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Magnitude of the diffusion coefficient anomaly in the critical region and its effect on supercritical fluid chromatogrpahy

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ABSTRACT

Literature measurements of diffusion in a supercritical fluid, especially those of naphthalene in supercritical fluid carbon dioxide, are discussed. These show that at very high dilution there is no measurable anomaly, but that large reductions in the apparent diffusion coefficient are observed at higher, though still low, concentrations. Three effects contributing to the anomaly are described: those of chemical potential, augmented density and fluid motion. Measurements were made of the effect of on-column naphthalene solute concentration on column efficiency in supercritical fluid chromatography using carbon dioxide as the mobile phase. The experiments were performed at 35°C (308 K) at a variety of mobile phase densities and a constant linear flow-rate. The results are interpreted in terms of the above-mentioned phenomena and their implications for the Van Deemter and Golay equations. Calculations of quantities related to chemical potential, augmented density and fluid motion were performed for the same system (naphthalene in carbon dioxide) in order to estimate their importance. The significance of the diffusion coefficient anomaly for analytical and preparative supercritical fluid chromatography is discussed.

INTRODUCTION

Since supercritical fluid chromatography (SFC) is usually carried out at flow-rates above the optimum for the minimum theoretical plate height, h_{min}, as a compromise between satisfactory resolution and workable analysis time, the C_m term in the Van Deemter equation for h in terms of the mean mobile phase velocity u,

$$h = A + B/u + C_m u + C_s u \qquad (1)$$

makes an important contribution. C_m is inversely proportional to the diffusion coefficient of the solute in the mobile phase, D_m, as it arises from the variation of velocity in the mobile phase and is reduced by the effect of diffusion across the velocity profile. The principal advantage of SFC over liquid chromatography is that D_m is higher in supercritical fluids, allowing greater efficiency of separation or shorter analysis times.

Transport properties, such as diffusion, in supercritical fluids can exhibit so-called anomalous behaviour in the critical region [1], meaning that their values undergo a variation, which is sometimes dramatic, at temperatures just above the critical temperature and around the critical density. The diffusion coefficient tends to zero at

the critical point and along an isotherm above the critical temperature exhibits a drop, which is a maximum close to the critical density. In the limit of infinite dilution, this "anomaly" becomes vanishingly small.

Thus, chromatographic peak widths in SFC should be greater in the region around the critical point than away from it, and some of its advantage over liquid chromatography may be lost. There are two reasons why this is often inconsequential. First, chromatography is usually carried out at low concentrations which are close enough to the infinite-dilution limit for the diffusion coefficient anomaly to be negligible. However, measurements of diffusion coefficients using the chromatographic peak-broadening effect have sometimes been found to be affected by the amount of solute injected [2]. (It should be noted that preparative-scale SFC uses moderate solute concentrations, so the diffusion coefficient anomaly may then be important.) Second, the maximum in the anomaly is associated with the critical density. SFC is carried out at pressures above the critical pressure: increasing the temperature above the critical temperature will shift the maximum to higher pressures. The purpose of this study was to investigate the extent of the anomaly in the diffusion coefficient for a solute in high dilution, both experimentally and by thermodynamic argument, using the system of naphthalene in carbon dioxide, and to discuss its significance for SFC.

LITERATURE MEASUREMENTS OF DIFFUSION COEFFICIENTS IN SUPERCRITICAL FLUIDS

The large number of experimental measurements of diffusion coefficients in supercritical fluids fall into two classes. First, there are those made by chromatographic peak broadening (also known as Taylor dispersion), under conditions which approximate infinite dilution and mostly show no measurable anomaly in the critical region. The latter include measurements made by a variety of measurements at higher concentrations, which can show large anomalies.

The results of measurements of the former type for naphthalene in carbon dioxide at 313 K, made by a number of workers [3–5], are shown in Fig. 1 as a graph of ρD_m *vs.* density, ρ. Also shown is a value of ρD_m close to zero density calculated from the value measured in air [6] using rigorous kinetic theory [7]. The continous line in Fig. 1 gives the predictions of Thorne–Enskog theory [7], which is expected to be valid, at least qualitatively, at lower densities. Hence, the quantity ρD_m does not change dramatically over the whole density range and its general form is given by the dashed line. The curve falls initially with density, in accordance with Thorne–Enskog theory, and then rises to a fairly level region. We suggest that the rising portion of the curve is due to the fall in the rate of rotational diffusion with density, whereas edgewise motion of the naphthalene molecules persists longer.

Measurements of the diffusion coefficient of naphthalene in carbon dioxide at higher concentrations have been made by Tsekhanskaya [8] at 308 K. These show a dramatic drop from a value of $4.8 \cdot 10^{-9}$ m^2 s^{-1} at a density of 250 kg m^{-3} to $0.006 \cdot 10^{-9}$ m^2 s^{-1} near the critical density and then a rise to a value of $6.9 \cdot 10^{-9}$ m^2 s^{-1} at a density of 592 kg m^{-3}. As is explained in the next section, this fall is not all due to a decrease in the diffusion coefficient itself.
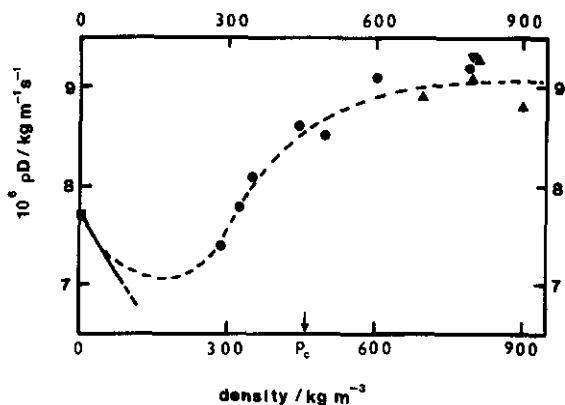
Fig. 1. Plot of the product of the diffusion coefficient, D_m, and density ρ, for naphthalene in dilute solution in carbon dioxide at 313 K; ■ = calculated from D_m in air [6]; ● = Feist and Schneider [3]; ▲ = Lauer *et al.* [4]; ▼ = Funazukuri *et al.* [5]. The arrow shows the critical density.

EXPERIMENTAL

The effects on peak width of solute concentration and mobile phase density in the critical region were studied using a Lee Scientific 501 supercritical fluid chromatograph (Dionex). Solutions of naphthalene (Gold Label, scintallation grade, 99 + %; Aldrich) in dichloromethane (DCM) (high-performance liquid chromatographic grade, 99.8 + %, May and Baker) were injected onto a phenyl-substituted polysiloxane capillary column, 15 m × 100 μm I.D. (Lee Scientific). The column dimensions were selected to maximize the residence time and facilitate the measurement of any anomalous effects.

The temperature of the system was maintained at 35.0°C by immersing the complete column in a water-bath. The temperature was monitored by a chromel thermocouple connected to a digital voltmeter (Keithly) with an accuracy of ± 0.001 mV. Measurements were made within a temperature range expressed as (35.000 ± 0.085)°C. The flow-rate of carbon dioxide (SFC grade; Air Products) was regulated by means of different lengths of linear restrictor tubing (12 μm I.D.) (Polymicro Technologies), butt-connected to the main capillary column. The lengths of linear restrictors were in the range 58.5–75.0 cm. The apparatus is shown schematically in Fig. 2. The pressure was programmed to give a retention time of the unretained peak (the injection solvent) of 19.67 min at each linear restrictor length, so that mean linear flow-rate, u, of the Golay equation was constant throughout the experiments. Densities corresponding to the experimental temperature and pressure were calculated using a principle of corresponding states method.

The pneumatic injection valve (A90; Valco) was fitted with a 60-nl sample loop. The long injection time of 6 s ensured that the entire contents of this loop were delivered onto the column. At the residence times used, this was assumed not to distort the peak shape appreciably from Gaussian.

Flame ionization at 400°C detection was applied. The flow-rate of hydrogen was 30 cm^3 min^{-1} and of air 300 cm^3 min^{-1}. The make-up gas was helium at 28 cm^3
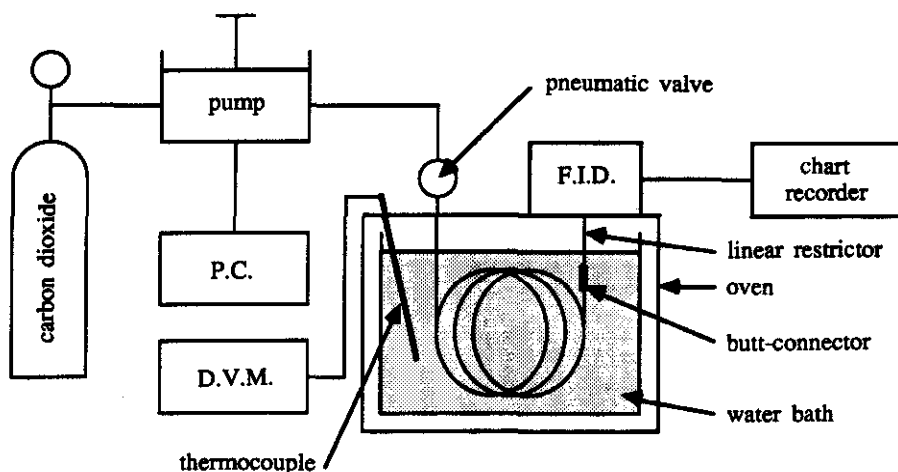
Fig. 2. Schematic diagram of the apparatus in which the experiments were performed. P.C. = personal computer; D.V.M. = digital voltmeter; F.I.D. = flame ionization detector.

min^{-1}. Output was relayed to a potentiometric chart recorder (Smiths) operating at speed of 120 mm min^{-1}. The baseline width of the solute peak was measured from the recorder trace. This, with a knowledge of the column dimensions and mean mobile phase flow-rate, permitted the calculation of the peak volume at elution.

The peak volume at detection was assumed to be representative of the solute peak volume travelling down the column, especially as peak broadening is a function of the square root of residence time, *i.e.*, half the broadening occurs after one quarter of the passage along the column. At a known density, and given a desired mole fraction of naphthalene in carbon dioxide on the column, the appropriate concentration of naphthalene in DCM to be injected can be determined.

At each density studied, at least five replicate runs were made for solutions of naphthalene in DCM equivalent to on-column mole fraction concentrations of $1 \cdot 10^{-4}$, $2 \cdot 10^{-4}$, $3 \cdot 10^{-4}$ and $4 \cdot 10^{-4}$. The differences in the retention times of the unretained injection solvent, DCM, and the solute, denoted $t_r - t_m$, and the width at half-height, $w_{d_{0.5}}$, were measured from the chart recorder traces to an accuracy of ± 0.05 cm, and used to determine the efficiency of the column as a function of solute concentration at a variety of densities.

RESULTS AND DISCUSSION

The expanded Golay equation for capillary columns is

$$h = \frac{2D_m}{u} + \frac{d_c^2(1 + 6k + 11k^2)u}{96(1 + k^2)D_m} + \frac{2kd_f^2 u}{(1 + k)^2 D_s} \qquad (2)$$

where u is the average mobile phase velocity along the column d_c is the column inside diameter, k is the capacity ratio, d_f is the stationary phase film thickness and D_m and

TABLE I

EXPERIMENTAL DATA, AT 35.0°C, FOR DIFFERENCES OF RETENTION OF THE SOLUTE PEAK AND UNRETAINED SOLVENT PEAK AT $t_r - t_m$ AND THE WIDTH AT HALF-HEIGHT, $w_{d0.5}$, OF THE NAPHTHALENE SOLUTE PEAK

35.0°C		Concentration (mole fraction of naphthalene)							
p (bar)	ρ (kg m^{-3})	$1 \cdot 10^{-4}$		$2 \cdot 10^{-4}$		$3 \cdot 10^{-4}$		$4 \cdot 10^{-4}$	
		$t_r - t_m$ (cm)	$w_{d0.5}$ (cm)	$t_r - t_m$ (cm)	$w_{d0.5}$ (cm)	$t_r - t_m$ (cm)	$w_{d0.5}$ (cm)	$t_r - t_m$ (cm)	$w_{d0.5}$ (cm)
78.0	407.1	17.02	3.45	17.12	3.55	17.05	3.65	16.89	3.73
79.8	458.5	16.17	3.54	16.15	3.69	16.18	3.87	16.16	4.08
80.4	474.6	16.13	3.55	16.12	3.71	16.19	3.98	16.22	4.16
81.7	507.3	16.11	3.47	16.15	3.56	16.22	3.73	16.22	3.85
83.0	547.6	15.70	3.29	15.63	3.37	15.71	3.52	15.76	3.72
85.5	602.9	15.53	3.21	15.60	3.27	15.64	3.34	15.72	3.37
90.0	671.0	14.74	2.91	14.86	2.98	14.91	2.93	14.99	3.02

D_s are the diffusion coefficients in the mobile and stationary phase, respectively. Under SFC conditions, which normally operate at flow-rates above the optimum for maximum efficiency (typically by a factor of ten), the term in C_m of the Van Deemter equation (eqn. 1) increases the significance of its contribution relative to the term in B.

In order to obtain results which could be compared in terms of diffusional effects on the Golay equation for column efficiency, it was essential to perform chromatographic separations at the same mean linear flow-rate of the mobile phase and with the same on-column concentration of naphthalene. The manner in which this was done is outlined under Experimental. The flow-rate used in this study was 1.277 cm s^{-1}.

Table I gives the retention differences of the solute peak and the unretained solvent peak (DCM) as $t_r - t_m$ and the width at half-height of the naphthalene solute peak. The former value was found to be in the region of 16 min. However, at densities above 474.6 kg m^{-3} the peaks of solute at high concentration were generally retained longer than those at low concentrations, whereas below this density the reverse applied. The effect was not marked under the conditions used. At all densities, the width at half-height, $w_{d0.5}$, was found to increase with increasing concentration. This phenomenon increased in magnitude with increasing density to a density close to 474.6 kg m^{-3} (note that the critical density, i.e., the density at the critical temperature and pressure, of carbon dioxide is 470.1 kg m^{-3}). Any further increase in density to the limit of the study (671.0 kg m^{-3}) was observed to reduce the magnitude of the effect. At densities higher than 671.0 kg m^{-3}, any effects were of the same order of magnitude as the experimental uncertainties.

Fig. 3 shows a plot of h, derived from the experimental values, versus the density of the mobile phase, ρ. The number of plates in the column, and the corresponding plate heights, determined from the experimental data are given in Table II. The heights evaluated under these experimental conditions are slightly larger than those generally used in SFC (typically of the order of 0.2 mm at ten times the optimum
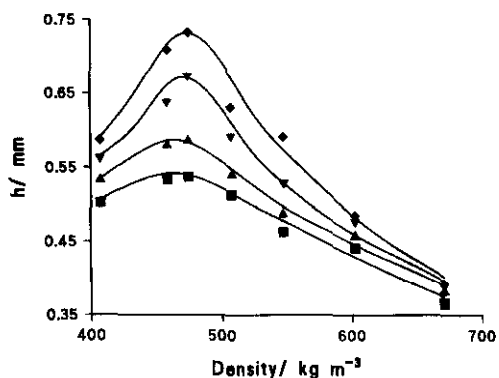
Fig. 3. Plot of the experimentally derived *h versus* density, ρ. Lines join data of the same on-column concentrations of naphthalene, x_2: ■, $x_2 = 1 \cdot 10^{-4}$ mole fraction; ▲, $x_2 = 2 \cdot 10^{-4}$ mole fraction; ▼, $x_2 = 3 \cdot 10^{-4}$ mole fraction; ◆, $x_2 = 4 \cdot 10^{-4}$ mole fraction.

mean linear flow-rate, $10u_{opt}$, on the preferred 50 μm I.D. column and 0.4 mm at $10u_{opt}$ on a 100 μm I.D. column). The effect of concentration on *h* is depicted in Fig. 4 over the range of densities studied.

Peak broadening arises from a reduction in the diffusive transport, behaviour typified by a heavier solute in a supercritical fluid in the critical region. Three factors contribute to this effect. The first is a reduction in the diffusion coefficient itself. According to non-equilibrium themodynamics [9,10], the diffusive flux is driven by the gradient of chemical potential rather than concentration, although it is defined in terms of the latter. The theoretical expression for D_m therefore contains the important factor

$$\zeta = (1/RT)(\delta\mu_2/\delta\ln x_2)_{p,T} \tag{3}$$

TABLE II

NUMBER OF PLATES IN THE COLUMN, *n*, DERIVED FROM THE EXPERIMENTAL DATA, AT 35.0°C, AND THE CORRESPONDING PLATE HEIGHTS, *h*

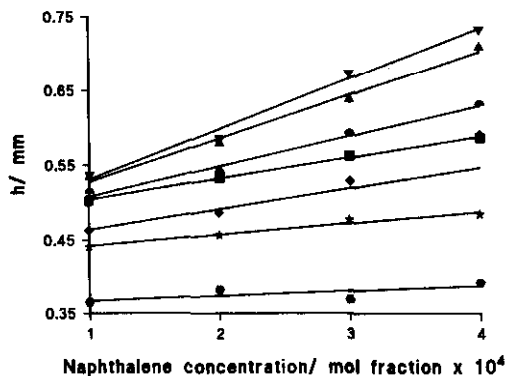| 35.0°C		Concentration (mole fraction of naphthalene)							
p (bar)	ρ (kg m^{-3})	$1 \cdot 10^{-4}$		$2 \cdot 10^{-4}$		$3 \cdot 10^{-4}$		$4 \cdot 10^{-4}$	
		n	*h* (mm)	*n*	*h* (mm)	*n*	*h* (mm)	*n*	*h* (mm)
78.0	407.1	29 798	0.503	28 165	0.533	26 629	0.563	25 534	0.587
79.8	458.5	28 112	0.534	25 869	0.580	22 243	0.638	21 161	0.709
80.4	474.6	27 945	0.537	25 584	0.586	22 243	0.674	20 463	0.733
81.7	507.3	29 244	0.513	27 793	0.540	25 331	0.592	23 776	0.631
83.3	547.6	32 425	0.463	30 887	0.487	28 329	0.529	25 374	0.591
85.5	602.9	34 016	0.441	32 797	0.457	31 447	0.477	30 909	0.485
90.0	671.0	41 134	0.365	39 259	0.382	40 627	0.369	38 266	0.392

Fig. 4. Plot of the experimentally determined h as a function of on-column mole fraction concentration, x_2, of naphthalene. The data are shown for a variety of densities: $\blacksquare$, 407.1; $\blacktriangle$, 458.5; $\blacktriangledown$, 474.5; $\curvearrowright$, 507.3; $\blacklozenge$, 547.6; $\bigstar$, 602.9; $\bullet$, 671.0 kg m^{-3}.

where μ_2 is the chemical potential of the solute and x_2 its mole fraction. At the critical point ζ tends to zero, except at the limit of infinite dilution. The physical explanation of this is that, towards the critical point, a situation is approached in which the fluid will split into two phases in which the solute will have the same chemical potential but different concentrations (except in the limit of zero concentration where both concentration are tending to zero).

The second factor is a smaller one, but it does reinforce the above effect. Arising because of the attraction of the heavier solute molecule for the solvent molecules, it results in a solvent density in the region of the solute peak which is higher than that in the column as a whole. This augmentation of local solvent density is largest in the critical region. As shown in Fig. 5, the quantity ρD_m usually does not change greatly with density, and the diffusion coefficient will be lower in the region of the solute peak by a factor of around ρ_0/ρ, where ρ is the density in the presence of solute and ρ_0 is the density of the pure solvent.

Finally, a more serious effect, which is difficult to quantify, concerns fluid motion during the diffusion process. The diffusion coefficient and the fluxes of solute to which it relates are defined barycentrically, *i.e.*, with respect to the mass of the fluid at any point, and therefore the frame of reference will be in motion. In chromatography, there will be the motion of the fluid along the column, with velocity increasing towards the centre of an open capillary or passage through a packed column, which is taken into account in the theory of chromatography. There will be additionally, however, a motion of the fluid towards any region in which the concentration is increased by the diffusion process, in order to achieve the higher density corresponding to the higher concentration. This motion will mean that the flux of solute with respect to space-fixed coordinates is different to that with respect to the barycentre. In accurate liquid diffusion studies in static cells, this effect is taken into account: a one-dimensional solution to the problem is sufficient [11]. In SFC in the critical region this is potentially a more serious effect, and a three-dimensional solution is required. It can be shown [12] that the fluid velocity, $\mathbf{v}$ arising from this effect is related to the flux of the solute, $\mathbf{J}_2$, by

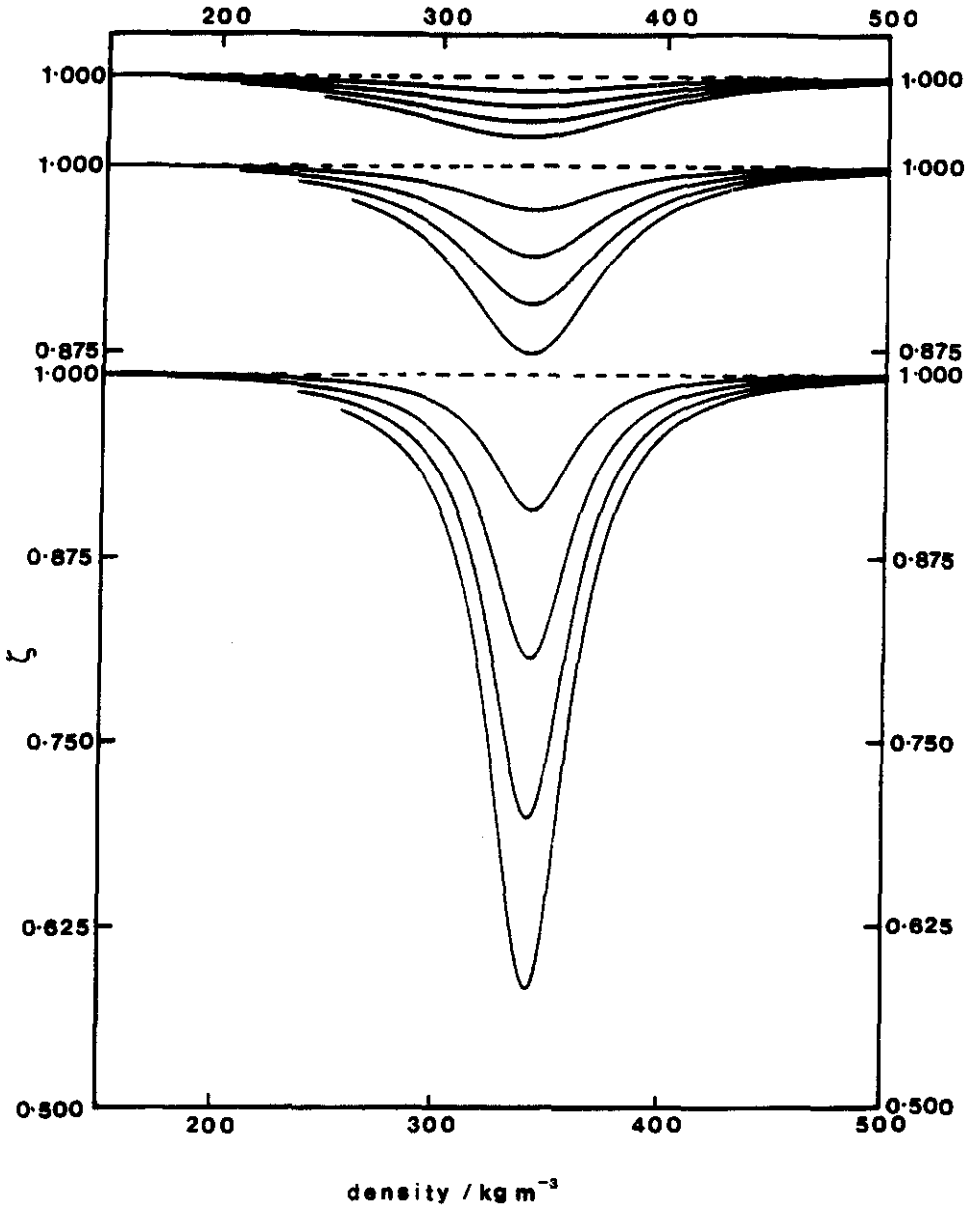$$\mathrm{div}\,\mathbf{v} = -\rho(V_2/M_2 - V_1/M_1)\mathrm{div}\mathbf{J}_2 \qquad (4)$$

Fig. 5. Plots of ζ *versus* density, ρ, for solutions of naphthalene in carbon dioxide at temperature 1, 3 and 9 K above the critical temperature of the pure solvent, calculated from the Van der Waals equation. Mole fractions of naphthalene are $1 \cdot 10^{-4}$, $2 \cdot 10^{-4}$, $3 \cdot 10^{-4}$, and $4 \cdot 10^{-4}$, with deviations of ζ from unity increasing with increasing concentration. The scale factor on the ζ axis is the same at all three temperatures. Note that the critical density according to the Van der Waals equation, with the parameters used, is 343 kg m^{-3}.

where V_1 and V_2 are partial molar volumes and M_1 and M_2 are the molar masses of the solvent and solute, respectively. In the critical region, the partial molar volumes of

typical solutes are large and negative, as will be discussed in more detail in the next section. The effect is therefore potentially a large one, but is also proportional to the rate of change of solute flux with distance, and thus will also become negligible in the limit of infinite dilution.

Two examples of this third effect are now discussed. First, when a solid is being dissolved into a supercritical fluid, the flux of solute falls off with increasing distance from the solid surface and so, according to eqn. 4, there is fluid motion towards this surface, reducing the solute transport away from the solid with respect to space-fixed coordinates. This contributes to the reduction in the diffusive flux observed in the Tsekhanskaya diffusion experiment [8], for example. As a second example, in the case of a one-dimensional Gaussian distribution of solute concentration, application of eqn. 4 shows that the fluid moves away from the centre of the distribution, with the velocity rising from zero at the centre to a maximum and then falling towards zero at the edges. These, therefore, are two contrasting examples. In the first, new solute is being introduced, which attracts solvent towards it, reducing the diffusive flux. In the second, the solute already in solution transports its associated solvent molecules with it as it moves, increasing the diffusive flux with respect to space-fixed coordinates.

The incorporation of this effect into the theory of chromatography is a daunting prospect, as the dependence of D_m, ρ and $\mathbf{v}$ on concentration make the diffusion equation, solved for example in the Golay treatment [13], non-linear. The situation is further complicated by the fact that, because of the fluid motion associated with diffusion, a full hydrodynamic analysis may be necessary, which takes into account viscous and inertial effects in addition to solving the diffusion equation. In the absence of a proper analysis, the following qualitative argument and conclusion seem likely to be valid. The solute peak, averaged over the cross-section of the tube, travels along an open chromatographic column in an approximately Gaussian form with respect to the longitudinal coordinate. As it travels it is spread by various effects corresponding to the terms in eqn. 1 and when this happens it is further spread by fluid motion away from the centre of the peak, as in the Gaussian example above. Thus, fluid motion will cause increased spreading in SFC, especially in the critical region. This effect is difficult to quantify, but will be less important for very dilute solutions.

Thermodynamic arguments for a diffusion coefficient anomaly

In this section estimates are made of the quantities illustrating the importance of the genuine reduction in mutual diffusion coefficient itself (via chemical potential), augmented density and fluid motion. The Van der Waals equation of state is used, and although this is less successful than later equations in predicting thermodynamic quantities which agree with experiment; it is adequate for the purpose of estimating the importance of the effects. The simpler form of the Van der Waals equation,

$$p = RT/(V-b) - a/V^2 \tag{5}$$

is used, where p is the pressure, V the molar volume and the constants a and b are given by

$$a = [(a_{11})^{1/2}x_1 + (a_{22})^{1/2}x_2]^2$$

$$a_{12} = (a_{11}a_{22})^{1/2}$$

$$b = b_1 x_1 + b_2 x_2 \tag{6}$$

The Van der Waals parameters used for carbon dioxide were $a_{11} = 0.364675$ J m^3 mol^{-1} and $b_1 = 42.7514 \cdot 10^{-6}$ m^3 mol^{-1}, calculated from a critical temperature of 304 K and a critical pressure of 7.39 MPa [14] (the large number of significant figures used ensures that the predicted critical temperature of the pure solvent is close to 304 K). The corresponding values for naphthalene used were $a_{22} = 3.97$ J m^3 mol^{-1} and $b_2 = 189 \cdot 10^{-6}$ m^3 mol^{-1} obtained from a critical temperature of 758 K and a critical pressure of 4.11 MPa [14].

Quantities related to these three effects are now made. For the first of these, the diffusion coefficient itself, the relevant parameter is ζ, defined by eqn. 3. This can be shown, by using standard thermodynamic procedures and the Van der Waals equation, to be given by

$$\zeta = 1 - [2x_1 x_2/RTV^2(V-b)^2\varphi]\{(a_{11}+a_{22}-2a_{12})V + a(b_1-b_2)/V \\ - 2[(a_{11}-a_{12})x_1 - (a_{22}-a_{12})x_2](b_1-b_2)\} \tag{7}$$

where

$$\varphi = 1(V-b)^2 - 2a/RTV^3 \tag{8}$$

Sample calculations were made and are shown in Figs. 5 and 6. Fig. 5 shows ζ falling below unity around the critical density to an extent increasing with concentration and proximity to the critical temperature. The curves are only shown for condition where correlations of experimental solubilities [15] using the Peng–Robinson equation of state [16] indicate that saturation has not occured. Fig. 5 shows that a decrease in ζ by about half can occur 1 K above the critical temperature of the pure solvent, but that the decrease is only a few percent 9 K above the critical temperature. These plots compare with Fig. 3, the variation of h with density at the same four concentrations, almost as inversions. Note, however, that results of calculations are not shown for the precise experimental temperature. Fig. 6 shows the values for the highest concentration plotted as a function of pressure. Here the effect is sharper and moves to higher temperature, both these features reflecting the p–V–T behaviour of the fluid.

For the second effect, that of increased density, calculations of ρ_0/ρ were made and are shown in Fig. 7 as a function of pressure. This is seen to be a smaller effect, which does, however, reinforce the first.

The third effect, arising from fluid motion, is a function of the differences in the partial molar volumes of the solute and solvent. Calculations of this quantity for the solvent, V_1, show that it is not markedly different from the molar volume of pure carbon dioxide at the same temperature and pressure. V_2, for the solute, is given by

$$V_2 = [1/(V-b) + b_2/(V-b)^2 - 2(a_{12}x_1+a_{22}x_2)/RTV^2]/\varphi \tag{9}$$
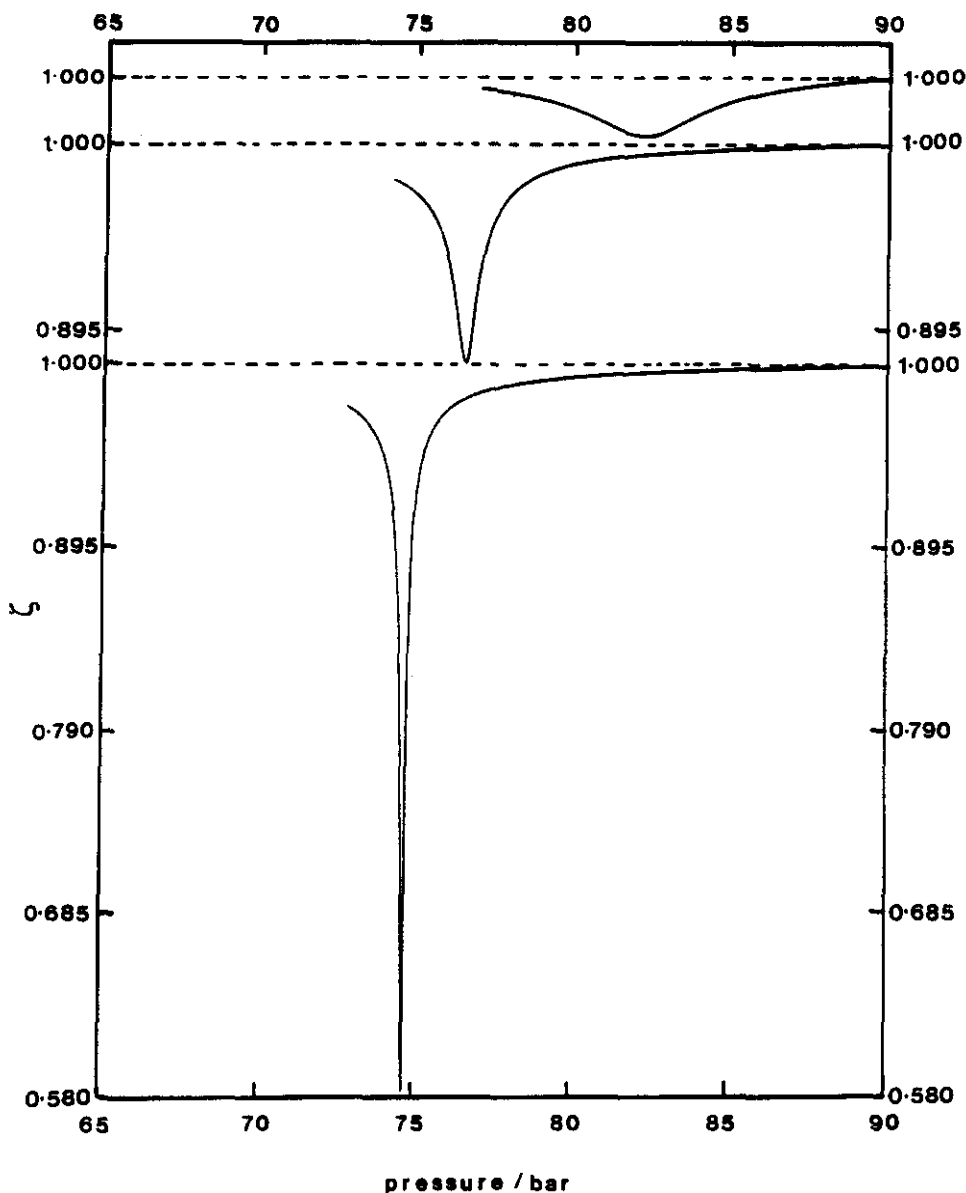
according to the Van der Waals equation.

Fig. 6. Plots of ζ *versus* pressure, p, for solutions of naphthalene (mole fraction $4 \cdot 10^{-4}$) in carbon dioxide at temperatures 1, 3 and 9 K above the critical temperature of the pure solvent, calculated from the Van der Waals equation. The scale factor on the ζ axis is the same at all three temperatures.

Calculations show that V_2 is not sensitive to concentration below the solubility limit for naphthalene. Values are plotted for $x_2 = 4 \cdot 10^{-4}$ in Fig. 8. These demonstrate large negative values even at the highest temperature considered, and a value of $-60 \ dm^3 \ mol^{-1}$ at 1 K above the critical temperature of carbon dioxide (this com-
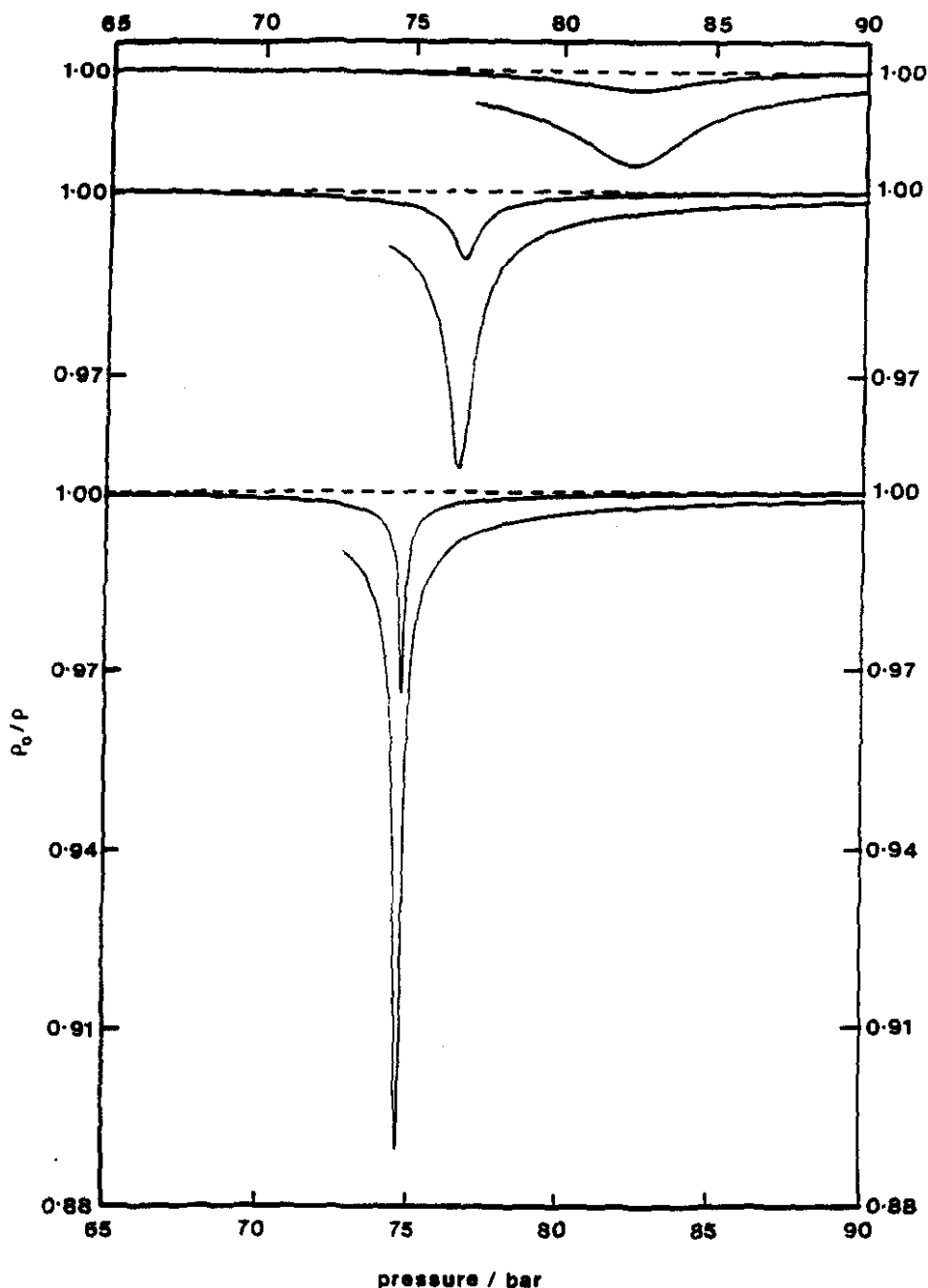
Fig. 7. Plots of ρ_0/ρ *versus* pressure, p, for solutions of naphthalene in carbon dioxide at temperatures 1, 3 and 9 K above the critical temperature of the pure solvent, calculated from the Van der Waals equation. ρ is the density of the mixture and ρ_0 that of the pure solvent at the same temperature and pressure. For the upper curves at each temperature $x_2 = 1 \cdot 10^{-4}$ and for the lower curves $x_2 = 4 \cdot 10^{-4}$. The scale factor on the ρ_0/ρ axis is the same at all three temperatures.
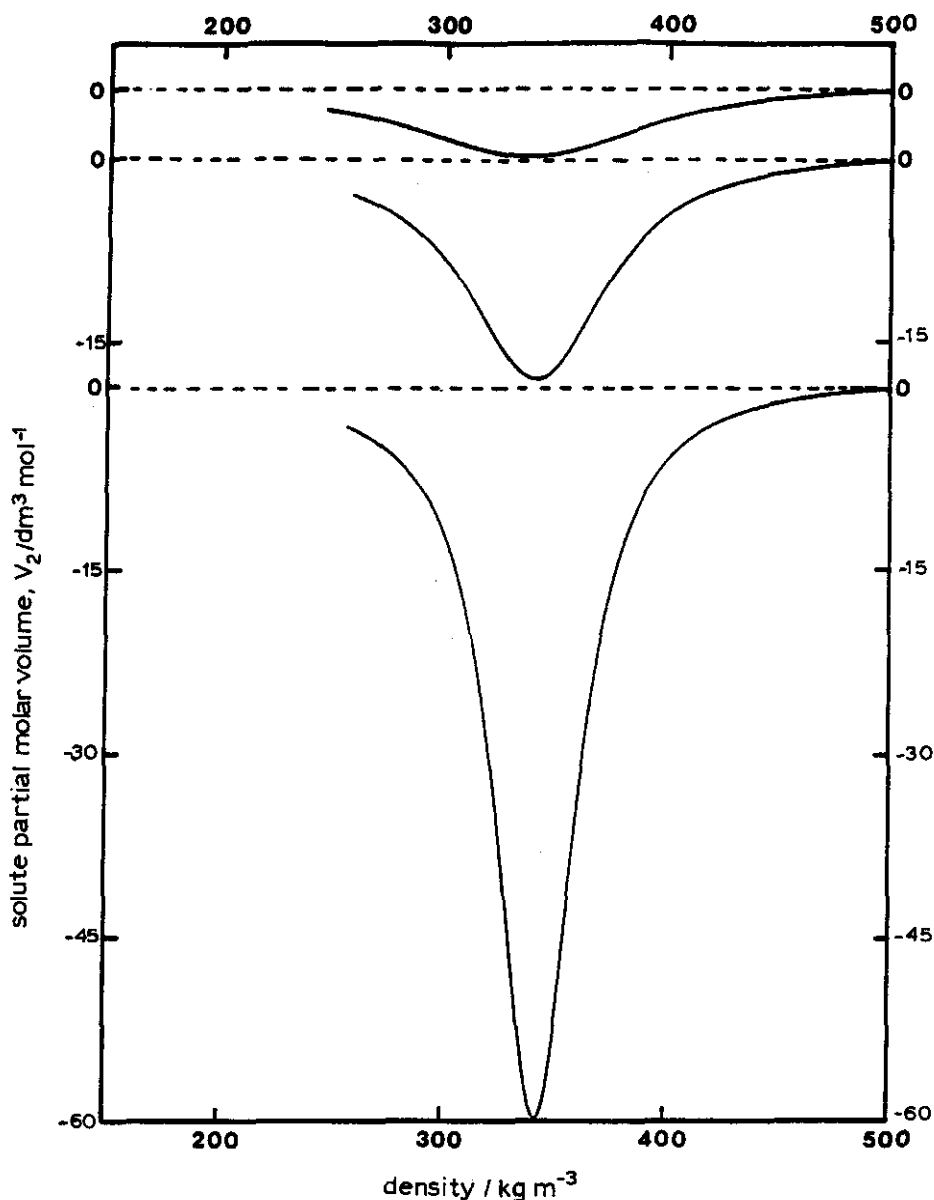
Fig. 8. Plots of the partial molar volume, V_2 of naphthalene of mole fraction $4 \cdot 10^{-4}$ in carbon dioxide at temperatures 1, 3 and 9 K above the critical temperature of the pure solvent, calculated from the Van der Waals equation. The scale factor on the V_2 axis is the same at all three temperatures.

pares with the molar volume of naphthalene of about $+0.2 \, dm^3 \, mol^{-1}$). Addition of naphthalene to carbon dioxide at its critical density and 1 K above the critical temperature, to form a solution of $4 \cdot 10^{-4}$ mole fraction (close to saturation), is predicted by the Van der Waals equation to reduce the volume to around half of its orginal value at the same pressure.

The results of calculations given above were obtained for naphthalene. For heavier solutes, the values of a_{22} and to a lesser extent a_{12}, which describe the attractive forces of solute–solute and solute–solvent interactions, respectively, will be greater. The consequence is, via eqns. 8 and 9, that the effects described above increase in magnitude.

CONCLUSIONS

From the calculations and experimental evidence above, it has been demonstrated that the effect of the anomaly in the diffusion coefficient on column efficiency in SFC can be avoided by starting a pressure programme some way above the critical pressure to avoid the region of critical density. The pressure yielding maximum peak broadening will increase from the critical pressure as the temperature is increased from the critical temperature, but the phenomenon diminishes in magnitude with this rise.

Even at 35°C, which is 4°C from the critical temperature, peak broadening was observed to be significant, particularly at a high mole fraction of injected solute, over part of the pressure range employed in the experimental study. Normally this effect should not be important in analytical SFC because of the low concentrations used; the calculations in the previous section show that the diffusion coefficient itself is not much affected with concentrations below mole fractions of 10^{-4} for naphthalene. If the mole fraction is below 10^{-5} the effect is negligible for naphthalene, and probably also for heavier solutes. The concentration limit above which solvent motion affects diffusion has not been quantified. If it is close to or more than that for the diffusion coefficient itself, then the arguments given in the next paragraph are valid. If not, then the limits given should be revised downwards.

In capillary SFC the solute is typically injected in a volume of *ca.* 0.1 μl to give a peak volume at the detector of *ca.* 1 μl. An approximate calculation shows that an injection of 10 ng or less of solute would, therefore, not bring about significant peak broadening in the critical region. For packed-column SFC the corresponding volumes are roughly an order of magnitude larger, and the injection limit would be *ca.* 100 ng. For preparative-scale SFC milligram amounts or higher are used, so the effects would be very significant, in spite of larger peak volumes.

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