

Determination of binary diffusion coefficients of organic compounds in supercritical carbon dioxide by supercritical fluid chromatography

N. DAHMEN, A. KORDIKOWSKI and G. M. SCHNEIDER*

Physical Chemistry Laboratory, Department of Chemistry, University of Bochum, D-4630 Bochum (F.R.G.)

SUMMARY

Binary diffusion coefficients, D_{12} , in supercritical carbon dioxide were determined in a supercritical fluid chromatographic apparatus by the peak-broadening method. Organic compounds belonging to three different classes, namely ketones, fatty acids and liquid crystals and additionally squalene were investigated as a function of pressure between 9.5 and 18 MPa at about 314 K. The resulting D_{12} values are of the order of $10^{-8} \text{ m}^2 \text{ s}^{-1}$ and $\ln D_{12}$ decreases approximately linearly with increasing density of the carbon dioxide.

INTRODUCTION

The determination of gaseous diffusion coefficients by the gas chromatographic peak-broadening method (PBM) was introduced by Giddings' in 1960. His results and those of other workers were summarized in a review by Marrero and Mason'. Later the method was extended to gas-liquid³, liquid^{4,5} and supercritical fluid systems^{6,7}. A critical review of the literature was given by Maynard and Grushka⁸.

The theory of diffusion in flowing fluids was first studied by Taylor⁹⁻¹¹ and Aris¹², who solved the problem in a more general form. According to Aris, a sharp band of solute, which is allowed to dissolve in a solvent flowing laminarily in an empty tube, can be described in the limit of a long column as a Gaussian distribution, the variance of which, σ^2 , in length units is

$$\sigma(x)^2 = 2D_{\text{eff}}t \quad (1)$$

where t is the time of migration of the peak. D_{eff} is an effective diffusion coefficient, given by

$$D_{\text{eff}} = D_{12} + \frac{r^2 u^2}{48D_{12}} \quad (2)$$

where u is the average solvent velocity, r the inner radius of the tube and D_{12} is the binary diffusion coefficient. The first term describes the longitudinal diffusion in the axial direction. The second term is called the Taylor diffusion coefficient and describes band broadening due to the parabolic flow profile and therefore radial diffusion. The height equivalent to a theoretical plate, H , is a measure of the relative peak broadening and is defined as

$$H = \frac{\sigma(x)^2}{L} \quad (3)$$

where L is the length of the tubing. Substituting eqns. 1 and 2 in eqn. 3 yields

$$H = \frac{2D_{12}}{u} + \frac{r^2 u}{24D_{12}} \quad (4)$$

Eqn. 4 can be rearranged to

$$D_{12} = \frac{u}{4} \left(H \pm \sqrt{H^2 - r^2/3} \right) \quad (5)$$

Of the two possible values of D_{12} only one is meaningful; in this work the negative sign is used.

EXPERIMENTAL

The measurements were carried out with a supercritical fluid chromatographic (SFC) apparatus first designed by Van Wasen *et al.*⁷ Since then, several improvements have been made.

Fig. 1 shows the apparatus used in this work. First the carbon dioxide was

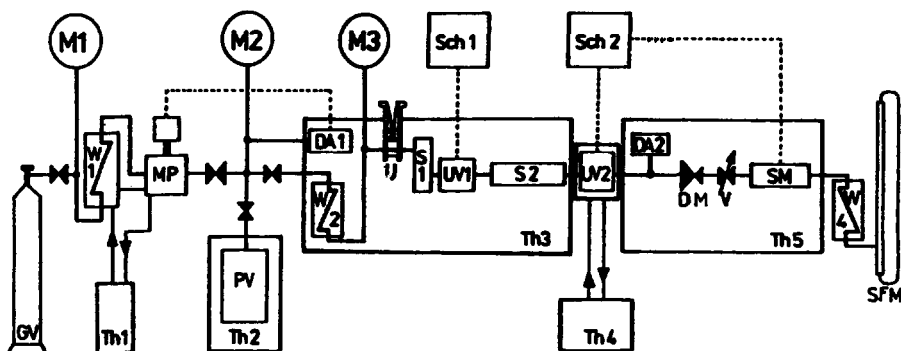


Fig. 1. SFC apparatus for the determination of binary diffusion coefficients. GV = Gas cylinder; W = heat exchanger; MP = diaphragm pump; Th₁ = cryostat; Th₂₋₅ = air- and water-baths; PV = buffer volume; M = pressure gauge; DA = strain gauge; IJ = injector; S = column; UV = UV detector; Sch = chart recorder; DM = pressure-reducing valve; V = needle valve; SM = thermal conductivity flow meter; SFM = soap-bubble flow meter.

liquefied and then compressed to the pressure of the experiment by a diaphragm pump (Orlita DMP-AE-10.4) the pulsations of which were eliminated by a volume of buffer. The sample was injected through a high-performance liquid chromatographic valve with a sample volume of cu. 0.5 μl . To eliminate the effects of the initial variance of the solute and of the dead volume on peak broadening, the subtraction method of Giddings as adapted by Wasik and McCulloh¹³ was used. A short pre-column, 1.26 m long, allowed the development of a symmetrical initial band, which was recorded with a UV detector. Behind the main diffusion column (46.23 m x 0.41 mm I.D.) the end variance was measured by means of a second UV detector. For the usual flow velocity of 0.5 cm s^{-1} a typical experimental run lasted about 2.5 h. The time between two injections was chosen in such a way that overlapping of the peaks was prevented. Finally the fluid was expanded and the flow velocity could be measured by means of a soap-bubble flow meter. The measurements were performed in the range 9-18 MPa at 313.5 and 314.5 K. This corresponds to densities of $0.53 \cdot 10^3$ – 0.8210^3 kg m^{-3} . The initial and the end bands were registered on a chart recorder.

To evaluate D_{12} values from eqn. 4, values of H had to be determined. They were available from the measured chromatograms obtained manually with eqn. 3 and

$$\sigma(x)^2 = \sigma_2(x)^2 - \sigma_1(x)^2 \quad (6)$$

where $\sigma_2(x)^2$ and $\sigma_1(x)^2$ are the variances in length units recorded with the second and first UV detector, respectively. For easier evaluation, the base width w was used instead of the variance:

$$w(x)^2 = 16\sigma(x)^2 \quad (7)$$

After transforming $\sigma(x)^2$ into $\sigma(t)^2$ by $a(x)^* = u^2\sigma(t)^2$, where u is the average flow velocity, the following expression for H was obtained:

$$H = \frac{[w_2(t)^2 - w_1(t)^2]u}{16t_r} \quad (8)$$

t_r being determined from the time difference of the two peaks as shown in Fig. 2.

The main sources of error were the initial peak dispersion, adsorption effects, in particular for low-volatile substances, and the manual determination of the chromatograms. The overall accuracy of the D_{12} values obtained was better than $\pm 6\%$.

Substances

The substances tested belonged to three different chemical classes. In the first group some homologous and branched ketones were measured. In particular these were the symmetric ketones 2-propanone, 3-pentanone, 4-heptanone, 5-nonanone and 6-undecanone, the 2-substituted ketones 2-butanone, 2-pentanone, 2-heptanone and 2-nonanone and the branched isomers 2,4-dimethyl-3-pentanone (DMP), 2,2,4,4-tetramethyl-3-pentanone (TMP) and tricyclo[3.3.1.1^{3,7}]decanone (adamantanone). The second group consisted of the fatty acids oleic acid, stearic acid and linolenic acid, all with 18 carbon atoms but a different number of double bonds. Finally, the two

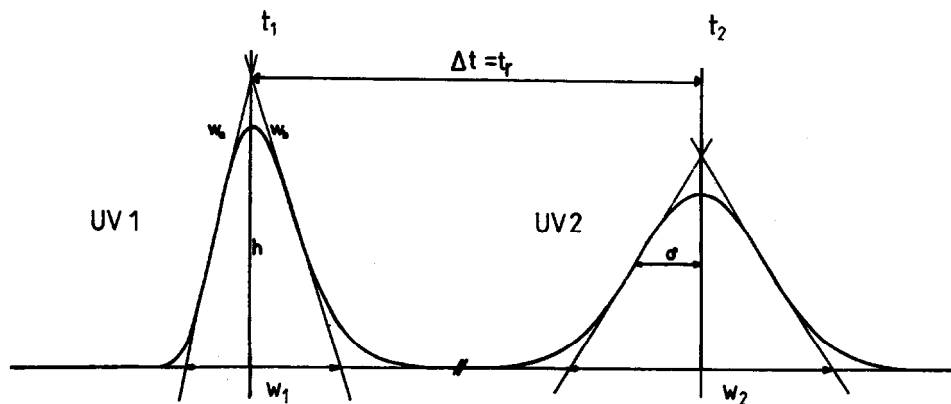


Fig. 2. Determination of D_{12} values from the chromatograms. σ = Variance; W = base width; w_a, w_b = inflection point tangents; h = peak height; t = migration time; $t_r = t_2 - t_1$.

liquid crystals N-(4-methoxybenzylidene)-4-n-butylaniline (MBBA) and 4-cyano-4'-n-pentoxybiphenyl (5-OCB), both having similar molar masses, and additionally 2,6,10,15,19,23-hexamethyl-2,6,10,14,18,22-tetracosahexaene (squalene) were measured.

Most of the substances were from Aldrich (Steinheim, F.R.G.) with purities 98% or better; DMP was from Fluka (Buchs, Switzerland) with a purity better than 98%. MBBA was obtained from Merck (Darmstadt, F.R.G.) and 5-OCB from BDH (Poole, U.K.) with purities of about 98% and better than 99%, respectively.

The mobile phase carbon dioxide was obtained from Linde (Höllriegelskreuth, F.R.G.) with a purity of better than 99.9%.

All low-volatile substances were dissolved before injection. The fatty acids were dissolved in ethanol and the liquid crystals and squalene in heptane and cyclohexane. The solvent had no influence on the value of D_{12} .

RESULTS AND DISCUSSION

In previous papers^{14,15}, results of measurements mostly on aromatic compounds in different mobile phases were reported. In this paper, new data on some ketones, fatty acids and liquid crystals and additionally squalene in supercritical carbon dioxide are presented. The results are compiled in Tables I, II and III.

In Figs. 3 and 4 the density dependence of the D_{12} values of the symmetric and non-symmetric ketones is shown. The same exponential behaviour is found for all the substances. For comparison, self-diffusion coefficients D_{11} of carbon dioxide^{16,17} are also given. They show a density dependence, which is similar to that of the binary diffusion coefficients. As expected the D_{11} values are higher mainly because of the lower molar mass of carbon dioxide. In Fig. 5 reduced diffusion coefficients, $D_k^{\text{red}} = D_k/D(3\text{-pentanone})$, are plotted against the molar mass of all ketones, k , under test. D_k^{red} are values obtained by dividing all D_{12} values of a substance by the corresponding D_{12} of 3-pentanone measured at the same density and subsequently taking the average. The resulting dependence for the homologous ketones is approximately linear. The

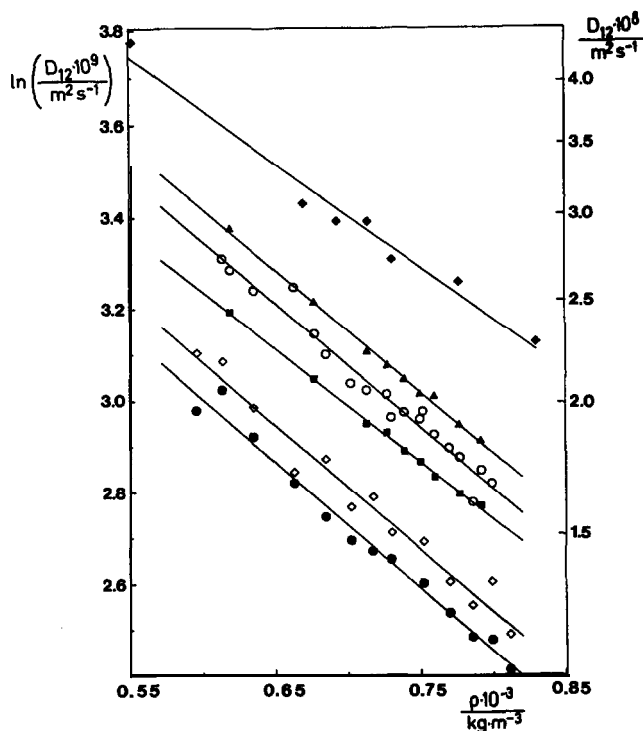


Fig. 3. Logarithm of binary diffusion coefficients, $\ln D_{12}$, of symmetric ketones as a function of density ρ at 314 K. A = 2-Propanone; O = 3-pentanone; ■ = 4-heptanone; □ = 5-nonanone; ● = 6-undecanone. ◆ = Self-diffusion coefficients, D_{11} , of carbon dioxide according to refs. 16 and 17. Densities of carbon dioxide are taken from ref. 18.

TABLE I

DIFFUSION COEFFICIENTS, D_{12} , OF SOME KETONES IN SUPERCRITICAL CARBON DIOXIDE AT 313.5 K AND DENSITIES, ρ

313.5 K		D_{12} ($\text{JO} \cdot \text{m}^2 \text{s}^{-1}$)					
p (MPa)	$\rho \cdot 10^{-3}$ (kg m^{-3})	2-Propanone	3-Pentanone	4-Heptanone	Adamantanone	DMP ^a	TMP ^b
16	0.792	1.84	1.72	1.59	~	1.58	1.43
15	0.777	1.90	1.77	1.64	1.44	1.60	1.44
14	0.760	2.03	1.86	1.70	1.50	1.70	1.54
13.5	0.750	2.04	1.93	1.76	1.59	1.73	1.58
13	0.739	2.10	1.96	1.79	1.59	1.71	1.63
12.5	0.727	2.17	2.07	1.87	1.64	1.83	1.67
12	0.713	2.23	2.05	1.91	1.68	1.89	1.78
11	0.677	2.49	2.32	2.11	1.77	2.10	1.91
10	0.619	2.92	2.68	2.43	1.41	2.45	2.22

^a 2,4-Dimethyl-3-pentanone.

^b 2,2,4,4-Tetramethyl-3-pentanone.

TABLE II
 DIFFUSION COEFFICIENTS, D_{12} , OF SOME KETONES IN SUPERCRITICAL CARBON DIOXIDE AT 314.5 K AND DENSITIES, ρ

314.5 K		$D_{12} (10^{-8} \text{ m}^2 \text{ s}^{-1})$						
p (MPa)	$\rho \cdot 10^{-3} (\text{kg m}^{-3})$	2-Butanone	2-Pentanone	2-Heptanone	2-Nonanone	3-Pentanone	5-Nonanone	6-Undecanone
18	0.812	1.75	1.53	1.40	1.31	—	1.20	1.12
17	0.799	1.70	1.69	1.42	1.29	1.68	1.35	1.19
16	0.786	1.79	1.69	1.46	1.19	1.61	1.29	1.20
15	0.770	1.86	1.84	1.49	1.42	1.81	1.35	1.27
14	0.752	1.90	1.81	1.60	1.44	1.97	1.44	1.35
13	0.730	2.13	1.93	1.72	1.48	1.93	1.51	1.38
12.5	0.717	2.18	1.97	1.71	1.64	—	1.63	1.45
12	0.702	2.20	2.12	1.81	1.76	2.09	1.59	1.48
11.5	0.685	2.49	2.24	2.01	1.74	2.22	1.77	1.56
11	0.663	2.55	2.25	2.11	1.92	2.58	1.86	1.68
10.5	0.635	2.59	2.58	2.27	2.00	2.55	1.99	1.96
10.2	0.614	2.94	3.28	—	2.15	2.74	2.19	2.06
10	0.586	2.86	2.79	2.71	2.16	3.17	2.23	1.97
9.7	0.562	3.42	3.28	2.70	—	—	—	—
9.5	0.531	3.46	3.30	2.92	—	—	—	—

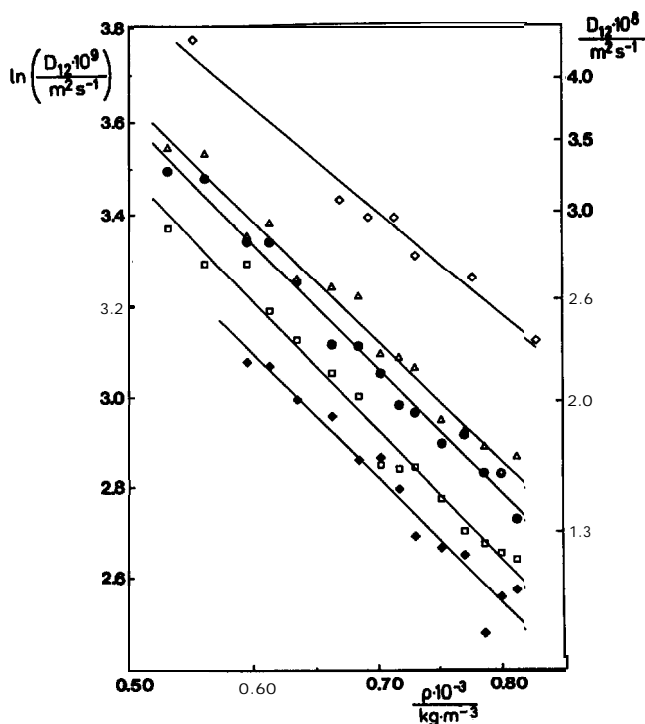


Fig. 4. $\ln D_{12}$ of non-symmetric ketones as a function of density ρ at 314 K. Δ = 2-Butanone; \bullet \square 2-pentanone; \square = 2-heptanone; \blacklozenge = 2-nonanone. \circ = D_{11} values of carbon dioxide.

D_{12} values of the branched C_7 ketone lay in the range of the linear isomers (Fig. 6), whereas for the tetramethylated C_9 isomer there is a trend to higher values (Fig. 7). Tricyclodecanone also shows higher values, as expected because of its nearly spherical shape.

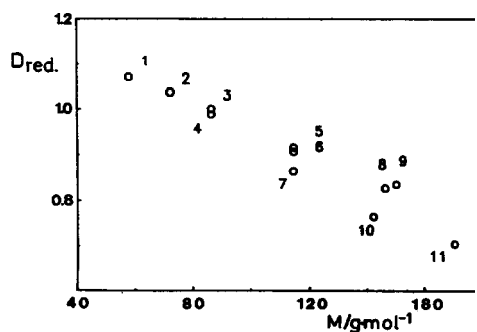


Fig. 5. Reduced diffusion coefficients, $D_k^{red} = D_k/D(3\text{-pentanone})$, as a function of molar mass, M_k . 1 = 2-Propanone; 2 = 2-butanone; 3 = 3-pentanone; 4 = 2-pentanone; 5 = 4-heptanone; 6 = 2,4-dimethyl-3-pentanone; 7 = 2-heptanone; 8 = 2,2,4,4-tetramethyl-3-pentanone; 9 = adamantanone; 10 = 2- and 5-nonanone; 11 = undecanone.

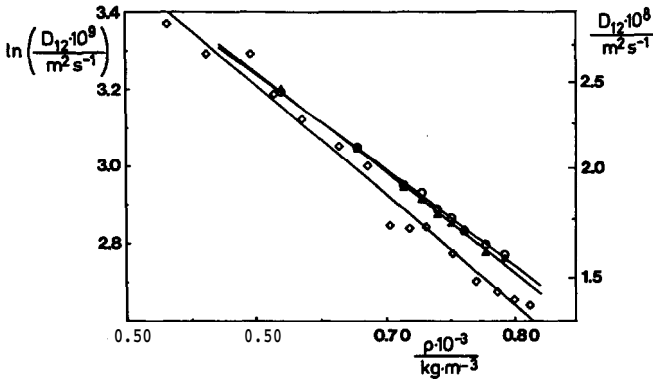


Fig. 6. Density dependence of $\ln D_{12}$ of the C_7 isomeric ketones at 314 K. \circ = 4-Heptanone; Δ = 2,4-dimethyl-3-pentanone; \diamond = 2-heptanone.

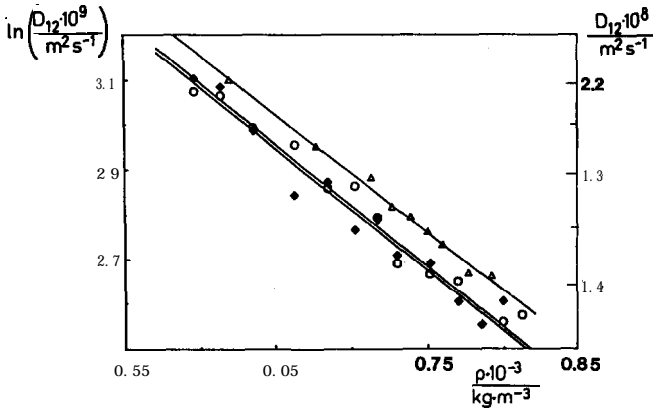


Fig. 7. Density dependence of $\ln D_{12}$ of the C_9 isomeric ketones at 314 K. Δ = 2,2,4,4-Tetramethyl-3-pentanone; \circ = 2-nonanone; \bullet = 5-nonanone.

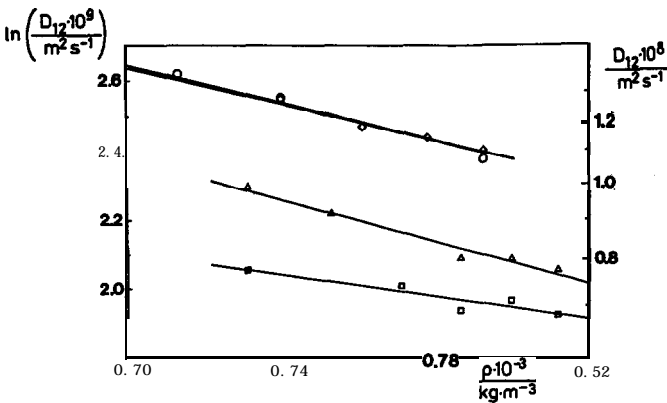


Fig. 8. Comparison of the density dependence of $\ln D_{12}$ of some fatty acids and squalene at 314 K. \circ = Stearic acid; \triangle = oleic acid; \blacklozenge = linolenic acid; \square = squalene.

TABLE III

DIFFUSION COEFFICIENTS, D_{12} , OF SOME LOW-VOLATILE SUBSTANCES IN SUPER-CRITICAL CARBON DIOXIDE AT 313.5 AND 314.5 K AND DENSITIES, ρ

313.5 K		$D_{12} (10^{-8} \text{ m}^2 \text{ s}^{-1})$		
$p \text{ (MPa)}$	$\rho \cdot 10^{-3} \text{ (kg m}^{-3}\text{)}$	MBBA ^a	Stearic acid	Oleic acid
16	0.792	1.00	1.10	1.08
15	0.777	1.04	1.15	—
14	0.760	1.10	1.19	1.19
13.5	0.657	—	—	1.29
13	0.739	1.15	1.28	1.37
12	0.713	1.23	—	1.54

314.5 K		5-OCB ^b Linolenic acid Squalene		
18	0.812	0.86	0.78	0.68
17	0.799	0.89	0.81	0.71
16	0.785	0.89	0.81	0.66
15	0.770	0.93	—	0.71
14	0.752	0.96	0.92	—
13	0.703	1.06	1.00	0.78

^a MBBA = N-(4-Methoxybenzylidene)-4-n-butylaniline.^b 5-OCB = 4-Cyano-4'-n-pentoxybiphenyl.

Owing to the strong solvent power of the highly compressed carbon dioxide, it was possible to measure some low-volatile substances such as the fatty acids. Three C_{18} acids were examined which differ only in the number of double bonds. For stearic acid and oleic acid with one double bond no difference exists, as can be seen in Fig. 8. Only linolenic acid with its three double bonds shows distinctly lower D_{12} values. It is evident that these double bonds make the molecule rigid, its effective cross-section increases and the diffusion process will be slower.

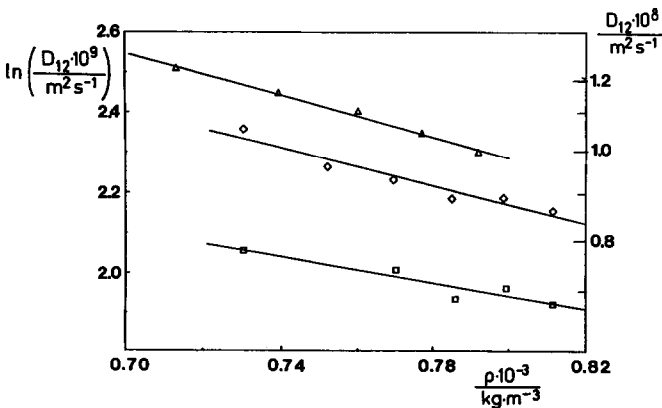


Fig. 9. Comparison of the density dependence of $\ln D_{12}$ of the liquid crystals Δ = MBBA and \circ = 5-OCB and also \square = squalene at 314 K.

For the liquid crystals MBBA and 5-OCB a similar effect can be seen. Although both have similar molar masses, their diffusion coefficients differ. The bridged phenyl rings should allow more mobility whereas the biphenyl is rigid. This results in lower diffusion coefficients for 5-OCB (Fig. 9). For squalene small D_{12} values are found as expected because of its high molar mass.

ACKNOWLEDGEMENT

Financial support of the Fonds der Chemischen Industrie is gratefully acknowledged.

REFERENCES

- 1 J. C. Giddings, *J. Phys. Chem.*, 33 (1960) 1579.
- 2 T. R. Marrero and E. A. Mason, *J. Phys. Chem. Ref. Data*, 1 (1972) 3.
- 3 G. L. Hargrove and H. J. Sawyer, *Anal. Chem.*, 39 (1967) 244.
- 4 E. Grushka and E. J. Kitka, *J. Phys. Chem.*, 78 (1974) 2297.
- 5 E. Grushka and E. J. Kitka, *J. Am. Chem. Soc.*, 98 (1970) 643.
- 6 Z. Balenović, N. M. Myers and J. C. Giddings, *J. Chem. Phys.*, 52 (1970) 915.
- 7 U. van Wasen, I. Swaid and G. M. Schneider, *Angew. Chem.*, 92 (1980) 585.
- 8 V. R. Maynard and E. Grushka, *Adv. Chromatogr.*, 12 (1975) 99.
- 9 G. Taylor, *Proc. R. Soc. London, Ser. A*, 219 (1953) 186.
- 10 G. Taylor, *Proc. R. Soc. London, Ser. A*, 223 (1954) 446.
- 11 G. Taylor, *Proc. R. Soc. London, Ser. A*, 225 (1954) 473.
- 12 R. Aris, *Proc. R. Soc. London, Ser. A*, 235 (1956) 67.
- 13 S. P. Wasik and K. E. McCulloh, *J. Res. Natl. Bur. Stand., Sect. A*, 73 (1969) 207.
- 14 R. Feist and G. M. Schneider, *Sep. Sci. Technol.*, 17 (1982) 261.
- 15 A. Kopner, A. Hamm, J. Ellert, R. Feist and G. M. Schneider, *Chem. Eng. Sci.*, 42 (1987) 2213.
- 16 H. A. O'Hern, Jr. and J. J. Martin, *Znd. Eng. Chem.*, 47 (1955) 2081.
- 17 S. Takahashi, H. Iwasaki, *Bull. Chem. Soc. Jpn.*, 39 (1966) 2105.
- 18 ZVPAC *International Thermodynamic Tables of the Fluid State: Carbon Dioxide*, Pergamon Press, Oxford, 1976.