

Universal set-up for measurement of diffusion coefficients in supercritical carbon dioxide with flame ionization detection

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ABSTRACT

Improvements to the chromatographic apparatus for diffusivity measurements in supercritical carbon dioxide with flame ionization detection have been designed and evaluated. Modifications concerned the injection with partial solvent evaporation in the injector loop, separation of solutes and solvent in a short precolumn coated with a thin film of PS 264 stationary phase, and a back-pressure device. Diffusion coefficients of C₁₅–C₁₈ *n*-alkanes, dodecanone, pentadecanone, methyl myristate and biphenyl in supercritical carbon dioxide at 100°C and 125°C at 100 atm were determined. The method of optimization of D_g to a plot of H vs. v was evaluated for the estimation of diffusion coefficients. The estimated diffusion coefficients have been compared with the average diffusion coefficients and diffusion coefficients calculated from the Wilke–Chang equation. Relatively good agreement of measured diffusion coefficients and those calculated from the modified Wilke–Chang equation has been obtained for biphenyl and polar solutes.

INTRODUCTION

During the past decade, supercritical fluid chromatography (SFC) has been developed as a widely accepted analytical separation method, which complements gas chromatography and high-performance liquid chromatography. A large number of applications [1,2] have been described. However, interactions of the solute with the supercritical mobile phase and the stationary phase, swollen with the mobile phase, are not yet fully understood [3,4]. It is believed that diffusion in the mobile phase has a

decisive influence on band broadening in SFC [5]. Knowledge of the diffusion in supercritical fluids may be useful also in areas other than SFC, such as supercritical fluid extraction and in industrial supercritical processes, *e.g.*, polymer fractionation and/or impregnation. Regardless of the many publications devoted to diffusivity measurements in supercritical fluids [6–24], diffusion data in the literature are still scarce and, often, inaccurate. Further, mathematical models for the prediction of diffusion coefficients are known to be unreliable in the region around the critical point [25]. The present state of diffusion and thermodynamic measurements by SFC has recently been reviewed [26].

The Taylor dispersion technique, also known as the chromatographic band-broadening method, has been applied to diffusion measurements in supercritical fluids. Measurements are based on the

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dispersion of a narrow concentration pulse in a fully developed laminar flow of the supercritical mobile phase through a tube of circular cross-section. Although the mathematical treatment is relatively complete [27–30], the experimental measurements are subject to many errors. These errors originate from non-ideal behaviour of the system, such as (1) non-zero width of the pulse at the tube inlet, (2) extra-column band broadening, (3) solute–solvent interactions, if the injected solute is dissolved in a solvent, (4) solute adsorption on the inner walls of the diffusion tube, (5) density changes due to the pressure drop along the diffusion tube, (6) coiling-induced secondary flow within the tube, and (7) concentration dependence of the diffusion coefficient.

The first diffusivity measurements in supercritical carbon dioxide were done by Swaid and Schneider [6]. Since that time, much effort has been devoted to the development of instrumentation for the determination of binary diffusion coefficients in supercritical fluids. Dahmen *et al.* [22] applied a subtraction method, originally proposed by Giddings and Seager [31]. In this method, the effects of the initial variance of the solute and of dead volume on peak broadening are eliminated. A symmetrical initial band of the solute, eluted from a short precolumn, was recorded with a UV detector. The observed variance was subtracted from the variance measured when the solute had passed the diffusion tube. This method is limited to UV-detectable solutes and necessitates the use of two UV detectors with identical time constants and dead volumes. The influence of extra-column band broadening has, in many cases, been decreased by the use of diffusion tubes with large volumes, and/or by the application of an off-line subtraction method, in which two diffusion tubes of different lengths are used [6]. The latter method can, however, give inaccurate data, as the dead volumes of the connections must be absolutely identical in both cases [32].

Some authors studied the effect of the solvent used for solute injection into the diffusion tube on the measurements of diffusion coefficients [9,19,20]. However, no solvent effect on the solute diffusion coefficients in supercritical CO₂ was observed [9,19,20,22]. Olesik *et al.* [33] recommended injection of the pure compound in the supercritical fluid in order to obtain exact binary diffusion coefficients. When a

solvent is used, interdiffusion coefficients of a solute in an undefined mixture of supercritical fluid and solvent are being measured; dissolution of the sample in the mobile phase can be achieved in an extraction cell [33].

The effect of solute adsorption is reduced with increasing tube diameter and solute concentration [11]. However, its presence can be easily recognized by the appearance of asymmetric peak shapes; it is difficult to avoid adsorption in SFC when the aim is the measurement of solute diffusion coefficients at a broad density interval. Recently, a method for the determination of solute diffusion coefficients in gases from diffusivity measurements affected by solute adsorption has been described [34].

A pressure drop in the column results in a drop in both density and viscosity. The diffusion coefficient of the solute in a supercritical mobile phase, D_m , is affected by density and viscosity, so that the term $D_m \nu^{-1}$, where ν is the kinematic viscosity, is constant at high densities. As the changes of ν^{-1} at pressures above 100 atm are small [35], D_m should be changed only slightly. In SFC with open tubular columns, the pressure drop under typical conditions is quite small [35]. The pressure drop in wide-bore tubes used for diffusivity measurements does not exceed 1 atm and can be neglected.

Under certain conditions ($De^2 Sc > 100$, where De and Sc are the Dean and Schmidt numbers, respectively), the peak variance is affected by the column coiling, which causes secondary flow effects [36]. This can easily be avoided if mobile phase velocities are used that are lower than the maximum calculated for the column diameter and coiling radius.

Recently, a method for processing the data obtained from diffusivity measurements in gas chromatography has been published [34]. For the evaluation of the band broadening in a diffusion tube, possible contributions from solute adsorption on the column wall, extra-column band broadening and non-laminar flow effects have been included. Thus, the height equivalent to the theoretical plate (H) can be expressed as:

$$H = 2D_{g0}f_1/\nu_0 + r^2f_1\nu_0/(24D_{g0}) + G_a f_2 \nu_0 + D(f_2 \nu_0)^2 \quad (1)$$

where D_{g0} is the diffusion coefficient in the gas phase

at the outlet pressure, v_0 is the carrier gas velocity at the outlet of the tube, r is the tube radius and f_1 and f_2 are pressure drop factors. The first two terms describe ideal band broadening in a diffusion tube due to actions of the molecular diffusion and the parabolic velocity profile. The effects of a v_0 -dependent adsorption and non-laminar flow are expressed by the C_a term, and the diffusion-independent extra-column band broadening contributes to H as the D term. An optimization programme has been used by means of a least-squares fit of the measured values (H_i , v_{0i}) to eqn. 1. Making a number of assumptions, D_{g0} , C_a and D have been estimated [34]. For low pressure drops, *i.e.*, f_1 and f_2 approach unity, the outlet velocity can be replaced by the average mobile phase velocity, and the diffusion coefficient at outlet pressure can be replaced by the average binary diffusion coefficient, D_g . Eqn. 1 becomes:

$$H = 2D_g/v + r^2v/(24D_g) + C_a v + D(v)^2 \quad (2)$$

If v approaches zero, then the last two terms of eqn. 2 approach zero and the diffusion coefficient in mobile phase can be calculated from eqn. 3 as if no adsorption and/or extra-column effects occurred:

$$D_g = L/(4t_r)[H \pm \sqrt{H^2 - (r^2/3)}] \quad (3)$$

where L/t_r is the average mobile phase velocity in the column.

It seems that chromatographic measurements at low mobile phase velocities are preferable for the determination of diffusion coefficients, although the effects that decrease the accuracy of the determination of diffusion coefficients, as mentioned above, become in most cases negligible at such velocities.

Attention must, however, be paid to the diffusion-dependent extra-column band broadening, originating from the injector and couplings. Although this has been proven to be negligible in GC [32], the contribution in SFC can be significant owing to the much lower diffusion coefficients in the mobile phase.

Instrumentation for diffusivity measurements in supercritical fluids should, for a given inlet pressure, provide a means for convenient changes of the mobile phase velocity. As the flow of mobile phase in SFC is controlled by a restrictor, a back-pressure device, regulating the pressure drop over the restrictor, has been used to adjust the mobile phase velocity

[26]. Back-pressure devices compatible with post-restrictor detection usually consist of a system of linear restrictors [24]. Back-pressure can be applied either by compressed gas from a tube or by carbon dioxide from a second syringe pump. Other devices, such as a high-pressure sheath-flow nozzle [38] and a back-pressure regulator based on a low-dead-volume high-speed switching solenoid valve [39], have not been proven to be suitable for flame ionization detection (FID).

This paper describes improvements to the apparatus for diffusivity measurements in supercritical carbon dioxide with FID. Average mobile phase diffusion coefficients were calculated from chromatographic data obtained at low mobile phase velocities. The method of optimization of D_g to a plot of H vs. v was further evaluated for an estimation of diffusion coefficients in supercritical carbon dioxide.

EXPERIMENTAL

Instrumentation

A schematic diagram of the apparatus is shown in Fig. 1. A Suprex SFC/200A supercritical fluid chromatograph (Pittsburgh, PA, USA) was equipped with a pneumatically actuated Valco injection valve (Model CI4W, Valco Instruments, Houston, TX, USA) with a 0.06- μ l internal loop. The waste line of the injector was equipped with a piece of fused-silica capillary tubing (0.10 m \times 50 μ m I.D.) (Polymicro Technologies, Phoenix, AZ, USA). A short precol-

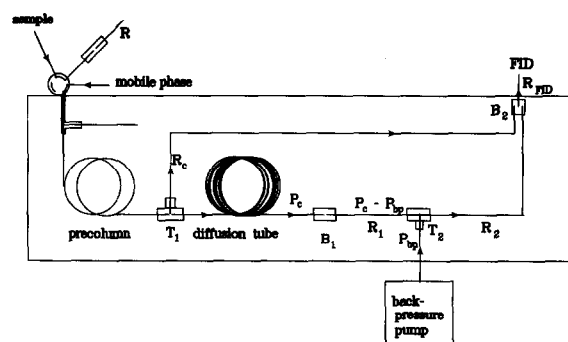


Fig. 1. Schematic diagram of the apparatus for the measurement of diffusion coefficients. R_c , R_1 , R_2 and R_{FID} are restrictors, T_1 and T_2 are T-pieces, B_1 is a low-dead-volume butt connector, and B_2 is an outlet splitter.

umn coated with methylpolysiloxane PS-264 (Fluka, Buchs, Switzerland) ($0.55 \text{ m} \times 259 \text{ }\mu\text{m}$ I.D., $d_f = 0.18 \text{ }\mu\text{m}$, or $1.50 \text{ m} \times 50 \text{ }\mu\text{m}$ I.D., $d_f = 0.24 \text{ }\mu\text{m}$) was connected at one end to the injection valve via a flow-splitter, the other end being connected to a linear restrictor R_c ($0.20 \text{ m} \times 11 \text{ }\mu\text{m}$ I.D.) and to the diffusion tube ($25.01 \text{ m} \times 259 \text{ }\mu\text{m}$ I.D.) with a coiling radius of 65 mm, via a low-dead-volume ZT.5 Valco T-piece (Valco Instruments). The mobile phase velocity was controlled by a variable-flow restrictor R_1 ($0.50 \text{ m} \times 21 \text{ }\mu\text{m}$ I.D.), which was connected to a feeding capillary from a back-pressure $\mu\text{LC-500}$ micropump (Isco, Lincoln, NE, USA) and restrictor R_2 ($0.50 \text{ m} \times 21 \text{ }\mu\text{m}$ I.D.) via another ZT.5 Valco T-piece. The variable-flow restrictor R_1 was coupled to the diffusion tube using a low-dead-volume butt connector MVSU 004 (SGE, Austin, TX, USA). The mobile phase flows issuing from restrictors R_c and R_2 were combined using a low-dead-volume VSOS outlet splitter (SGE) into a restrictor R_{FID} ($21 \text{ }\mu\text{m}$ I.D.) ending in the jet of the flame ionization detector. The chromatograph was connected to an ELDS 900 laboratory data system (Chromatography Data Systems, Kungshög, Stenhamra, Sweden).

Diffusivity measurements

A solution of one to three solutes in pentane, 10 mg/ml , was injected on the precolumn at 40°C by partial evaporation of the solvent in the internal loop of the injector. The loop was washed out with the sample and the syringe was withdrawn, thus allowing evaporation through the injector inlet. After a delay of 30–60 s, the injection was carried out using a 50–100 ms injection period and a split ratio of 1:4 to 1:6. The mobile phase velocity, 4–20 mm/s, was adjusted by the back-pressure of supercritical carbon dioxide. Each solute was injected three to five times under the same conditions, the time between two injections being chosen so that overlapping of the peaks from the precolumn and the diffusion tube was avoided. After alteration of the test parameters, an equilibration time of 30 min was sufficient to attain stable conditions. The diffusivity measurements were performed for C_{15} – C_{18} *n*-alkanes, dodecanone, pentadecanone, methyl myristate and biphenyl at 100 atm and at 100°C and 125°C .

Data handling

Chromatograms were registered at 3.03 Hz, and FID chromatograms were obtained first from the precolumn and then after the precolumn and the diffusion tube. Band broadening arising from the diffusion tube was estimated by computerized subtraction of the square of the peak width at half height from the precolumn from the square of the peak width at half height after the precolumn and diffusion tube. The HETP was then calculated from the estimated peak width at half height, and the binary diffusion coefficients corresponding to each mobile phase velocity were calculated by use of eqns. 2 and 3.

RESULTS AND DISCUSSION

Instrumentation

The requirement of generally applicable, accurate measurements of binary diffusion coefficients in supercritical carbon dioxide made some modifications of the chromatograph necessary. These modifications concerned the injection, the separation of solute(s) and solvent, and the back-pressure device.

The on-line subtraction procedure was modified by use of a small precolumn for the separation of solute and solvent. In general, this is not a problem [40,41], but for diffusivity measurements, band broadening in the precolumn must be very low,

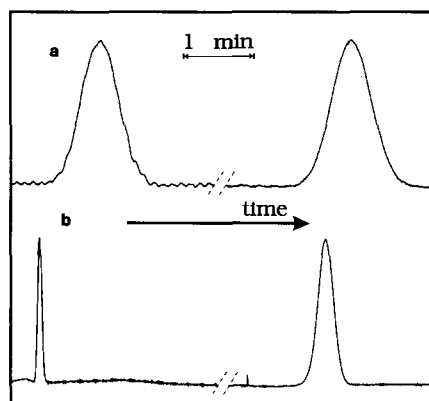


Fig. 2. SFC-FID chromatograms of pentadecane. On-line elution of the solute from (a) a precolumn ($4.50 \text{ m} \times 250 \text{ }\mu\text{m}$ I.D.) coated with PS 264 stationary phase, $d_f = 1.57 \text{ }\mu\text{m}$, and (b) a precolumn ($1.50 \text{ m} \times 50 \text{ }\mu\text{m}$ I.D.) coated with PS 264 stationary phase, $d_f = 0.24 \text{ }\mu\text{m}$, and a diffusion tube ($25.01 \text{ m} \times 259 \text{ }\mu\text{m}$ I.D.). Temperature, 100°C ; pressure, 100 atm.

otherwise the accuracy of the measurements will be decreased. Thus, the attempt to use a thick-film precolumn (4.50 m × 250 μm I.D., $d_f = 1.57 \mu\text{m}$) failed (Fig. 2a). Even when the length of the precolumn was only one fifth of that of the diffusion tube, it can be seen from the comparison of the peak widths from the precolumn and from the total bandwidth in Fig. 2a, that the precolumn contributed more to the total bandwidth than the diffusion tube. In addition to the diffusion in supercritical fluids, other factors (excluding extra-column effects) contributing to the band broadening in SFC seem to be more significant than is commonly considered. In Fig. 2b, a short 1.50 m × 50 μm I.D. column, coated with a thin film, 0.24 μm, was used as the precolumn.

Two precolumns were used. The first was coated with a thin film of PS-264, the I.D. being the same as the I.D. of the diffusion tube; the second had an I.D. of 50 μm. The contribution of this precolumn to the peak width was significantly lower than that of the first type of column. However, it was sensitive to overloading, and sometimes distorted peaks were generated. Further, the separation of solutes from the solvent was more difficult, owing to very high mobile phase velocities in the precolumn. These factors caused a higher standard deviation of the measured diffusion coefficients than when the first precolumn was applied.

Both precolumns had rather low retention power, and they could accept only small volumes of solvent. In this case, the total separation of early eluting solutes from the solvent under isobaric conditions is difficult. In order to facilitate the separation, partial evaporation of solvent and a preconcentration of the solutes in the internal loop of the injector have been applied. The injector was accordingly thermostatted at around the boiling temperature of the solvent. It was thus possible to inject similar amounts of solute and solvent (Table I). Consequently, their separation in the precolumn was readily achieved (Fig. 3). The degree of solvent evaporation and solute concentration in the sample was dependent on several factors, such as the time between the filling of the loop with the test solution and the moment of injection (Table I), the length of the restrictor in the waste line of the injector, and the type of solute and its concentration in the solvent. It is evident that this technique has low reproducibility from a quantitative point of view and most likely suffers from discrimination effects.

TABLE I

EFFECT OF SAMPLE EVAPORATION TIME IN THE INJECTOR LOOP ON THE SOLVENT EVAPORATION AND SOLUTE PRECONCENTRATION

Conditions: timed split 50 ms; separation on a 1.50 m × 50 μm I.D. column coated with PS 264, $d_f = 0.23 \mu\text{m}$, at 100°C, 100 atm; mobile phase velocity, 43 mm/s; sample, 10 mg/ml naphthalene in dichloromethane; injector loop thermostatted at 40°C.

Time (s)	Injected sample (%) ^a	Injected solute (%) ^a	c_s (%) ^b	Preconcentration factor
0	15 ± 5	17 ± 8	3 ± 2	1.1 ± 0
15	5 ± 1	67 ± 7	53 ± 2	4.7 ± 0.4
30	7 ± 2	100 ± 18	54 ± 3	6.7 ± 1.2
60	4 ± 1	53 ± 3	47 ± 1	3.5 ± 0.6

^a The amounts of injected sample and solute compared with those injected with the injector cooled to 15°C.

^b Solute concentration in the preconcentrated sample (w/w %).

A plain back-pressure device has been applied for the control of the mass flow-rate in the column (Fig. 1). A similar device has been proposed by Hirata and Nakata [42] and tested using UV detection. In the present work, a slightly modified set-up was used with post-restrictor FID. The mass flow-rate in the column is identical with a mass flow-rate in a variable-flow restrictor. With high pressure at the restrictor outlet, it can be assumed that mobile phase behaviour is more liquid-like than gas-like and that the mass flow-rate, F , in a linear type of restrictor R_1 , can be approximated by the Poiseuille equation for laminar flow:

$$F = [(\pi\rho d^4)/(128\eta L)](P_c - P_{bp}) \quad (4)$$

where ρ and η are the fluid density and viscosity, respectively, d and L are the restrictor diameter and length, respectively, and P_c and P_{bp} are the column inlet pressure and back-pressure, respectively. Accordingly, the mass flow-rate in the column is proportional to the pressure drop over the variable-flow restrictor. Fig. 4 shows the linear dependence of the mass flow-rate in the column on the pressure drop over the variable-flow restrictor for high pressures at the restrictor outlet (curve 1 in Fig. 4). For back-pressures lower than 150 atm (at an oven temperature of 100°C) deviations from the linearity of the dependence appear, because reciprocal kine-

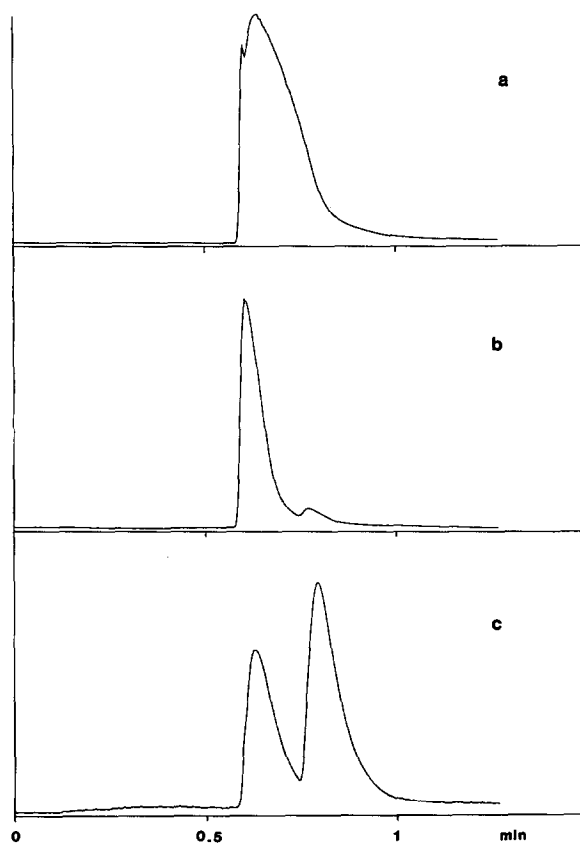


Fig. 3. Influence of injection temperature and sample evaporation time in the injector loop on the separation of dichloromethane (solvent) and naphthalene (solute) on a precolumn (1.50 m \times 50 μ m I.D.). (a) Injection at 15°C; (b) injection at 40°C, evaporation time 0 s; (c) injection at 40°C, evaporation time 30 s.

matic viscosity is markedly dependent on the pressure [35]. The stability of the whole system resulted in low standard deviations of solvent as well as solute hold-up times in the diffusion tube (Table II). Reproducible adjustment of the back-pressure was tested by the measurement of solvent (pentane) hold-up time in the diffusion tube. Good reproducibility was obtained, as shown in Table II. Adequate control of the mass flow-rate was obtained.

The present back-pressure device is much simpler than the one designed for use with FID by Janssen *et al.* [24]. The column flow is not split, and consequently, the detection limit is not decreased with increasing mobile phase velocity. Further, the back-pressure flow also functions as a make-up fluid and

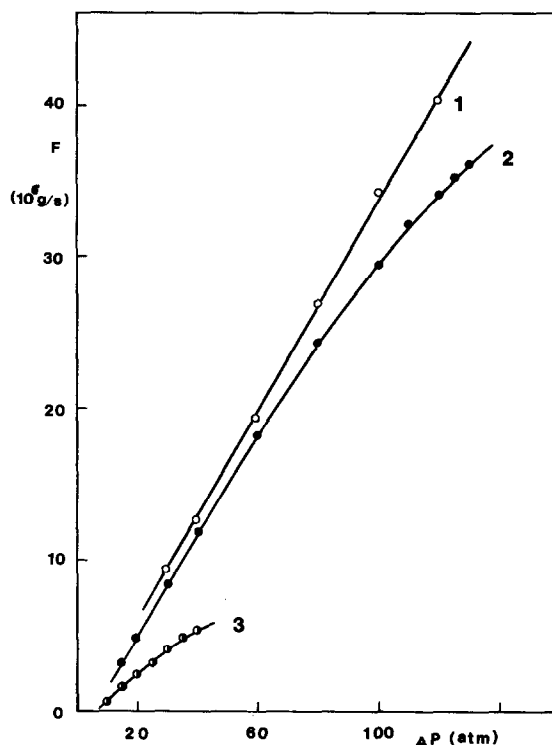


Fig. 4. Column mass flow-rate at different pressure drops, ΔP , over the variable-flow restrictor for different column-inlet pressures: (1) 300 atm; (2) 200 atm; (3) 100 atm.

decreases possible extra-column band broadening. It is easy to match the dimensions of restrictors to the desired range of column flow-rates. Easy control of the maximum column velocity was achieved by changing the restrictor R_{FID} .

Extra-column band broadening of the whole apparatus was either minimized and/or subtracted from the column band broadening. Subtraction was applied in order to exclude the influence of band broadening in the injector and the first T-piece. Band broadening in the second T-piece, in butt connector B_2 and in the detector was decreased by application of the back-pressure flow. In order to investigate possible band broadening in connector B_2 , measurements have been made without restrictor R_{FID} ; restrictors R_c and R_2 were thereby inserted into the jet of the detector. Such an arrangement resulted in an unstable baseline, but peak widths were unaffected. It can therefore be anticipated that the connector B_2 has no effect on the band broad-

TABLE II
SOLUTE AND SOLVENT HOLD-UP TIMES IN THE DIFFUSION TUBE AT DIFFERENT VELOCITIES

t_r = Solute hold-up time in diffusion tube, 25.01 m \times 259 μ m I.D.; t_m = pentane hold-up time considered as dead time at 125°C and 100 atm; k'_i = solute capacity factor at the given mobile phase velocity; \bar{k}' = average capacity factor. Solutes: C₁₅–C₁₈ = *n*-alkanes; C_{12on} = 2-dodecanone; C_{15on} = 2-pentadecanone; C_{14es} = methyl myristate.

Solute	$v = 14.6$ mm/s				$v = 12.4$ mm/s				$v = 10.4$ mm/s				$v = 8.3$ mm/s				\bar{k}'
	t_r (s)	S.D. (%)	t_m (s)	$10^2 k'_i$	t_r (s)	S.D. (%)	t_m (s)	$10^2 k'_i$	t_r (s)	S.D. (%)	t_m (s)	$10^2 k'_i$	t_r (s)	S.D. (%)	t_m (s)	$10^2 k'_i$	
C ₁₅	1730	0.06	1721	0.52	2016	0.06	2008	0.40	2416	0.15	2408	0.33	3008	0.12	2994	0.47	0.0043 \pm 0.0009
C ₁₆	1735	0.34	1721	0.81	2030	0.09	2019	0.54	2429	0.07	2418	0.46	3020	0.12	2999	0.70	0.0063 \pm 0.0018
C ₁₇	1718	0.06	1704	0.82	2032	0.09	2017	0.74	2398	0.08	2381	0.71	3031	0.08	3009	0.73	0.0075 \pm 0.0006
C ₁₈	1722	0.12	1704	1.06	2038	0.05	2017	1.04	2408	0.10	2381	1.13	3041	0.06	3009	1.06	0.0107 \pm 0.0004
C _{12on}	–	–	–	–	2027	0.09	2019	0.40	2431	0.04	2418	0.54	3011	0.03	2994	0.57	0.0050 \pm 0.0007
C _{15on}	1748	0.17	1721	1.57	2033	0.12	2008	1.25	2442	0.10	2408	1.41	3039	0.08	2994	1.50	0.0143 \pm 0.0016
C _{14es}	1742	0.12	1721	1.22	2037	0.09	2008	1.44	2447	0.03	2418	1.20	3031	0.03	2994	1.24	0.0127 \pm 0.0013
Biphenyl	1711	0.03	1704	0.41	2026	0.05	2017	0.45	2390	0.05	2381	0.38	3023	0.04	3009	0.46	0.0042 \pm 0.0004
S.D. ^a		0.44					0.35				0.75				0.27		

^a Standard deviation of solvent hold-up time resulting from reproducibility of back-pressure adjustment.

TABLE III
SOLUTE DIFFUSION COEFFICIENTS IN SUPERCRITICAL CARBON DIOXIDE AT 125°C AND 100 ATM

\bar{D}_m = Average measured solute diffusion coefficient, data from eqn. 3; $D_m(\text{opt})$ = solute diffusion coefficient calculated by optimization of eqn. 2; $D_m(\text{opt } C_a = 0)$ = solute diffusion coefficient calculated by optimization of eqn. 2 with the C_a term set to zero; D_mW and D_mW' = solute diffusion coefficient calculated from Wilke–Chang equation and modified Wilke–Chang equation, respectively.

Solute	\bar{D}_m (mm ² /s)	$D_m(\text{opt})$ (mm ² /s)	$D_m(\text{opt } C_a = 0)$ (mm ² /s)	k'	C_a (μs)	D_mW (mm ² /s)	D_mW' (mm ² /s)
C ₁₅ ^a	0.0404 (± 0.0034)	0.0406	0.0406	0.0043	–10	0.0290	0.0344
C ₁₆ ^b	0.0386 (± 0.0036)	0.0389	0.0389	0.0063	7	0.0285	0.0331
C ₁₇ ^a	0.0374 (± 0.0045)	0.0379	0.0379	0.0075	14	0.0275	0.0320
C ₁₈ ^c	0.0375 (± 0.0039)	0.0373	0.0372	0.0107	90	0.0266	0.0309
C _{12on} ^d	0.0420 (± 0.0026)	0.0427	0.0427	0.0050	–3	0.0337	0.0392
C _{15on} ^c	0.0346 (± 0.0026)	0.0355	0.0355	0.0143	45	0.0296	0.0344
C _{14es} ^e	0.0371 (± 0.0022)	0.0373	0.0373	0.0127	11	0.0290	0.0336
Biphenyl ^e	0.0499 (± 0.0014)	0.0502	0.0502	0.0042	–3	0.0427	0.0496

^a $n = 14$.

^b $n = 13$.

^c $n = 11$.

^d $n = 8$.

^e $n = 10$.

ening. Thus, the only section sensitive to extra-column band broadening is the low-dead-volume butt connector B₁, connecting the diffusion tube and the variable-flow restrictor.

Diffusivity measurements

Diffusion coefficients of each solute at 100 atm and 125°C, calculated from measured data according to eqn. 3, are summarized in Table III. An average diffusion coefficient was obtained for each solute as an average of all values estimated at low mobile phase velocities. Possible effects of solute adsorption on the walls of the diffusion tube, of insufficient solute solvation at low densities, of extra-column band broadening and of other possible effects described above have thus been neglected. Relatively good precision was obtained for biphenyl (2.8% relative standard deviation). The standard deviation of D_m for other solutes was much higher, increasing to almost 10%. This is quite high in

comparison with the precision obtained in some investigations [19,20,33], and could be due to the above-mentioned effects. However, the spread of values measured at individual velocities was not significantly lower. In several investigations of D_m in supercritical media, the diffusion tube has been immersed in a thermostatted bath [19,20,33], and it was thought that the less stringent temperature control, $\pm 1^\circ\text{C}$, applied in this work might make a contribution to the standard deviation. However, the diffusion coefficients are, at given conditions, not very dependent on small temperature differences (calculated from Wilke–Chang equation [43] for pentadecane $D_m(124^\circ\text{C}) = 0.0295 \text{ mm}^2/\text{s}$, $D_m(126^\circ\text{C}) = 0.0296 \text{ mm}^2/\text{s}$). A much stronger effect can be expected from adsorption and condensation of the solutes. Another source of errors may be asymmetric solute bands in the inlet of the diffusion tube. At low carbon dioxide densities, the precolumn was easily overloaded. Leading peaks were, however, not eval-

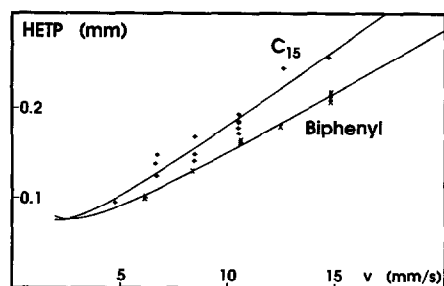


Fig. 5. Optimized HETP versus v plots for pentadecane and biphenyl at 125°C and 100 atm.

uated. Both effects probably contributed to the increased standard deviations of diffusion coefficient measurements for polar and higher-molecular-mass solutes.

Solute diffusion coefficients obtained by optimization of D_m or C_a and D_m to the best fit of H vs. v , according to eqn. 2 are presented in Table III. Either the coefficient of adsorption, C_a , was set to zero or the computer had to optimize both D_m and C_a , respectively (third and fourth column in Table III). As can be seen in Table III, the contribution of a C_a term to the total band broadening is negligible. Thus, the D_m values are not significantly affected by column adsorption for any of the solutes at 125°C. A close fit of the optimized HETP curve to the data points was observed for all solutes. An example is demonstrated in Fig. 5 where two optimized HETP curves, derived from n -pentadecane and biphenyl at 125°C, are shown.

Diffusion coefficients in liquids can be calculated according to the Wilke–Chang equation [43]:

$$D_{12} = (1.9 \cdot 10^{-18}) \frac{(\phi M)^{1/2} T}{\eta V_b^{0.6}} \quad (5)$$

where η is the viscosity of the liquid (in Pa s), V_b is the molecular volume of the solute at its boiling temperature at atmospheric pressure (in m^3/mol), M is the molecular mass of the liquid, and ϕ is the association factor of the liquid. When applying this equation for supercritical fluids, some uncertainty originating from prediction of the association factor, the viscosity of the fluid and the solute molar volume at its boiling temperature can be expected. Sassiati *et al.* [19] have modified the Wilke–Chang equation for estimation of diffusion coefficients in supercritical carbon dioxide, introducing molar volume at am-

bient temperature instead of V_b . As these molar volumes obey eqn. 6:

$$V_b = -5.31 + 130V \approx 1.3V \quad (6)$$

the modified Wilke–Chang equation gives higher values for solute diffusion coefficients than the original equation. Good agreement between measured diffusion coefficients and those calculated according to the modified Wilke–Chang equation has been found for aromatic compounds in high-density supercritical carbon dioxide [19]. Funazukuri *et al.* [20] have applied the modified equation for calculation of diffusion coefficients of linoleic acid methyl ester in supercritical CO_2 at different temperatures for a given pressure and for a given density. Good agreement with the measured values was obtained for the dependence at constant pressure, but at constant density the measured values gave steeper temperature dependence.

In Table III, diffusion coefficients calculated according to Wilke–Chang and according to the modified Wilke–Chang equation are given. As the modified equation was derived from the diffusion coefficients measured for aromatic compounds, very good agreement was obtained for biphenyl. Measured values for polar compounds are in most cases somewhat higher but, within experimental error, they fit to the values calculated from the modified equation. Relatively large differences have been found between the measured and the calculated values for alkanes, the measured values being higher. In Fig. 6, D_m values for the alkanes are plotted versus carbon number. The optimized values are signifi-

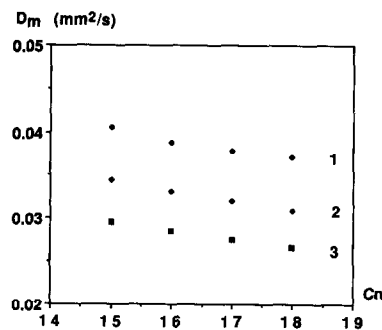


Fig. 6. Correlation of solute diffusion coefficients of n -alkanes with the carbon number at 125°C: (1) optimized diffusion coefficients; (2) calculated from modified Wilke–Chang equation; (3) calculated from Wilke–Chang equation.

TABLE IV

SOLUTE DIFFUSION COEFFICIENTS IN SUPERCRITICAL CARBON DIOXIDE AT 100°C AND 100 ATM

Symbols as in Table III; $n = 7-11$.

Solute	\bar{D}_m (mm ² /s)	$D_m(\text{opt})$ (mm ² /s)	$D_m(\text{opt } C_a = 0)$ (mm ² /s)	k'	C_a (μs)	$D_m W$ (mm ² /s)	$D_m W'$ (mm ² /s)
C ₁₅	0.0342 (± 0.0026)	0.0312	0.0333	0.006	375	0.0277	0.0322
C ₁₆	0.0329 (± 0.0041)	–	0.0351	0.008	–	0.0267	0.0310
C ₁₇	–	–	–	0.010	–	0.0257	0.0299
C ₁₈	0.0305 (± 0.0067)	–	0.0343	0.014	–	0.0249	0.0289
C _{12on}	0.0387 (± 0.0058)	0.0405	0.0403	0.007	100	0.0316	0.0367
C _{15on}	0.0296 (± 0.0034)	0.0297	0.0295	0.025	160	0.0277	0.0322
C _{14es}	0.0283 (± 0.0071)	0.0289	0.0288	0.021	120	0.0272	0.0316
Biphenyl	0.0373 (± 0.0044)	0.0412	0.0407	0.007	150	0.0400	0.0465

cantly higher than those obtained by the Wilke–Chang and the modified Wilke–Chang equations. However, the shapes of the curves are similar.

The same approach as for data obtained at 125°C was applied to data obtained at 100°C. However, the peak shapes were not of the same quality as at 125°C, *i.e.*, adsorption appeared to be greater.

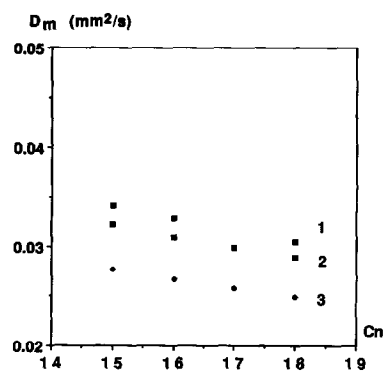


Fig. 7. Correlation of solute diffusion coefficients of *n*-alkanes with the carbon number at 100°C: (1) average diffusion coefficients; (2) calculated from modified Wilke–Chang equation; (3) calculated from Wilke–Chang equation.

Solute diffusion coefficients obtained at 100°C are listed in Table IV, and it can be seen that the C_a term has some influence on the optimized diffusion coefficients. Though only symmetrical peaks were evaluated, the number of measurements at different velocities was too small to be able to optimize D_m and C_a from eqn. 2 for all solutes. However, in Fig. 7, the calculated average diffusion coefficients from Table IV and the D_m values from Wilke–Chang and from the modified Wilke–Chang are plotted *versus* carbon number for the alkanes. A similar trend as at 125°C is observed at 100°C, but the calculated values are closer to the modified Wilke–Chang values at 100°C than at 125°C. No literature data can be found for diffusion coefficients of the alkanes measured at the same conditions as applied in the present work.

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