications of the concept have often concerned the solvent effects on UV-Vis spectra, the numerical constants describing the individual substances’ involvement in the individual interactions are called solvatochromic parameters. Although the early versions [33,34] of the LSER concept were aimed at processes occurring in incompressible solvents (liquids), many applications to gas–liquid partitioning [35,36] and GLC retention data [37,38] were also described. The applications of LSERs involving supercritical fluids were concerned with density dependence of solvatochromic parameters of CO₂ [39], spectroscopy of solvatochromic probes in pure [40–42] and cosolvent-modified [43] supercritical fluids, solid–scCO₂ equilibria [44], supercritical fluid–water partitioning [45,46], and solute retention in packed [47,48] and open tubular [49] column SFC with pure [49] and cosolvent-modified [47,48] CO₂.

Employing an octadecylsilane bonded phase in packed capillary column SFC with 35 test solutes, Pyo et al. [47] used the LSER regression to discern between two different effects of addition of methanol to scCO₂. They concluded that small amounts of methanol serve predominantly to coat the free silanol groups on the surface of the stationary phase, and when more methanol is added, the increase in density of the mobile phase becomes more important. Cantrell et al. [48] measured the retention factors of sixteen 1-substituted naphthalenes on a packed column with a cyano-bonded stationary phase using pure CO₂ and CO₂ modified with 10 different cosolvents. LSER treatment of the retention data results in ranking the cosolvents with respect to their lipophilicity, dipolarity, and basicity, and it suggests that selection of a cosolvent may be used to either promote or suppress a particular type of molecular interactions.

Weckwerth and Carr [49] employed LSER to interpret the retention factors of 86 solutes of diverse chemical structures in SFC with pure CO₂ mobile phase on an open tubular column with PDMS stationary polymer. The measurements were carried out at constant temperature and column inlet pressure, with the temperature ranging from 60 to 120 °C

and the pressure ranging from 7.6 to 11.7 MPa. The resultant solvatochromic coefficients confirm the dominance of dispersion interactions and cavity formation processes in the mechanism of retention, and suggest that scCO₂ can act as both a Lewis base and a Lewis acid.

Adopting a concept similar to LSERs, Heaton et al. [50] applied a multicomponent solubility parameter approach [51] to correlate and predict the retention factors of mono- and disubstituted benzenes in packed column SFC with methanol-modified CO₂ as the mobile phase. Comparison with experimental data made it possible to predict the contributions from individual kinds of intermolecular forces to the overall solubility parameters in a series of disubstituted aromatics.

2.1.4. Correlation of solute retention with other properties of the solute

Brauer et al. [52] used a solubility parameter model of partition coefficient [53] for correlation and prediction of retention factors of alkylated ferrocenes in terms of solute solubility parameter, solute molar volume, and phase ratio of the column. The cohesive energies and molar volumes of substituted ferrocenes were estimated from the group contribution method of Fedors [54].

2.2. Properties derived from changes in solute retention with pressure, temperature, or mobile phase composition

Unlike the properties discussed in Sections 2.1.1 and 2.1.2, determination of the properties described below does not require the knowledge of the exact amount of the principal component of the stationary phase in the column. However, the amount of the principal component of the stationary phase has to remain constant during the measurements (no washout or bleeding).

The change in solute retention factor with *pressure* at a constant temperature can be used to obtain the difference between the partial molar *volumes* of the solute at infinite-dilution in the mobile and the stationary phase (Section 2.2.1).

The change in solute retention factor with *temperature* at a constant pressure can be used to obtain the difference between the partial molar *enthalpies* of the solute at infinite-dilution in the mobile and the stationary phase (Section 2.2.2).

The change in solute retention factor with *composition* of a binary mobile phase fluid at a constant temperature and pressure can be used to obtain the composition derivative of the *fugacity coefficient* of the solute at infinite-dilution in the binary fluid (Section 2.2.3). This quantity may be very useful in quantifying the cosolvent effects [55] in near-critical fluids.

2.2.1. Effect of pressure

Under the conditions mentioned in the introduction to section 2, the isothermal change of the solute retention factor

with pressure in a (1 + 2 + 3) system (without a cosolvent) is given by [21,22,56–60]:

$$\left(\frac{\partial \ln k_1}{\partial P}\right)_T = \frac{\bar{v}_{1m}^\infty - \bar{v}_{1s}^\infty}{RT} - \beta_{m,T} - \frac{V_s}{V_m} \beta_{s,T,\sigma} - \frac{1}{RT} \left(\frac{\partial \mu_{1s}^\infty}{\partial w_{3s}}\right)_{T,P,n_{2s}} \left(\frac{\partial w_{3s}}{\partial P}\right)_{T,\sigma} \quad (6)$$

where R is the molar gas constant, T the temperature, P the pressure, \bar{v}_{1m}^∞ and \bar{v}_{1s}^∞ are the infinite-dilution partial molar volumes of the solute in the mobile and the stationary phase, respectively, $\beta_{m,T}$ is the isothermal compressibility of the pure mobile phase fluid (3), $\beta_{s,T,\sigma}$ is the isothermal compressibility of the stationary phase at saturation with the mobile phase fluid, μ_{1s}^∞ is the infinite-dilution chemical potential of the solute in the stationary phase, and w_{3s} is the mass fraction of the mobile phase fluid in the stationary phase. Subscript n_{2s} refers to insolubility of component 2 in the mobile phase fluid, and subscript σ emphasises saturation of the stationary phase with the dissolved mobile phase fluid. The reason for using mass fraction in the last term is that, in SFC, component 2 is often a high-molar-mass polymer ($M_2 \rightarrow \infty$) which makes mole-fraction an inconvenient composition variable for the stationary phase.

At the temperatures and pressures near the critical point of the mobile phase fluid, the quantities \bar{v}_{1m}^∞ , $\beta_{m,T}$, $\beta_{s,T,\sigma}$, and $(\partial w_{3s}/\partial P)_{T,\sigma}$ in Eq. (6) display near-critical anomalies resulting in complex non-linear variations of $\ln k_1$ with pressure such as shown in Fig. 1. Therefore, Eq. (6) is an awkward starting point for the analysis of retention data to obtain \bar{v}_{1m}^∞ , and the data analysis is commonly based on variation of $\ln k_1$ with density of the mobile phase fluid. The isothermal variations of $\ln k_1$ with the pressure and with the density are related to each other by:

$$\left(\frac{\partial \ln k_1}{\partial P}\right)_T = \beta_{m,T} \left(\frac{\partial \ln k_1}{\partial \ln \rho_m}\right)_T \quad (7)$$

In the near-critical region, \bar{v}_{1m}^∞ scales as $\beta_{m,T}$ [61–63], and the same applies to $\beta_{s,T,\sigma}$ and $(\partial w_{3s}/\partial P)_{T,\sigma}$. Therefore, the ratio $\bar{v}_{1m}^\infty/\beta_{m,T}$ is relatively insensitive to density [64,65]. Since neither \bar{v}_{1s}^∞ nor $(\partial \mu_{1s}^\infty/\partial w_{3s})_{T,P,n_{2s}}$ display the near-critical anomalies, the result is that the $\ln k_1$ versus $\ln \rho_m$ plots are nearly linear as illustrated in Fig. 2. Although Fig. 2 shows somewhat exotic system involving an ionic liquid, the overall appearance of such plots is essentially independent of the nature of the stationary phase since, in the near-critical region, the value of the slope $(\partial \ln k_1/\partial \ln \rho_m)_T$ arises primarily in the mobile phase. The near-linearity of the plots over short intervals of density can also be inferred from the unified molecular theory of chromatography [66].

The analysis of retention data via Eqs. (6) and (7) requires a high-accuracy equation of state (EOS) for the pure mobile phase fluid (Section 4.1.3) to describe the fluid's $P\rho_m T$ behaviour and to calculate $\beta_{m,T}$. The partial molar volume of the solute at infinite-dilution in the stationary phase, \bar{v}_{1s}^∞ , is often substituted by the molar volume of the pure solute that

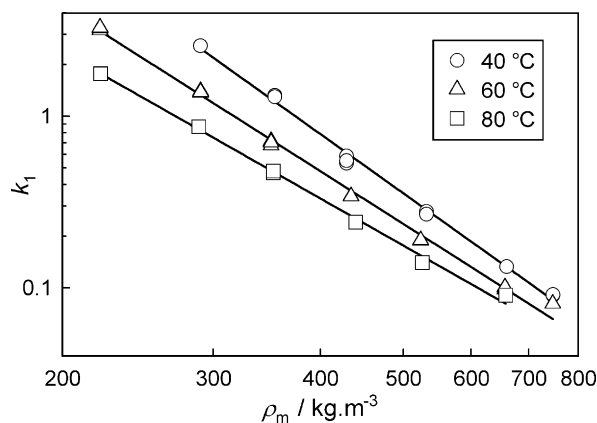


Fig. 2. Retention factor of naphthalene as a function of density of CO₂. Open tubular column 4.2 m × 85 μm i.d., [bmim][PF₆] film thickness 0.16 μm [30].

can be estimated using group-contribution methods (Section 4.1.1). At the temperatures and pressures near the critical point of the mobile phase fluid, \bar{v}_{1s}^{∞} is often negligible compared to \bar{v}_{1m}^{∞} that acquires large negative values [56,67]. If the effects of dissolution of the mobile phase fluid in the stationary phase are to be taken into account, a thermodynamic model is needed to calculate $(\partial\mu_{1s}^{\infty}/\partial w_{3s})_{T,P,n_{2s}}$ and to correlate V_s/V_m , $\beta_{s,T,\sigma}$, and $(\partial w_{3s}/\partial P)_{T,\sigma}$ (Section 4.1.4). Because $(\partial\mu_{1s}^{\infty}/\partial w_{3s})_{T,P,n_{2s}}$ cannot be obtained without resorting to a thermodynamic model, the correction for uptake of the mobile phase fluid by the stationary phase cannot be carried out in a definite and conclusive way.

Eqs. (6) and (7) were used extensively to determine the partial molar volumes of diverse solutes at infinite-dilution in scCO₂. The selection of solutes included aromatic hydrocarbons [21,22,56–58,68–73], C₆–C₁₆ *n*-alkanes and alkylated cyclohexanes [68], benzoic acid and 2-methoxynaphthalene [69,71], C₃–C₉ aliphatic and C₁₀ terpenic alcohols [74], coenzyme Q₁₀ [75], polyunsaturated long-chain carboxylic acids [76,77] and their ethyl esters [78], C₂₁–C₄₀ *n*-alkanes [79], and β -carotene and vitamin E [80]. The effect of the correction for uptake of scCO₂ by the stationary phase could only be tested in naphthalene [73] where sufficient amount of independent \bar{v}_{1m}^{∞} data were available [81]. Fig. 3 suggests that the correction brings the SFC-derived results closer to the \bar{v}_{1m}^{∞} values derived from high-precision density measurements [81].

The determinations of solute partial molar volumes described above were accomplished using partition SFC. Akman et al. [82] presented a thermodynamic model for adsorption SFC, and adsorption SFC with silica gel adsorbents was employed to determine \bar{v}_{1m}^{∞} for several aromatic solutes in scCO₂ [83,84] as well as in CO₂–ethane mixtures [85].

Once the infinite-dilution partial molar volume of the solute in a near-critical fluid is known, it can either be used to obtain unlike-interaction parameters in EOS models and to test the EOS-based correlations for \bar{v}_{1m}^{∞} [86,87], or it can be converted to some fundamental thermodynamic de-

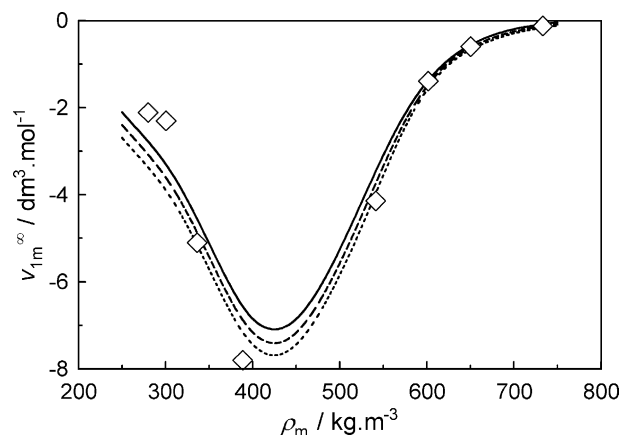


Fig. 3. Effect of the correction for uptake of scCO₂ by PDMS on \bar{v}_{1m}^{∞} of naphthalene in scCO₂ at 35 °C [73]. (◇) Data from vibrating-tube densitometry at 35.23 °C [81]; (solid line) SFC without uptake correction; (dashed line) SFC with correction from the Scatchard–Hildebrand–Flory–Huggins theory; (dotted line) SFC with correction from the Panayiotou–Vera lattice fluid model [294].

scriptors of the interaction between the non-volatile solute (1) and the near-critical fluid (3). The descriptors include, e.g., the δ -value [88], the Krichevskii function [89], and the Krichevskii parameter [90]. The δ -value is related to \bar{v}_{1m}^{∞} by:

$$\delta = \frac{\bar{v}_{1m}^{\infty} \rho_m}{\beta_{m,T}} \quad (8)$$

where ρ_m is the molar density of the mobile phase fluid, and it had been used for classification of dilute binary mixtures near the solvent's critical point [88]. In a binary mixture of components 1 and 3, the Krichevskii function [89] is the isothermal, isochoric derivative of pressure with respect to mole-fraction of the solute (1) in the limit of infinite-dilution of the solute ($x_1 \rightarrow 0$), and it is related to δ through:

$$\left(\frac{\partial P}{\partial x_1}\right)_{T,v} = \delta - \frac{1}{\beta_{m,T}} \quad (9)$$

The value of the Krichevskii function at the fluid's critical temperature and pressure has been called Krichevskii parameter [90]. Because the isothermal compressibility $\beta_{m,T}$ diverges to $+\infty$ at the fluid's critical temperature and pressure, the Krichevskii parameter of a solute can be estimated by extrapolating the SFC-derived values of δ to the fluid's critical temperature and pressure. This route has been used [91] to obtain the Krichevskii parameters of C₂₁ to C₄₀ *n*-alkanes in scCO₂ but the results show significant departures from those derived from supercritical solubility data [92,93] using the theory of dilute near-critical mixtures [94,95].

Within the frame of fluctuation theory of solutions, certain thermodynamic properties of binary mixtures, including partial molar volume and isothermal compressibility [96,97], can be expressed in terms of integrals of molecular correlation and distribution functions [98]. These can further be used to express mean cluster sizes in dilute near-critical mixtures [99]. Consequently, the pressure- and density-quotients

of solute retention factor (Eqs. (6) and (7)) are simply related to the correlation function integral and mean cluster size in solute–mobile phase fluid systems [100]. Fluctuation solution theory was also employed to describe solute–solute interactions as a possible source of inconsistency between the \bar{v}_{1m}^∞ values derived from solubility measurements and those from SFC [101].

Yet another use of high-pressure partial molar volumes includes their conversion via an EOS model to second cross-virial coefficients for solute–fluid interactions. Although this approach [102] depends again on a particular thermodynamic model, it can be used in systems with very large disparities in solute/fluid molecular size where it is nearly impossible to measure the cross-virial coefficients by any other experimental approach, at least at the relatively low temperatures accessible by SFC. In the context of the virial coefficients, it is also worth noting that, when introducing the virial EOS to express \bar{v}_{1m}^∞ in the low pressure limit, Eq. (6) would reduce to the expressions that had long ago been used to derive the solute–carrier gas second cross-virial coefficients from GLC retention data [103,104].

2.2.2. Effect of temperature

The isobaric change of the solute retention factor with temperature in a (1 + 2 + 3) system (without a cosolvent) may be expressed as [21,22,58–60,105]:

$$\left(\frac{\partial \ln k_1}{\partial T}\right)_P = \frac{\bar{h}_{1s}^\infty - \bar{h}_{1m}^\infty}{RT^2} + \alpha_{m,P} + \frac{V_s}{V_m} \alpha_{s,P,\sigma} - \frac{1}{RT} \left(\frac{\partial \mu_{1s}^\infty}{\partial w_{3s}}\right)_{T,P,n_{2s}} \left(\frac{\partial w_{3s}}{\partial T}\right)_{P,\sigma} \quad (10)$$

where \bar{h}_{1m}^∞ and \bar{h}_{1s}^∞ are the infinite-dilution partial molar enthalpies of the solute in the mobile and the stationary phase, respectively, $\alpha_{m,P}$ is the isobaric expansivity (thermal expansion coefficient) of the pure mobile phase fluid (3), and $\alpha_{s,P,\sigma}$ is the isobaric expansivity of the stationary phase at saturation with the mobile phase fluid. The quantities in Eq. (10) displaying anomalous behaviour at the temperatures and pressures near the critical point of the mobile phase fluid include \bar{h}_{1m}^∞ , $\alpha_{m,P}$, $\alpha_{s,P,\sigma}$, and $(\partial w_{3s}/\partial T)_{P,\sigma}$. The anomalies result in complex non-linear plots of $\ln k_1$ versus temperature at a constant pressure. In order to avoid difficulties in non-linear curve fitting, therefore, the analysis of retention data to obtain \bar{h}_{1m}^∞ or the transfer enthalpy $\bar{h}_{1m}^\infty - \bar{h}_{1s}^\infty$ is usually based on the density-involving derivatives of solute retention rather than directly on Eq. (10). The relationship between $(\partial \ln k_1/\partial T)_P$ and the density-involving derivatives may be written as:

$$\left(\frac{\partial \ln k_1}{\partial T}\right)_P = -\alpha_{m,P} \left(\frac{\partial \ln k_1}{\partial \ln \rho_m}\right)_T - \frac{1}{T^2} \left(\frac{\partial \ln k_1}{\partial (1/T)}\right)_{\rho_m} \quad (11)$$

where the isobaric expansivity $\alpha_{m,P}$ can again be calculated from an accurate EOS for the pure mobile phase fluid. As

suggested by the molecular theory of chromatography [66] and confirmed by ample experimental evidence [106,107], the constant-density plots of $\ln k_1$ versus $1/T$ are nearly linear. The slopes of such plots are composite quantities lacking a straightforward physical significance [108–110].

Eqs. (10) and (11) were occasionally employed to obtain $\bar{h}_{1,m}^\infty$ or $\bar{h}_{1m}^\infty - \bar{h}_{1s}^\infty$, mostly for aromatic hydrocarbon solutes [21,22,58,72,73] and hexasubstituted benzenes [110] in scCO₂ with the use of both packed [21,22,58,110] and open tubular [72,73] columns. A related approach using solute adsorption was also used to obtain infinite-dilution partial molar enthalpies of aromatic hydrocarbons in scCO₂–ethane mixtures [85].

The requirements for auxiliary information needed to process the retention data are the same as in the preceding section on determination of partial molar volumes. In addition, determination of \bar{h}_{1m}^∞ or $\bar{h}_{1m}^\infty - \bar{h}_{1s}^\infty$ from the temperature dependence of $\ln k_1$ requires a careful and accurate control of the column temperature, preferably over large temperature intervals. Therefore, the accuracy of the partial molar enthalpies determined in this way is certainly lower than the accuracy of the partial molar volumes discussed in Section 2.2.1.

In the field of adsorption SFC, Afrane and Chimowitz [111,112] developed a molecular thermodynamic model to describe adsorption from high-pressure fluids on solid surfaces. Although the model has not been used explicitly to obtain \bar{h}_{1m}^∞ or $\bar{h}_{1m}^\infty - \bar{h}_{1s}^\infty$, it provides a good representation of the complex isobaric temperature dependence of the retention factors for aromatic solutes on octadecyl silica.

2.2.3. Effect of composition of binary mobile phase

The primary domain for the use of cosolvents (modifiers) is certainly in analytical SFC where the cosolvents are used to mask residual silanol groups or other active sites on silica surface, and to tune the ability of the mobile phase fluid for individual types of intermolecular interactions [113,114] to optimise selectivity in SFC [115]. In principle, however, SFC can also provide useful information on cosolvent effects to meet the needs of non-analytical applications of supercritical fluids [55]. Ekart et al. [116] employed SFC to measure the effect of methanol addition on solubility of anthracene and 2-naphthol in scCO₂, and noted a good agreement with independent data [117] on cosolvent-induced solubility enhancement.

At a constant temperature and pressure, the change in solute retention factor with the mole-fraction of cosolvent in the mobile phase fluid is given by [118]

$$\begin{aligned} \left(\frac{\partial \ln k_1}{\partial x_{4m}}\right)_{T,P,n_{2s}} &= \left(\frac{\partial \ln \varphi_{1m}^\infty}{\partial x_{4m}}\right)_{T,P} - \zeta_{4m} - \frac{V_s}{V_m} \zeta_{4s} \left(\frac{\partial x_{4s}}{\partial x_{4m}}\right)_{T,P,n_{2s},\sigma} \\ &\quad - \frac{1}{RT} \left(\frac{\partial \mu_{1s}^\infty}{\partial x_{4s}}\right)_{T,P,n_{2s}} \left(\frac{\partial x_{4s}}{\partial x_{4m}}\right)_{T,P,n_{2s},\sigma} \end{aligned} \quad (12)$$

where φ_{1m}^∞ is the fugacity coefficient of the solute (1) at infinite-dilution in the binary mobile phase fluid (3 + 4), x_{4m} is the mole-fraction of cosolvent in the binary mobile phase fluid, and x_{4s} is the mole-fraction of cosolvent in the stationary phase. The quotient:

$$\zeta_{4m} = \frac{1}{\rho_m} \left(\frac{\partial \rho_m}{\partial x_{4m}} \right)_{T,P} = - \frac{1}{v_m} \left(\frac{\partial v_m}{\partial x_{4m}} \right)_{T,P} \quad (13)$$

is sometimes termed “mixing expansivity”, and the quantity ζ_{4s} is defined by

$$\zeta_{4s} = - \frac{1}{V_s} \left(\frac{\partial V_s}{\partial x_{4s}} \right)_{T,P,n_{2s}} \quad (14)$$

In deriving Eq. (12), it has been assumed that bulk dissolution of the solute in the stationary phase is the only mechanism of retention, i.e., that interfacial adsorption of the solute is absent. Further, Eq. (12) is only valid if the principal component of the stationary phase (2) is a high-molar-mass polymer ($M_2 \rightarrow \infty$); a more general form of Eq. (12) can be found elsewhere [118]. An experimental application of Eq. (12) would include at least two chromatographic runs, one with a pure mobile phase fluid (3) without any cosolvent, and the other with a small amount of cosolvent (4) added. Ekart et al. [116], for example, used CO₂ modified with 3.5 mol% of methanol. If Δx_{4m} is the mole-fraction of cosolvent in the binary fluid (3+4) in the other run, Eq. (12) may be integrated to yield the shift in solute retention factor between the two runs,

$$\Delta \ln k_1 \approx \Delta \ln \varphi_{1m}^\infty - \zeta_{4m} \Delta x_{4m} - \frac{V_s}{V_m} \zeta_{4s} \Delta x_{4s} - \frac{1}{RT} \left(\frac{\partial \mu_{1s}^\infty}{\partial x_{4s}} \right)_{T,P,n_{2s}} \Delta x_{4s} \quad (15)$$

The “valuable” quantity that can be obtained from Eq. (12) or Eq. (15) is the first term on the right-hand side that measures the effect of the change in composition of the near-critical fluid on the fluid’s intermolecular interactions with the solute. This quantity may be very useful for fundamental understanding as well as for technological applications of cosolvent-modified supercritical fluids.

The application of SFC to study the cosolvent effects via Eq. (12) or Eq. (15) presents an experimental challenge because it requires a stable pumping system capable of delivering the binary fluid of a well-defined composition at a carefully controlled temperature and pressure. This may be one of the reasons why, to the author’s knowledge, there has been just a single application of this approach to date [116]. In their study, Ekart et al. [116] employed a simplified form of Eq. (15), retaining only the first term on the right-hand side. The good agreement of their results with the literature data [117] suggests a cancellation among the remaining terms in Eq. (15) in the systems investigated. For a general application of Eqs. (12) and (15), a quantitative understanding of the relative weights of the individual terms is needed. Unfortunately, except the mixing expansivity ζ_{4m} that can

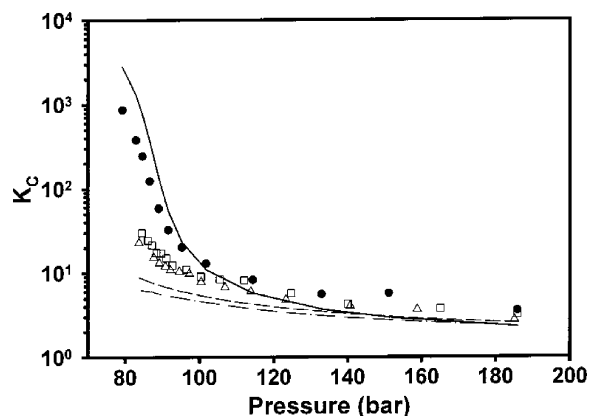


Fig. 4. Pressure dependence of the partition coefficient of acridine between PDMS and fluid at 40 °C [120]: (●) pure CO₂; (□) 0.30 M [2H₄]methanol-modified CO₂; (Δ) 0.30 M [2H₈]2-propanol-modified CO₂. The lines are the Sanchez–Lacombe EOS fit of acridine partitioning. Solid line, pure CO₂; dotted-dashed line, 0.30 M [2H₄]methanol-modified CO₂; dashed line, 0.30 M [2H₈]2-propanol-modified CO₂. Reprinted with permission from [120]. © 1999 American Chemical Society.

be estimated from a cubic EOS for the (3 + 4) binary fluid (Section 4.1.3), the correction terms in Eqs. (12) and (15) are very difficult to access.

In order to delineate and quantify the individual correction terms in Eq. (12), Eckert et al. carried out a series of ingenious IR [119,120] and UV [120] spectroscopic studies combined with measurements of swelling of crosslinked PDMS [119,120] and poly(cyanopropyl methyl siloxane) (PCPMS) [120] polymers by the dissolved CO₂ and cosolvent. They designed a special high-pressure optical cell allowing separate measurements of the fluid and polymer phases under identical conditions [121]. The cosolvents used were methanol, 2-propanol [119,120] and acetone [119] together with their deuterated analogues needed to separate the IR-spectral characteristics of the cosolvents from the absorbances due to scCO₂ and the polymer phases. Anthracene [119], naphthalene [120], acridine [120] and 2-naphthol [119,120] served as model solutes. The results indicate that the corrections increase with increasing proximity of the operating temperature and pressure to the critical point of CO₂ and with decreasing polarity of the solute. In 2-naphthol and CO₂ modified with 3.5 mol% of methanol at 35 °C, for example, the total correction ranges between +30 and –10%, depending on pressure [119]. The pronounced effect of cosolvent on spectroscopically determined solute partition coefficient is illustrated by Fig. 4. A similar methodology was later applied to study the partitioning of azo dyes between water-modified scCO₂ and poly(methyl methacrylate) (PMMA) [122,123].

2.2.3.1. Helium head pressure CO₂. In SFC or supercritical fluid extraction (SFE) with CO₂, the working cylinder of the syringe pump has to contain liquid CO₂ for smooth operation. For an efficient liquefaction of CO₂, the pump cylinder has to be cooled down to about +5 °C or below.

In order to avoid cooling of the cylinder when filling it, the CO₂ supply tanks have sometimes been pressurised with helium to about 14 MPa. Such “helium head pressure CO₂” (HHPCO₂) tanks have been marketed to provide for a convenient delivery of liquid CO₂ at a pressure exceeding the vapour pressure of CO₂ at ambient temperature. Apparently, this practice involves a tacit assumption that the added helium merely works as an inert piston squeezing the liquid CO₂ out of the tank through a dip tube.

The issue of HHPCO₂ tanks is an interesting story showing the lack of links between physical chemistry and thermodynamics on one side and everyday analytical practice on the other. Phase equilibrium data for helium–CO₂ system [124,125] indicate that, under the conditions prevailing in an HHPCO₂ tank, the equilibrium solubility of helium in the liquid phase may reach up to 5 mol%. Also, in the course of usage of HHPCO₂ tanks, it has become apparent that the assumption mentioned above is not valid. Experimental evidence has been accumulated of irreproducible retention times in SFC [126–128] and extraction efficiencies in SFE [129–131] suggesting that the entrained helium acts as a negative modifier (antisolvent). Other unexpected deleterious effects that might occur with HHPCO₂ were discussed by Parcher and Xiong [132] and by Wells et al. [133]. Although thermodynamic implications of entrained helium may simply and fairly accurately be treated by a cubic EOS [134], the principal cause of the unexpected effects of HHPCO₂ is probably the lack of thermodynamic equilibrium in HHPCO₂ tanks [135]. The estimated low diffusivity of helium in liquid CO₂ suggests that, after a rapid pressurisation of a CO₂ tank with helium, equilibration may take months, if not years [135]. Therefore, the composition of the liquid drawn from the tank through a dip tube depends not only on temperature and pressure within the tank but also on storage history and liquid level in the tank. To illustrate the important effects of entrained helium, Fig. 5 shows the density differences between pure CO₂ and HHPCO₂ as obtained from acoustic measurements [135]. Consequently, a growing number of authors have concluded that the use of HHPCO₂ tanks should be discouraged [128,131,132,134–136]. Wells et al. [136] utilised the high-pressure behaviour of He–CO₂ system (type III phase behaviour) in a remarkable demonstration of gas–liquid chromatography with a dynamic stationary phase formed by the CO₂-rich liquid at temperatures below the critical point of the He–CO₂ mixtures and pressures above the vapour pressure of pure CO₂.

2.3. Uptake of the mobile phase fluid by the stationary phase

At the temperatures and pressures near and above the critical point of the mobile phase fluid, most stationary phases in current use absorb significant amounts of the fluid. Uptake of the mobile phase fluid by the stationary phase results in two interconnected effects:

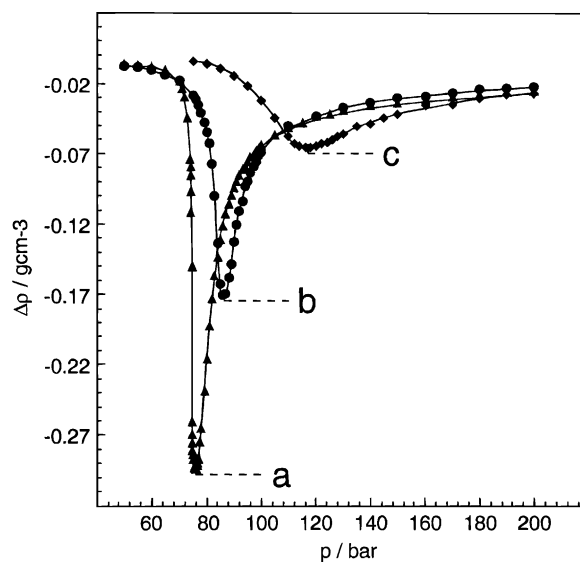


Fig. 5. Density differences between pure CO₂ and HHPCO₂ as a function of pressure at different temperatures: (a) 304.6 K, (b) 309.5 K, and (c) 324.3 K [135]. Reprinted with permission from [135]. © 1996 American Chemical Society.

- (i) a decrease in phase ratio V_m/V_s because of swelling of the stationary phase with the absorbed fluid, and
- (ii) a change in the molecular environment “sensed” by the solute in the stationary phase because of temperature- and/or pressure-induced variations in solubility of the mobile phase fluid in the stationary phase.

While the effects (i) and (ii) are of no direct concern in analytical SFC, their possible extent makes them important for a correct conversion of the retention data to the properties discussed in Sections 2.1.2 and 2.2. This statement applies to “traditional” as well as to “neoteric” systems that lend themselves to thermodynamic measurements by SFC. An example in traditional systems is provided by uptake of scCO₂ by crosslinked PDMS—the associated increase in the polymer volume may exceed 80% [22], the percentage linear dilation exceeds 20% at 42 °C and >20 MPa [137], and the percentage mass uptake of CO₂ by PDMS exceeds 125% at the same conditions [137]. An example in neoteric systems is provided by solubility of scCO₂ in RTILs—although there is still some scatter in the published data on this rapidly growing topic, several studies [138–140] show that the mole-fraction solubility of CO₂ in [bmim][PF₆] may exceed 0.6.

Besides, there appears to be no unique general correlation between the composition (sorption) data and the volumetric (swelling) data. In the traditional system with PDMS mentioned above, high solubility of CO₂ in PDMS is accompanied by significant swelling of the polymer phase. On the contrary, in the neoteric system [bmim][PF₆]-CO₂, high solubility of CO₂ in [bmim][PF₆] is accompanied by relatively little swelling of the ionic liquid phase [138,141] with the dissolved CO₂.

Some earlier studies of uptake of scCO_2 by the stationary phases in SFC were reviewed by Yonker and Smith in 1991 [142] but this field has received an increasing attention in the last decade. More recent work on the subject will be discussed in Section 2.3.1 (bulk polymers) and Section 2.3.2 (reversed phases). Applications of SFC to probe polymer–fluid interactions will be reviewed in Section 2.3.3. The correlation and/or prediction of the composition and volume of stationary polymers swollen with CO_2 require some thermodynamic model. The models used for this purpose will briefly be discussed in Section 4.1.4.

Apart from their relevance for thermodynamic measurements by SFC, the studies of polymer–supercritical fluid interactions are certainly more important in polymer processing. Absorption of supercritical fluids may be helpful for plasticisation of polymers [143–147] and for impregnation of polymers with dyes [123,148] or other additives [149].

2.3.1. Uptake by bulk polymers

2.3.1.1. Pure fluids. Of the vast literature on interactions between polymers and compressed gases or supercritical fluids, only the work with some relevance to SFC will be mentioned here. Therefore, most of this section deals with siloxane polymers. Further, a major part of the studies to be mentioned below concerns the uptake of CO_2 . The few studies with other fluids of interest to SFC, such as hydrofluorocarbons, have usually either been carried out at subcritical temperatures of the fluid [150,151] or with polymers that have not been used as stationary phases in SFC [151,152].

At low pressures of the gas, both the absorbed amount of the gas and the relative change in volume of the polymer phase are proportional to pressure [143,153,154], and the quantitative differences in solubility coefficients among the individual gases are clearly apparent [155]. It appears that replacement of the methyl groups in PDMS by bulkier substituents tends to decrease the low-pressure solubility of CO_2 because of increased stiffness of the siloxane chain and decreased fractional free volume of the polymer [156]. The only exception seems to be the low-pressure solubility of CO_2 in poly(methyl trifluoropropyl siloxane) where the specific CO_2 –polymer interaction increases the sorption above that in PDMS [157]. Although CO_2 can act as both a Lewis acid and a Lewis base when interacting with polymers containing polar moieties [158], such specific interactions are probably absent from CO_2 –poly(alkylsiloxane) systems.

The measurements of solubility (sorption) or swelling in polymer– scCO_2 systems [159,22] are a natural extension of the studies with CO_2 at subcritical pressures. At higher pressures, the swelling isotherms [159,137] and the sorption isotherms [137] deviate from linearity to produce S-shaped patterns, especially at temperatures not far above the critical point of the gas. Unlike the glassy polymers [143,160], the rubbery siloxanes [143,23] do not display hysteresis during the sorption/desorption cycles.

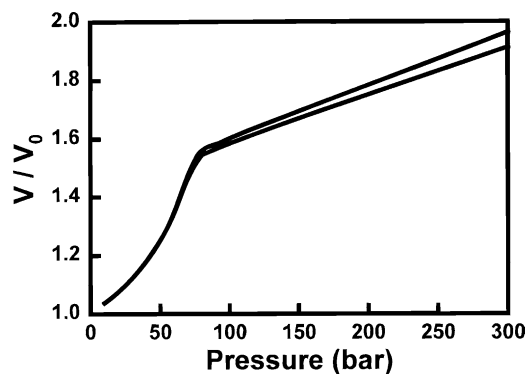


Fig. 6. Effect of crosslinks on equilibrium swelling of PDMS by scCO_2 at 35°C calculated [164] from the Sanchez–Lacombe EOS. Top curve, liquid PDMS; bottom curve, lightly cross-linked PDMS. Reprinted with permission from [164]. © 1998 American Chemical Society.

In a PDMS elastomer filled with glass beads, both elastomer–filler interfacial restrictions on sorptive dilation and volumetric restrictions on sorptive dilation reduce the CO_2 sorption capacity of the PDMS elastomer [161]. Although it is potentially relevant to chromatography, this finding has not yet been reflected in thermodynamic interpretation of SFC retention data.

The gas sorption and swelling of crosslinked siloxane elastomers [155] generally differ from the corresponding properties of the respective non-crosslinked (linear) polymers [152]. An increase in the crosslink density causes the elastomer to expand less freely [162,163]. In thermodynamic measurements employing commercial open tubular columns, the crosslink density in the siloxane polymer film on the column wall is often unknown but it is probably low enough to be negligible [23]. An indirect support for this opinion comes from the work of West et al. [164] who used the Sanchez–Lacombe (S–L) mean-field lattice fluid model (Section 4.1.4) to explain the very small difference between swelling of lightly crosslinked [23] and non-crosslinked (liquid) [152] PDMS (see Fig. 6).

The recent studies of sorption and swelling in PDMS– scCO_2 systems have focused on non-crosslinked (liquid) PDMS samples rather than on crosslinked elastomers. The optical measurements of kinetics and extent of swelling with scCO_2 of three samples of linear PDMS with different molecular mass indicated that, within the range of molecular masses studied ($M_w = 95$ – 284 kg/mol), the equilibrium swelling was essentially unaffected by molecular mass [165]. Sirard et al. [163] carried out swelling measurements by spectroscopic ellipsometry of thin films (approx. $0.1\ \mu\text{m}$) of non-crosslinked PDMS ($M_w = 188,000$, $M_w/M_n = 1.17$) coated on silicon substrate. The extent of sorption of CO_2 in PDMS could be estimated from refractive index measurements. Both swelling and sorption in the thin non-crosslinked films exceeded the values in bulk crosslinked films by 20–40% at 50°C . The increased swelling and sorption were attributed to excess CO_2 at the polymer– scCO_2 and polymer–substrate interfaces, and

possibly also to a change in the polymer chain conformation near the solid wall. These findings may be significant for interpretation of SFC retention data but no attempt in this respect has yet been made. Flichy et al. [166] employed attenuated total reflectance infrared (ATR-IR) spectroscopy for a simultaneous measurement of sorption of CO₂ and the consequent swelling of non-crosslinked PDMS. As the ATR-IR spectroscopy probes a layer of about 1 μm in thickness, it measures essentially the bulk properties of the polymer phase. The results of swelling measurements confirm again that the non-crosslinked PDMS samples expand more freely than crosslinked silicone elastomers. Xu et al. [167] used mass spectrometric tracer pulse chromatography (MSTPC) with pulses of isotopically labelled CO₂ (¹³C¹⁸O¹⁶O) to measure the solubility of scCO₂ in non-crosslinked PDMS (SE 30) coated on Chromosorb W HP (60–80 mesh) support as a film with an average thickness of 0.23 μm. These measurements complemented an earlier study by the same method [168]. At pressures below the critical of CO₂, the results agreed with the barometric [143], dilatometric [159,119], and piezoelectric [137] data but there was a marked disagreement at supercritical pressures, especially in the near-critical isotherms. The probable cause of the disagreement could again be traced to the polymer film thickness. In MSTPC [167], the thickness of the polymer layer was several orders of magnitude smaller than in the other methods [119,137,143,159]. Consequently, the effects of possible interfacial excesses of CO₂ [169] were much more apparent in MSTPC. Clearly, the interfacial adsorption of near-critical CO₂ in thin polymer films may be an important issue in thermodynamic applications of SFC.

2.3.1.2. Binary (modified) fluids. Because of associated experimental and interpretation difficulties, investigations of the uptake of binary near-critical fluids by polymers in systems relevant to SFC have been rare. Eckert et al. employed dilatometric and spectroscopic measurements to investigate swelling and sorption, respectively, in cosolvent-modified scCO₂–PDMS [119,120] and cosolvent-modified scCO₂–PCPMS [120] systems at temperatures close to 40 °C. At pressures below 9 MPa, swelling of crosslinked siloxane polymers with methanol-modified CO₂ was more pronounced as compared to pure CO₂, and there was very little difference in the swelling between PDMS and PCPMS. At pressures above ~10 MPa, the chemical identity and concentration of the cosolvent had little effect on the swelling of PDMS. Fig. 7 shows the swelling of crosslinked PDMS with acetone-modified CO₂ at 41.5 °C as a function of pressure and concentration of acetone in the fluid phase [119]. At saturated conditions when three phases (swollen polymer, liquid and vapour) are present, the swelling isotherm displays a local maximum and minimum. The systems with methanol and 2-propanol as cosolvents show qualitatively the same behaviour as the system with acetone.

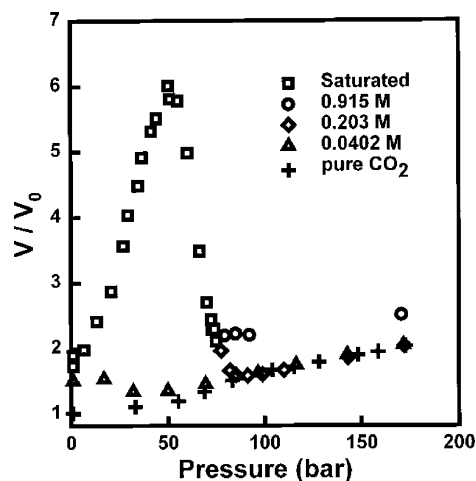


Fig. 7. Pressure dependence of the equilibrium swelling of crosslinked PDMS in acetone-modified CO₂ at 41.5 °C [119]. The values given in the legend are the concentrations of acetone in the fluid phase. The '+' signs represent the swelling of crosslinked PDMS in pure CO₂. Reprinted with permission from [119]. © 1998 American Chemical Society.

Regardless of the similarity in the swelling behaviours of the PDMS and PCPMS polymers, the partition coefficients for methanol in the scCO₂–PCPMS system were considerably higher than in the scCO₂–PDMS system, apparently because of a specific interaction between methanol and PCPMS [120].

2.3.2. Uptake by silica and bonded silica phases

Compared to the large number of studies on supercritical fluid–polymer interactions, the measurements of uptake of supercritical fluids by silica or chemically modified silica have been scarce, possibly because the applicability of such measurements is essentially limited to chromatography itself. The studies with silica sorbents were mostly performed by MSTPC [168,170–172], and they complemented the applications of tracer pulse chromatography to fluid–crosslinked polymer interactions in open tubular columns [173–176]. The MSTPC measurements with pure CO₂ at 30–50 °C and pressures up to 15 MPa [168,170,171] showed maxima in the surface excess isotherms near the critical pressure of CO₂. Consequently, under the conditions commonly used in SFC with CO₂, the solid adsorbent is covered with a layer of adsorbed CO₂, and thickness of the adsorbed layer is 1–3 molecular diameters. The investigations with octadecyl-, cyano-, and diol-bonded silicas [170] showed that the type of bonded phase had little or no effect on CO₂ adsorption isotherms. The measurements with methanol-modified CO₂ on octadecyl-bonded silica [172] revealed large variations in adsorption isotherms, especially those of CO₂, even with small changes in composition of the binary fluid. The variations might reflect the fact that, in CO₂ modified with polar, subcritical cosolvents, even small changes in composition of the CO₂–cosolvent binary mixture could cause marked shifts along the liquid–vapour critical curve of the mixture.

2.3.3. Use of supercritical fluid chromatography to probe polymer–fluid interactions

The sorption of compressed gases and supercritical fluids into glassy polymers has been known to produce plasticisation effect marked by depression of the glass transition temperature (T_g) [177,178,144]. Even at subcritical pressures, CO₂ can cause T_g depressions of several tens of °C. The glass transition temperature of the stationary polymer at a particular pressure of the fluid can be obtained from isobaric temperature dependence of the specific retention volume of a solute (“molecular probe”). Employing *iso*-octane as the probe solute, Edwards et al. [179] studied plasticisation of PMMA by CO₂ at temperatures within 0–180 °C and pressures within 0.1–7.6 MPa, and noted T_g depressions of up to 40 °C. The observed retention volume of the solute on glassy PMMA could be correlated with an adsorption model based on theory of fluid–solid chromatography [180]. Edwards et al. [181] also investigated the PMMA–CO₂ interaction by MSTPC with isotopically labelled CO₂ (¹³C¹⁸O¹⁶O) at temperatures within –10 to 180 °C and pressures up to 9.1 MPa. In this investigation, CO₂ was in a gaseous or supercritical fluid state, and PMMA was either in a glassy or rubbery state. The MSTPC data on solubility of CO₂ in PMMA were equivalent in accuracy and precision with the results of classical methods, and the sorption isotherms were fitted by three mean-field lattice fluid models to be discussed in Section 4.1.4.

Alessi et al. employed SFC to investigate the plasticisation effects of scCO₂ on PMMA, polystyrene, bisphenol A–polycarbonate [182], and poly(2,6-dimethylphenylene oxide) (PPO), poly(acrylic acid), and vinylpyrrolidone–vinyl acetate copolymer [P(VP–VA)] [183] at 8 and 10 MPa within 309–430 K. The polymers were coated on a Chromosorb 100–120 mesh support and packed into a 250 mm × 3.7 mm i.d. column. The probe solutes, 1-butanol, acetone, benzene, and ethyl acetate, were detected by an UV detector. In PPO–CO₂, PVP–CO₂, and P(VP–VA)–CO₂ systems the authors observed retrograde vitrification. This peculiar phenomenon, involving a liquid-to-glass transition with *increasing* temperature at a constant pressure, has previously been predicted theoretically [184] and confirmed experimentally [185,186] in other polymer–fluid systems.

2.4. Thermodynamic applications of chromatographic instrumentation

This section includes the applications utilising SFC instrumentation without making use of chromatography itself, i.e., without the solute partitioning between the stationary and the mobile phase. In a broader context of physicochemical measurements, the foremost of such applications is the determination of solute diffusion coefficient in supercritical mobile phase fluid by what is called the chromatographic band broadening technique or the Taylor–Aris dispersion method [187–189]. The diffusion studies are outside the

scope of the present survey that is limited to thermodynamic properties.

2.4.1. Phase behaviour of binary mobile phase fluids

In the search for suitable cosolvents to modify the properties of scCO₂ to fit the needs of analytical applications, it soon became apparent that the knowledge of high-pressure phase behaviour of the binary fluid was of ultimate importance, and that the literature compilations of high-pressure phase equilibrium data (Section 4.1.2) on CO₂–cosolvent mixtures did not cover all cosolvents of potential interest. Consequently, methods were sought of a rapid estimation of the missing phase equilibrium data and, as the impetus for the search came from the needs of analytical applications of supercritical fluids, attempts were made to utilise the equipment available in analytical laboratories.

Phase transitions in fluid mixtures have been known to be accompanied by changes in intensity of scattered light [190]. Page et al. [191] employed laser light scattering in fixed volume view cell to probe the transition pressures from single-phase to two-phase region in CO₂–methanol mixtures. The transition from the single-phase to the two-phase region was marked by an abrupt increase in the intensity of scattered light. At first glance, the method would seem to suffer from an uncertainty as to what was actually measured—equilibrium line (binodal) or stability limit (spinodal)? However, comparison with independent results showed a good conformity to equilibrium data. The method was modified to include a variable-volume view cell with a stirrer to enable a rapid equilibration of the cell contents, and used to study phase behaviour in CO₂–propylene carbonate mixture [192] and in pure CO₂ and CO₂–methanol mixture [193]. Subsequently, a view cell enabling the use of either scattered or transmitted light was employed to evaluate the phase behaviour in mixtures of CO₂ or chlorodifluoromethane with methanol, water, and triethylamine [194].

During their work on solvent selection and dynamic film formation in open tubular SFC, Chester and Innis [195] noted a distinct dependence of the solvent peak shape on miscibility of CO₂ with the solvent at the particular temperature and pressure. In CO₂–cosolvent mixtures with a continuous critical curve (type I and type II phase behaviour [196]), this observation gave rise to the “peak-shape method” for a rapid determination of the *P–T* projection of the critical locus. Validation of the method with CO₂–toluene and CO₂–methanol systems [197] showed a very good agreement of the results with independent data as illustrated in Fig. 8. The peak-shape method was applied to estimate the *P–T* projections of the critical loci in 23 different CO₂–cosolvent systems [197,199].

2.4.2. Solubilities in supercritical fluids

Miller and Hawthorne [200] used a direct coupling of a saturation cell to a flame ionisation detection (FID) system to determine the solubility of low-volatility organic solutes in scCO₂. The solubility was determined from the FID

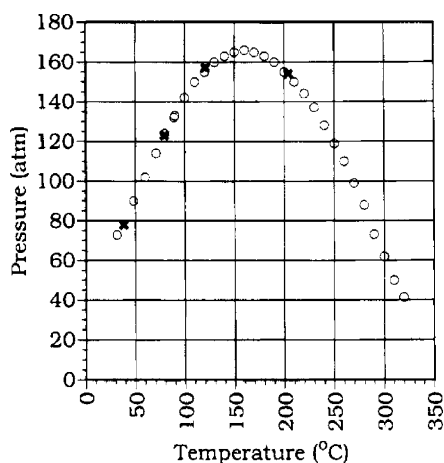


Fig. 8. Comparison of the P - T projection of the critical locus in CO_2 -toluene mixture as obtained by the peak-shape method (○) [197] and by a high-pressure view cell technique (×) [198]. Reprinted with permission from [197]. © 1995 American Chemical Society.

response and the flowrate of scCO_2 through the cell containing the solute. With anthracene and tripalmitin as the test solutes, the resultant solubilities were in good agreement with the literature data obtained by gravimetric or spectroscopic methods. The method allowed for determination of mole-fraction solubilities down to 1×10^{-8} with day-to-day reproducibility better than 5%. Subsequent applications of this method involved the solubility measurements in scCO_2 of PAHs [201] and chlorinated hydrocarbons and pesticides [202]. In an analogous study of solubility of PAHs in scCO_2 , Lou et al. [203] also used helium as the carrier fluid to separate the contributions of the solute vapour pressure and the solute–fluid interaction to the overall solubility in scCO_2 .

3. Instrumental considerations

Although several experimental set-ups have been constructed for the sole purpose of physicochemical measurements by high-pressure GC [204] or SFC [9,205–207], most thermodynamic applications of SFC have been carried out using commercial equipment for analytical SFC, GC, and high-performance liquid chromatography (HPLC). As might be expected, to obtain correct values of thermodynamic properties from solute retention data, one has to pay attention to some specific experimental precautions that may be less important in analytical SFC. Therefore, the following sections discuss the individual features that have to be taken into account in thermodynamic measurements by SFC.

3.1. Pressure drop effects

In any thermodynamic measurements involving flow methods, the associated pressure gradients present a fundamental problem in the near-critical region of high compressibility because the control over the fluid density is lost

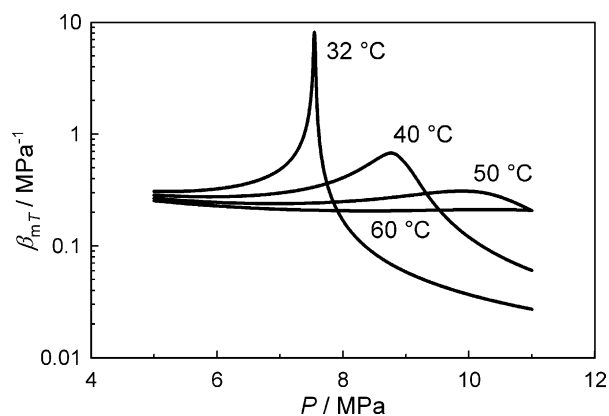


Fig. 9. Isothermal compressibility of CO_2 ($t_c = 30.978^\circ\text{C}$, $P_c = 7.3773\text{ MPa}$) as a function of pressure at several supercritical temperatures. Calculated from the EOS of Span and Wagner [276].

at a certain level of approach to the vapour–liquid critical point of the fluid [208]. When selecting the operating temperature and column inlet pressure for a thermodynamic study by SFC, it is therefore advisable to start with a check of the isothermal compressibility of the mobile phase fluid using a high-precision EOS for calculations. In such a way, one can avoid working at the pressures in the immediate vicinity of the compressibility maximum for the particular near-critical isotherm. The locus of compressibility maxima starts at the fluid's critical point ($\beta_{m,T} \rightarrow +\infty$) and extends into the supercritical region, with the maximum value of compressibility decreasing rapidly with the raising temperature as shown in Fig. 9. Previous calculations suggest that, as the temperature and pressure are increased from their respective critical values, the supercritical maxima in compressibility of CO_2 and hydrofluorocarbons fade away at a reduced temperature of about 1.11 and a reduced pressure of about 1.36 [209].

In SFC, numerous studies have appeared of the pressure drop effects, both with the purpose to relate the measured retention factor to the mean pressure in the column [210–213], and with the purpose to optimise the efficiency of packed columns [214–218]. Martire et al. [211,212] treated the pressure drop effects in terms of spatial and temporal density distribution functions and showed that, in columns with large pressure drop values typical of packed columns, the observed retention factor corresponded to that in a hypothetical zero-pressure-drop system at a density equal to the temporal average density of the real system [213]. In order to obtain a meaningful value of the pressure derivative of solute retention factor, however, it is clear that keeping the *actual* pressure drop at a minimum is advisable. Therefore, owing to their low hydrodynamic resistance, open tubular columns are generally preferable over packed columns in thermodynamic measurements by SFC. Estimations of the pressure drop along an open tubular column have been based on Poiseuille equation [219], and the pressure drop in a packed column may be estimated, e.g., from the Ergun

equation [220]. For open tubular capillaries, in-depth discussions were published of the departures from the Poiseuille equation because of compressibility of the fluid [221] and because of thermal effects [222], albeit without a direct reference to supercritical fluids. A simple treatment [223] suggests that the secondary effects detracting from applicability of the Poiseuille equation are negligible under usual operating conditions in open tubular SFC.

Thermodynamic applications of chromatography are carried out with predefined samples so that separation efficiency of the experimental set-up does not present a problem. Therefore, it may be easy to minimise the pressure drop by sacrificing some of the column efficiency, e.g., by selecting the linear velocity of the mobile phase below the optimum of the van Deemter curve or by using a higher internal diameter of the column.

3.2. Packed vs. open tubular columns

In thermodynamic measurements by both packed and open tubular columns, it is ultimately important that the principal component of the stationary phase is non-volatile and non-extractable by the mobile phase fluid. The current level of column technology meets these requirements very well. Historically, most thermodynamic applications of SFC prior to about 1990 were performed with packed columns similar to those used in HPLC at the time. In addition to the pressure drop problem mentioned above, the packed columns suffered from several adverse features including:

- (i) very large area of the fluid–packing interface and the resultant danger of spurious adsorption of polar solutes,
- (ii) uncertainty as regards the role in solute retention of the alkyl chains in typical packing materials (alkyl-bonded silica particles),
- (iii) limited compatibility with the detectors operating at atmospheric pressure because of excessively high flowrates of the mobile phase fluid after decompression, and
- (iv) high consumption and possibly high costs of the fluid.

Naturally, items (i) and (ii) above result in questions regarding the dominance of bulk absorption in the stationary phase as the only and exclusive mechanism of solute retention. These adverse features of packed columns have driven the gradual shift to open tubular columns in thermodynamic applications of SFC after 1990. The recent developments in microcolumn format [224] can alleviate some of the above problems to some extent. This, together with interesting analytical applications of packed column SFC [225] such as separation of enantiomers on chiral sorbents and the questions ensuing thereof, may revive some interest in thermodynamic measurements by packed column SFC. However, open tubular capillary columns with relatively thick films of the stationary phase will certainly remain the preferred choice in thermodynamic measurements by SFC. Apart from the low hydrodynamic resistance, another reason is that open

tubular columns provide the best compliance with the requirement for bulk partitioning as the exclusive mechanism of solute retention.

Regardless of the column type, the connections of the column to the injector and to the detector should comply with two requirements that may sometimes be contradictory:

- (a) the connections should have a minimum volume to minimise extracolumn broadening of solute peaks, and
- (b) the connections should have a defined internal geometry to allow the calculation of corrections to the measured hold-up time for extracolumn contributions.

3.3. Determination of the column hold-up time

Determination of the correct value of the column hold-up time (t_0 in Eq. (1)) to be used in thermodynamic applications of chromatography presents a long-standing fundamental problem [226–230]. In most thermodynamic applications of SFC, the column hold-up time has been approximated by the retention time of a suitable marker mimicking the hypothetical non-retained substance. In SFC, the marker method has prevailed over the more laborious procedure involving extrapolation of t_0 from retention times of a homologous series of solutes [226,229]. The hold-up time marker has been selected so as to fit the particular detection principle employed. For example, in MSTPC that uses an isotopically labelled tracer in a background of unlabelled mobile phase fluid, neon has been used as the marker [168,172].

Many thermodynamic measurements by SFC, especially those with open tubular columns, have employed FID. This detector is compatible with pure CO₂ and also with water in various states of aggregation [231–233]. With respect to the use in SFC, the most serious drawback of FID is the incompatibility with the CO₂ modified by most organic cosolvents although some compatible cosolvents do exist [234]. With FID, methane has been used almost exclusively to mark the hold-up time. The retention times t_R and t_0 to be used in Eq. (1) should preferably be obtained simultaneously from a single injection. To this end, it is expedient, albeit difficult, to inject a tiny amount of methane together with the injection solution of the solute(s). The simultaneous injection may be accomplished by flushing the sampling loop of the injection valve with methane prior to partial filling of the loop with the injection solution. Further, to obtain a true value of k_1 from Eq. (1), care should be taken to eliminate the extracolumn contribution to t_0 , i.e., the time needed for the marker to travel the connections between the injector and the column and between the column and the point of detection. The correction becomes important whenever the internal volume of the connections is not negligible with respect to the void volume of the column. In the adjusted retention time of the solute, $t_R - t_0$, the extracolumn contributions cancel provided there is no retention of the solute in the connections (e.g., by spurious adsorption).

3.4. Flow control

Flow restriction downstream of the column is needed to maintain the operating pressure in the column. The properties and performance required from the flow restriction device depend on the detector employed or, more precisely, on the relative positions in the flow path of the restriction device and the detector.

With the optical detectors operating at the column pressure, the fluid flow only needs to be restricted downstream of the detector cell. Then, the restriction device only serves to adjust and maintain a steady, uniform flow of the mobile phase fluid, and the internal volume of the device, operating temperature, and nucleation of the solutes from the expanding fluid do not constitute primary concerns.

In turn, when the detector operates at the ambient pressure (e.g., FID) or reduced pressure (e.g., mass spectrometer), the fluid flow has to be restricted upstream of the point of detection. With the low-pressure detectors, the restrictor does not only serve to maintain the uniform flow but it also has to secure a smooth transfer of the expanding fluid to the detector. The internal volume of the restrictor should be as low as possible to minimise the extracolumn broadening of solute peaks. Also, the detection of a solute should be completed while the solute–fluid mixture is still homogeneous because formation of molecular aggregates or even particles of the solute results in deterioration of the detection process (peak spiking, restrictor clogging, etc.). These considerations explain the lingering perception of the restrictor as an “Achilles’ heel” of SFC instrumentation. Currently, the flow restriction has usually been accomplished using a length of narrow-bore fused silica tubing that may be tapered or may contain a porous frit. The fused-silica restrictor is connected to the end of the column but an integral restrictor formed at the end of a fused-silica capillary column was also described [235]. The pros and cons of the tapered, frit, and integral restrictor designs were discussed by Pinkston and Henschel [236]. These restrictor designs, however, are not easily tailored to provide a desired flowrate at a particular temperature and pressure of the fluid. Vejrosta et al. [237,238] developed a multichannel restrictor that can be prepared to fit a particular flowrate required. The individual types of capillary restrictors are shown in Fig. 10 [239].

In binary mobile phase fluids, additional problems may result from phase separation of the main fluid and the co-

solvent in the restrictor. Chester and Innis [240] tested and discussed several pressure-regulating interface arrangements at the column outlet to avoid phase separation when using binary fluids.

3.5. Binary fluids and purity of CO₂

Determination of cosolvent effects by SFC (Section 2.2.3) would require a stable delivery to the column of the CO₂–cosolvent mixture of a defined composition. The various methods for preparation of cosolvent-modified CO₂ have been a subject of considerable attention in analytical SFC. As shown by Schweighardt and Mathias [241], the “premixed” supply tanks containing a CO₂–cosolvent mixture cannot deliver a mixture of constant composition unless an azeotrope is formed. The reason is a shifting vapour–liquid equilibrium as either phase is being drained from the tank. A simple method for preparation of cosolvent-modified CO₂ consists in saturation of the CO₂ stream with the cosolvent [242,243]. An obvious limitation of this technique is that it only yields a mixture of a single composition determined by the temperature and pressure in the saturator. Preparation of mixtures of varying, adjustable composition requires an independent control of the CO₂ and the modifier flowrates using a dual pump system [244] or a pulsed valve [245]. In order to monitor the concentration of water or methanol cosolvents in CO₂, Pyo and Hwang [246] developed an amperometric microsensor made of a thin film of perfluorosulphonate ionomer.

With highly sensitive detection methods such as FID, the presence of trace-level contaminants may present a concern also when pure CO₂ is to be used. As demonstrated, e.g., by Planeta [239], low-volatility contaminants such as lubricant residues tend to concentrate in the liquid phase contained in a CO₂ tank. Fig. 11 shows that application of tanks with dip tubes to feed the SFC pump can cause a marked increase in the background response of FID. Moreover, Fig. 11 suggests that the use of a dip-tube tank may even lead to increased background response of FID when compared to a tank with lower-grade CO₂ but without the dip tube. Consequently, the CO₂ from the vapour phase of a supply tank should preferably be used in SFC, and the use of dip tubes is not recommended for measurements requiring very high sensitivity of FID.

3.6. Detection

Some considerations regarding the solute detection have already been mentioned above, and so this section may be limited in its coverage. In SFC with cosolvent-modified CO₂, FID cannot be used because it responds to most organic cosolvents. If the use of low-pressure detection is desired with a binary fluid, the evaporative light scattering detector [247] may present a viable option. This detector is universal in its solute coverage, and its sensitivity is similar to that of FID.

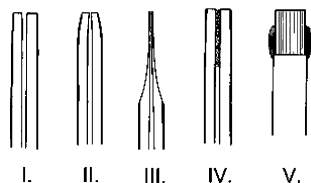


Fig. 10. Fused-silica capillary restrictors for SFC. I, linear restrictor; II, integral restrictor; III, tapered restrictor; IV, frit restrictor; V, multichannel restrictor. Reprinted with permission from [239].

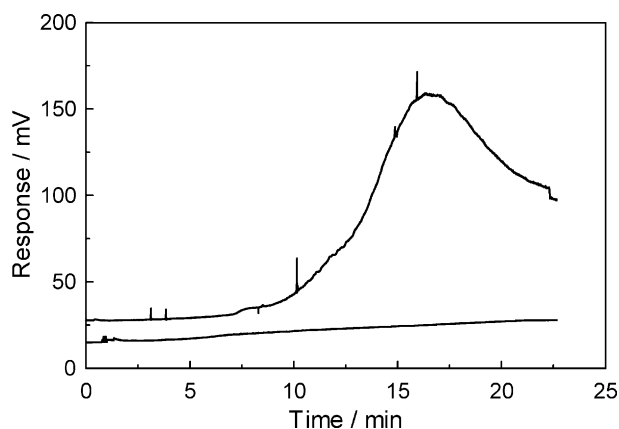


Fig. 11. FID response baseline in pressure-programmed SFC. Upper line: syringe pump filled from the liquid phase of a CO₂ tank with dip tube; supplier-specified purity of CO₂ = 4.8. Lower line: syringe pump filled from the vapour phase of a CO₂ tank; supplier-specified purity of CO₂ = 4.5. Column 15 cm × 250 μm i.d. packed with 5 μm octadecyl silica particles, 60 °C, pressure program 8–35 MPa. Reprinted with permission from [239].

The early thermodynamic studies by SFC mostly employed packed columns coupled to UV detectors. Although UV detection is much less universal compared to FID, it can operate at the column pressure and, therefore, it does not suffer from the restrictor-induced problems mentioned above. With the arrival of open tubular capillary columns to thermodynamic applications of SFC, the flow cells of conventional UV detectors proved to be too large for an efficient detection. A solution of this problem has been known from capillary separation techniques of analytical chemistry. It consists in removing the protective polyimide coating from a short (a few mm) section of a fused-silica capillary, and using the resultant transparent window as an optical detection cell, with the light passing in a perpendicular direction to the capillary axis. Since this configuration involves curved optical boundaries, it responds not only to a UV-absorbing solute but also to changes in the refractive index of the fluid [248]. For application in SFC, the cell temperature and pressure should be carefully controlled. This makes the construction technically difficult although suitable cell blocks for insertion into the cell compartment of a UV spectrophotometer were described [249]. The problem of temperature and pressure control can be somewhat alleviated by using optical waveguides to couple the cell to the detector. The capillary flow cells with optical fibres were used successfully in liquid-phase separation techniques such as electrophoresis [250] and high-temperature HPLC [251]. Bruno et al. [252] developed a capillary flow cell with optical fibres for use in open tubular column SFC. On the basis of a ray tracing algorithm, they formulated the guidelines for selecting proper diameters of the source and the collecting fibres to fit a particular capillary tube.

Optical detection in supercritical fluids has one more aspect that is partly relevant to thermodynamic measurements by SFC. When using spectrophotometry to quantify a so-

lute in a supercritical fluid, one should bear in mind that, in general, molar absorptivity of the solute varies with the fluid density. Examples of the variation were demonstrated in both IR [253] and UV [254] spectroscopy. Therefore, the absorbance–concentration proportionality constant is not readily transferable from one set of temperature and pressure conditions to another.

3.7. Uniqueness of the retention mechanism

The working equations given in Sections 2.1.1 and 2.2 rely on the underlying assumption that bulk partitioning of the solute between the stationary and the mobile phases is the only and exclusive mechanism of retention. Polar solutes, however, adsorb on interfaces within the column. As the interfacial area between the two phases in an open tubular capillary column is much smaller than in a packed column, the requirement to minimise interfacial adsorption again favours the open tubular columns over packed columns. Further, because of the growing correlation length, the density of a near-critical fluid at an interface generally differs from the bulk density regardless of the fluid's polarity. In a particular theoretical picture of the vapour–liquid interface near the critical point of a pure fluid [169], the interfacial thickness is supposed to be proportional to the correlation length. In the context to SFC, these phenomena probably modify the effective properties of the stationary phase, and they may be partly responsible for the different results on uptake of scCO₂ by stationary phases when studied by MSTPC [167,168,170,171] and by non-chromatographic methods (Sections 2.3.1 and 2.3.2). However, the effects of near-critical surface excesses of the mobile phase fluid on solute retention in SFC have yet to be explored.

4. Sources of auxiliary information

As a rule, the conversion of SFC retention factors to thermodynamic properties requires accurate data on diverse thermophysical properties of the various subsystems of the solute–mobile phase–stationary phase system. In this section, selected sources of such auxiliary information are briefly reviewed.

4.1. Thermodynamic data and models

4.1.1. Pure component properties

A reputed, critical collection of estimation methods for pure component properties has been prepared by Poling et al. [255]. Group contribution methods are of particular interest as they provide estimates of the properties for which no experimental data exist. For example, the EOS parameters for a pure component are often obtained from the component's critical properties and, in a number of important solutes, their critical parameters cannot be measured because of thermal decomposition. The appendices

of the book list the most important thermodynamic properties for organic substances containing up to 24 carbon atoms. A comprehensive compilation of critical parameters and phase change data is contained in the NIST Chemistry Webbook (<http://webbook.nist.gov/chemistry>), an Internet-based resource developed and maintained by the US National Institute of Standards and Technology (NIST) [256]. The NIST Chemistry Webbook is a public-domain source of information. More information on other thermophysical and thermochemical databases marketed by NIST can be found at <http://www.nist.gov/srd/thermo.htm> or at <http://trc.nist.gov>. Other commercial database products containing pure-component data include, e.g., the results of the DIPPR projects by the American Institute of Chemical Engineers (<http://www.aiche.org/dippr>, <http://dippr.byu.edu>) and the DETHERM database by DECHEMA e.V. (Society for Chemical Engineering and Biotechnology) (<http://www.dechema.de>).

In the important field of solute vapour pressure data, the most recent general compilation is probably that of Dykyj et al. [257]. Specific collections of vapour pressure data have been available for some important classes of low-volatility substances including higher alkanes [258,259], PAHs [260], polychlorinated biphenyls, polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans [261], and pesticides [262].

The $P\rho T$ data for organic liquids, including low-volatility liquids amenable to SFC, have been summarised and evaluated by Cibulka and Takagi [263,264].

The scope of SFC as a property measurement technique also includes synthetic oligomers and polymers in the roles of solutes and stationary phases, respectively. There are several useful compilations of solubility parameters and related properties of macromolecular substances [265–268]. Group contribution methods to estimate the thermodynamic properties of polymers are also available [269].

4.1.2. High-pressure phase equilibrium data for binary mixtures

In thermodynamic measurements by SFC, high-pressure phase equilibrium data serve a twofold purpose. The data on solute–fluid binary and/or ternary mixtures may be useful for checking the results obtained by SFC, either directly or after reduction to parameters of an EOS model. The data on interaction between the mobile phase fluid (CO₂) and small, often polar molecules may be useful for prediction and/or correlation of cosolvent effects when using modified mobile phases.

There are several recent compilations of both types of high-pressure phase equilibrium data mentioned above [270–273]. In addition to the general surveys, a large amount of scattered but useful information can be found in the proceedings of recent meetings dealing with supercritical fluids and with phase-equilibrium thermodynamics. A comprehensive review of phase equilibria in the CO₂–cosolvent mixtures of interest to SFC was published

by Page et al. [274]. As regards the specific topic of solubility of low-volatility solids and liquids in scCO₂, Bartle et al. [275] published a data compilation complemented with a correlation of solubility in terms of temperature, pressure, and density of pure CO₂.

4.1.3. Equations of state for PVT_x description of the mobile phase

Recently, thermodynamic properties of pure CO₂ have frequently been calculated from the wide-range, multiparameter EOS of Span and Wagner [276] (see also <http://www.ruhr-uni-bochum.de/thermo>). In chromatographic applications of pure hot (subcritical) water, wide-range thermodynamic formulation of Wagner and Pruss [277] will be of interest, possibly together with the correlations for the relative permittivity (dielectric constant) [278] and the ionic product [279] of water as functions of temperature and density. Selections of recommended EOS formulations for other potential mobile phase fluids, including hydrofluorocarbons, may be found elsewhere [280,281].

In modelling the fluid–solute or fluid–cosolvent mixtures and interactions in the mobile phase, the high-precision, multiparameter equations recommended for pure fluids are no longer applicable. Instead, a cubic EOS is a common choice here. There are several recent texts on cubic equations of state and their mixing rules [282–284]. For modelling of phase equilibrium data using a variety of EOSs and mixing rules, Pfohl et al. [285] developed PE, a freely downloadable, continuously expanded software package (<http://www.tu-harburg.de/vt2/pe2000>). The package is very useful for optimisation of binary parameters in multiple EOS models using a set of phase equilibrium data for the binary system concerned.

Employing the solubility data for 12 aromatic solutes in 5 supercritical fluid solvents, Caballero et al. [286] tested the ability of three cubic equations with two different sets of mixing rules to fit the data, and published the resultant sets of binary interaction parameters. On the basis of solubility data for 19 solutes of varied chemical type in scCO₂, Bartle et al. [287] developed a correlation of the unlike interaction parameter for the Peng–Robinson EOS [288] with conventional quadratic mixing rule.

4.1.4. Statistical thermodynamic models for stationary phase–mobile phase interactions

The cubic equations mentioned in the preceding section are only applicable to the mobile phase of a SFC system. In order to correlate the solute partition coefficients or to quantify the effects of uptake of mobile phase fluid by the stationary phase, a model is needed that would be applicable to both phases and capable of describing the distribution of any component of the system between the two phases. Considering that the system contains a non-volatile solute, a supercritical fluid, a crosslinked polymer or a bonded phase, and possibly a cosolvent, one concludes that the associated modelling is far from being a simple task. In principle, current molecular

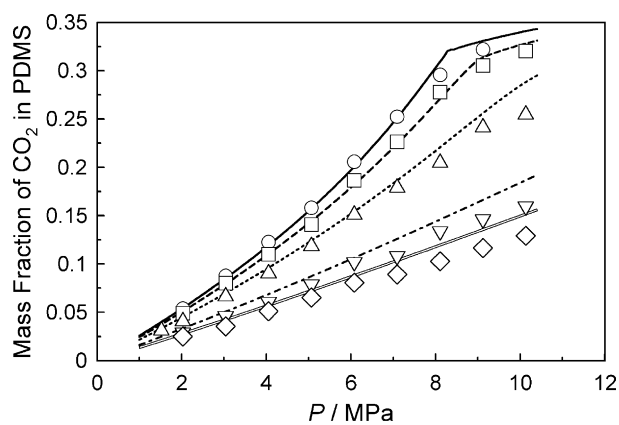


Fig. 12. Equilibrium solubility of CO₂ in PDMS. Points: calculated from experimental sorption data [167], lines: calculated from Panayiotou–Vera lattice fluid model [294] with parameters from [295]. (○) Solid line: 35 °C; (□) dashed line: 40 °C; (Δ) dotted line: 50 °C; (▽) dash-and-dotted line: 80 °C; (◇) double line: 100 °C.

thermodynamics provides several approaches compatible with the task. However, the perturbation theory-based models such as the statistical associating fluid theory [289,290] have not yet been used for the purpose, and the subject has been dominated by various kinds of mean-field lattice fluid models, with the S–L [291–293] and the Panayiotou–Vera (P–V) [294] models being used most often. Both models are descendants of the Flory–Huggins theory, and they can treat the mixtures of compressible fluids with polymers. The two models differ somewhat in their basic assumptions. The S–L model employs a composition-dependent volume of the lattice site and the approximation of an infinite coordination number of the lattice. The P–V model makes use of a fixed volume of the lattice site and a finite coordination number of the lattice (=10), and it contains a quasichemical term to account for non-random mixing. Because of the mean-field approximation, neither model can perform well in the immediate vicinity of the critical point, and both models tend to overestimate the critical compressibility factor. This problem can be partly bypassed by a suitable selection of the parameters for the near-critical fluid, however, at the expense of a decreased performance at temperatures farther above the critical as illustrated by Fig. 12. The original versions of the S–L and P–V models do not account for crosslinks in polymers but this may be settled by incorporating an elastic contribution [296] to the free energy into the models [23].

In order to correlate their experimental results or to calculate some auxiliary properties, many authors cited in Section 2 of this review used the S–L model [23,120,154,164,165,183,184], the P–V model [72,73,79], or both [152,181]. Xu et al. [167] and Edwards et al. [181] also employed the Martire–Boehm [66] model that is similar to but mathematically simpler than the S–L model. On the whole, the performance of all these models in fitting the experimental data is comparable, and it is also truly

remarkable, particularly in the systems containing polar cosolvents [120,164].

After 1990, the theoretical tools for interpretation of SFC retention data, especially in systems containing polar components, have been strengthened considerably by important new developments in lattice fluid models. However, neither advanced lattice fluid models accounting for hydrogen bonds [297,298] nor the combination [299] of lattice fluid approach with the recently popular, quantum mechanics-based COSMO models [300,301] have yet been applied to process SFC retention data.

In the author's knowledge, the most fitting assessment of the role of lattice fluid models in the interpretation of SFC retention data is that by Parcher and Chester [4]: "Again, the lattice fluid models are complex, but their ability to describe such complex systems involving a solute, supercritical CO₂ and a polar liquid modifier, all in equilibrium with a polymeric stationary liquid phase, is quite remarkable and bodes well for our ability to develop a truly comprehensive theory for a hypothetical unified chromatography".

4.2. Viscosity models

Viscosity of the mobile phase fluid as a function of temperature and density of the fluid is needed to calculate the pressure drop along the column. The correlation for viscosity of pure CO₂ within wide range of conditions was developed by Vesovic et al. [302] with a subsequent improvement in the liquid phase region [303]. Viscosity of alternative refrigerants, if needed, may be calculated from a recent modification [304] of an earlier correlation based on extended corresponding states principle [305]. Predictive methods for viscosity of dense fluid mixtures are also available [306,307] although modelling of binary mixtures containing polar cosolvents may be difficult.

5. Conclusion

SFC will certainly never become a prevailing, stand-alone, self-sufficient technique for thermodynamic measurements in systems comprising non-volatile solutes and supercritical solvents. The principal reasons for that include:

- (i) dynamic character of chromatography,
- (ii) dependence of certain results derived from the retention factors (e.g., solute partial molar properties) on the particular thermodynamic models employed in the data reduction, and
- (iii) wide variety of auxiliary information needed when interpreting the retention data.

However, in solute–solvent systems with a high degree of asymmetry (=size difference between the solute and solvent molecules) and in the limit of infinite-dilution of the solute, SFC provides a potentially powerful complement to conventional techniques of high-pressure phase equilibrium

studies. SFC can provide thermodynamic data fairly rapidly, it can handle multiple solutes within a single experimental run, and it usually requires less material as compared to other measurement techniques.

In addition to yielding the “mobile phase-rooted” thermodynamic data on solute–supercritical fluid interactions, SFC in its inverse mode is also a valuable source of information on the stationary phase. The foremost among such applications has been the use of solute (“molecular probe”) retention to monitor the supercritical fluid-induced depression in the glass transition temperature of the stationary polymer.

To date, an overwhelming part of thermodynamic applications of SFC have used CO₂ as the mobile phase fluid (=solvent) but there is no fundamental reason that would preclude the use of other fluids. For example, refrigeration industry may be interested in the interactions between lubricants and fluorinated refrigerants (CFC replacements). In principle, such data could be obtained by SFC using the lubricant as the solute and the refrigerant as the mobile phase fluid. Applications of SFC to probe solute partitioning in biphasic, “green”, reaction/solvent systems formed by room-temperature ionic liquids and scCO₂ also appear promising.

The overall position of SFC as a source of thermodynamic data may perhaps be described as follows: SFC is a tool to obtain “difficult-to-access” thermodynamic properties using solute retention factors and literature (or model-derived) values of some “easier-to-access” thermodynamic properties. Perhaps, this description applies to the whole of unified chromatography [4] rather than being restricted to the traditional domain of SFC.

6. Nomenclature

c	molar concentration
C	quantity defined in Eq. (4)
\bar{h}	partial molar enthalpy
H	Henry’s constant
k	retention factor
K_c	partition coefficient
M_n	number-average molar mass
M_w	weight-average molar mass
n	amount of substance (mole number)
P	pressure
R	gas constant
t_0	column hold-up time
t_R	solute retention time
T	absolute temperature
v	molar volume
\bar{v}	partial molar volume
V	volume
w	mass fraction
x	mole fraction
y	mole fraction (gas phase)

Greek letters

α	thermal expansivity
β	compressibility
δ	quantity given by Eq. (8)
φ	fugacity coefficient
μ	chemical potential
ρ	molar density
ζ	mixing expansivity

Subscripts

c	critical property
g	glass-transition property
m	mobile phase property
n	constant amount of substance
P	constant pressure
s	stationary phase property
T	constant temperature
v	constant molar volume
σ	saturation
1	solute
2	principal component of the stationary phase
3	mobile phase fluid
4	cosolvent (modifier, additive to the mobile phase fluid)

Superscripts

∞	infinite-dilution
σ	saturation

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