Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Determination of Binary Diffusion Coefficients of Benzene, Phenol, Naphthalene and Caffeine in Supercritical CO_2 between 308 and 933 K in the Pressure Range 90 to 160 gar with Supercritical Fluid Chromatography (SFC)

Reinhard Feist[a]; Gerhard M. Schneider[a]
[a] Institute of Physical Chemistry University of Bochum, Bochum, Federal Republic of Germany

To cite this Article Feist, Reinhard and Schneider, Gerhard M.(1982) 'Determination of Binary Diffusion Coefficients of Benzene, Phenol, Naphthalene and Caffeine in Supercritical CO_2 between 308 and 933 K in the Pressure Range 90 to 160 gar with Supercritical Fluid Chromatography (SFC)', Separation Science and Technology, 17: 1, 261 — 270
To link to this Article: DOI: 10.1080/01496398208058150
URL: http://dx.doi.org/10.1080/01496398208058150

SEPARATION SCIENCE AND TECHNOLOGY, 17(1), pp. 261-270, 1982

Determination of Binary Diffusion Coefficients of Benzene, Phenol, Naphthalene and Caffeine in Supercritical CO_2 between 308 and 333 K in the Pressure Range 80 to 160 Bar with Supercritical Fluid Chromatography (SFC)

REINHARD FEIST and GERHARD M. SCHNEIDER
INSTITUTE OF PHYSICAL CHEMISTRY
UNIVERSITY OF BOCHUM
4630 BOCHUM, FEDERAL REPUBLIC OF GERMANY

ABSTRACT

Binary diffusion coefficients D_{12} have been determined for benzene, phenol, naphthalene and caffeine in supercritical CO_2 at 40°C between 80 and 160 bar using the chromatographic peak-broadening method (CPB). The observed diffusion coefficients are of the order of 10^{-4} cm^2/s and decrease by about 50% for a pressure rise from 80 to 160 bar. For naphthalene in CO_2 the effect of temperature on D_{12} was investigated between 35 and 60°C at a constant CO_2 density of 0.6 g/cm^3; the energy of activation was found to be 4.7 kJ/mol. With increasing molecular size and polarity of the diffusing compound, adsorption effects are observed which can lead to serious errors.

INTRODUCTION

In Supercritical Fluid Chromatography (SFC) highly compressed fluid phases mostly at temperatures somewhat above their critical temperatures are used as mobile phases. Since the early sixties SFC has found interesting and important applications, especially in the separation of low volatile and thermolabile compounds (for a review and references see (1)).

However, diffusion data of medium molecular weight compounds in compressed gases are still rather scarce though they play an important role concerning mass transport phenomena in chromatographic columns as well as in technical plants for the extraction of natural products with supercritical phases (fluid extraction). In the present paper we shall present and discuss some recent results (2) on the effect of pressure and temperature on binary diffusion coefficients in supercritical CO_2 which we have obtained using the chromatographic peak-broadening method (CPB). This technique which is based on the fundamental work of Taylor (3) and Aris (4) was independently developed by Giddings and Seager (5), Bohemen and Purnell (6) and other workers in 1960 and was first used to determine diffusion coefficients in gaseous mixtures. Later the CPB technique was extended to dense gases (7,8) and, more recently, to liquid systems (9,10).

The theoretical foundations of the method will only be shortly discussed because detailed reviews have already been published (11,12).

THEORY

As shown by Taylor (3) the dispersion of a pulse of a solute in a fully developed laminar flow is the result of the combined action of convection along the axis of the column and molecular diffusion in the radial direction. The solution of the basic mass balance equation obtained under certain assumptions and boundary conditions (4,7) leads to an expression which represents the profile of the average concentration $\bar{c}$ as a function of the axial distance x and time t. Levenspiel and Smith (13) showed that this concentration profile becomes Gaussian when

$$\frac{D_{eff}}{\bar{u}l} < 0.01 . \qquad (1)$$

The variance in length units is then a function of the socalled effective diffusion coefficient and the time of flow t_R:

$$\sigma^2(x) = 2\, D_{eff} \cdot t_R \tag{2}$$

where

$$D_{eff} = D_{12} + \frac{r_o^2\, \bar{u}^2}{48\, D_{12}} \quad . \tag{3}$$

D_{12} is the binary diffusion coefficient, $\bar{u}$ the average velocity of the mobile phase, r_o the inner radius of the tube and l its length. Using the definition of plate height in chromatography

$$H = \frac{\sigma^2(x)}{l} \; , \tag{4}$$

one obtains the plate height equation for an empty straight column with circular cross-section

$$H = \frac{2\, D_{12}}{\bar{u}} + \frac{r_o^2\, \bar{u}}{24\, D_{12}} \tag{5}$$

which is identical to the results obtained from the van Deemter, Golay or Giddings equations in the case of $\gamma = 1$ (no packing) and $k' = 0$ (no sorbent phase) (14). The velocity which minimizes H is called the optimum velocity and given by

$$\bar{u}_{opt} = \sqrt{48}\, \frac{D_{12}}{r_o} \quad . \tag{6}$$

Rearrangement of Eq. (5) yields:

$$D_{12} = \frac{\bar{u}}{4} \left[H \pm (H^2 - \frac{r_o^2}{3})^{1/2} \right] \; . \tag{7}$$

According to Giddings and Seager (15) the negative root of Eq. (7) is physically meaningful at velocities higher than $\bar{u}_{opt}$ which is usually the case in liquid and dense gas systems where $\bar{u}_{opt}$ is very small. The plate height H can be easily obtained from experiment using the expression (see, e.g., (16))

$$H = \frac{1 \cdot w_{1/2}^2}{5.545 \cdot t_R^2} \qquad (8)$$

where $w_{1/2}$ is the peak width at half height in time units directly taken from the recorder plot and t_R the retention time. D_{12} is then obtained from Eq. (7) using the negative root.

EXPERIMENTAL

Apparatus

The apparatus was a self-designed fluid chromatograph identical to that used by Swaid (8). Modifications were only made concerning the injection system (see below). The mobile phase was CO_2 ($T_c = 31.1^{\circ}C$) which was compressed by an electrically driven double plunger pump. A sensitive electronic regulator kept the pressure constant within ±0.01 bar. The conditioning system, the injection system and the column were mounted in an air thermostat, the temperature being constant within ±0.02 K. In order to avoid additional solvents in the case of solid test compounds (e.g., naphthalene) the sample was first dissolved in compressed CO_2 in a separate autoclave and then samples of this solution were introduced into the flow by means of a commercial 6-port valve combined with a sample loop. Detection was carried out using a high pressure UV detector whose optical cell was held at column temperature. Leaving the detector the mobile phase was expanded by a two-stage reducing valve providing a constant flow rate (±1%) which was measured with a soap bubble flow meter. For pVT calculations an equation of state given by IUPAC was used (17).

To eliminate the initial variance of the solute pulse and the additional peak broadening caused by dead volumes, the two column method (15) was applied. The lengths of the columns were 9666 and 175.5 cm respectively both having an internal radius of 0.0246 cm. We made about six subsequent injections during one run at a flow rate of about 1 cm/s where according to previous investigations (8) the influence of secondary flow is negligible. The variances of such a series of peaks agreed within 3% ; the overall precision of the presented D_{12} values is estimated to be about 6%.

Sources of Errors

As this subject has already been treated extensively by other authors (7,10,11,16) only the most important effects shall be mentioned here:

a) initial peak dispersion
b) dead volume
c) secondary flow
d) pressure drop
e) adsorption

The effects a) and b) which lead to D_{12} values being too low were eliminated by use of the two column subtraction technique. As shown by Swaid (8) secondary flow caused by column coiling can be neglected if the linear flow velocity is sufficiently small. In this case also the pressure drop ($\leq$ 0.4 bar) is negligible. However, effect e) may lead to serious errors in the case of rising molecular size and polarity of the diffusing compound especially in the low density region where the solvent power of the mobile phase is appreciably reduced. Fig. 1 shows the separation of caffeine from unretarded benzene as a consequence of adsorption on the inner column walls. The shape of the caffeine peak indicates a curved adsorption isotherm which makes an evaluation of diffusion data impossible. By raising the pressure of the mobile phase this effect could be eliminated nearly

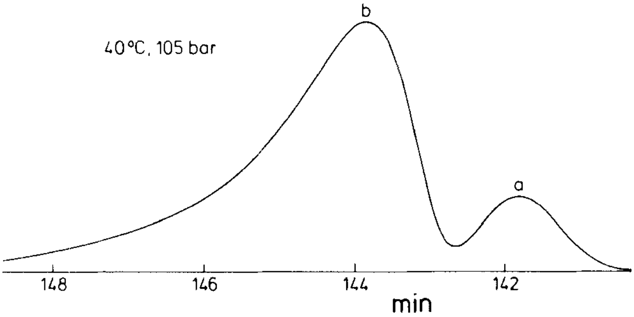

FIGURE 1. Effect of wall adsorption. Separation of caffeine (b) from unretarded benzene (a). Unpacked steel capillary column, l = 9666 cm; velocity of mobile phase, 1.135 cm/s.

completely. However, elution profiles with a pronounced tailing were always taken as an indicator for interaction between the diffusing species and the column surface and only symmetrical peaks were used for the calculation of diffusion coefficients.

RESULTS AND DISCUSSION

D_{12} as a Function of Density at Constant Temperature

The binary diffusion coefficients of benzene, phenol, naphthalene and caffeine have been determined as a function of the CO_2 density at 40°C. The density range extended from 0.3 to 0.8 g/cm^3, the corresponding pressures being 80 and 160 bar respectively. The results are plotted in Fig. 2. Measurements on caffeine were limited to the high pressure region ($\geq$ 125 bar) because of considerable adsorption effects which have already been discussed above. The diffusion coefficients are all of the order of 10^{-4} cm^2/s and decrease with increasing molecular weight and size of the diffusing compound. By raising the pressure from 80 to 160 bar the diffusion

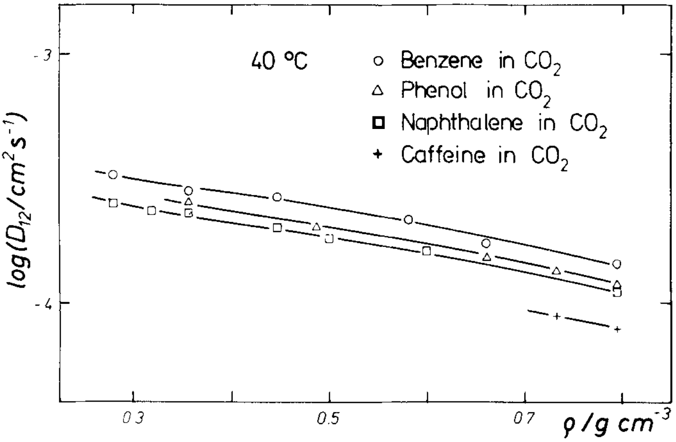

FIGURE 2. D_{12} of benzene, phenol, naphthalene and caffeine in supercritical CO_2 as a function of CO_2 density at 40°C.

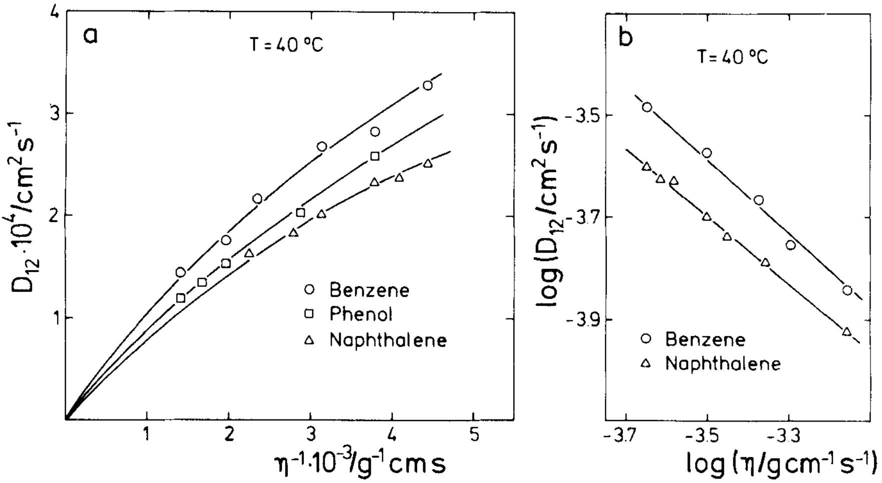

FIGURE 3. Dependence of D_{12} on solvent viscosity.

a. D_{12} versus reciprocal viscosity. Test of the Stokes-Einstein equation

b. $\log D_{12}$ versus $\log \eta$

coefficients decrease by about 50% because of the increasing collision frequency and the reduced mean free path.

Fig. 3a shows D_{12} as a function of the reciprocal CO_2 viscosity which was taken from Reference 18. Obviously the Stokes-Einstein equation does not hold in the density range investigated leading to a decrease of the apparent molecular diameter of the solute with increasing density. In Fig. 3b log D_{12} is plotted versus log η. The points can fairly well be fitted by straight lines corresponding to $D_{12} \sim \eta^{-q}$ where $q \approx 0.66$. An analogous correlation between D_{12} and the solvent viscosity has already been proposed for some liquid systems (19).

A comparison with the Enskog-Thorne theory (20) showed that in all cases the measured diffusion coefficients lie well above the theoretical values; these findings are consistent with previous results of other authors (7,8). Values for F were found to be 0.8 to 1.2 where $F \equiv (D_{12}\cdot\rho)/(D_{12}\cdot\rho)_{id}$ with $(D_{12}\cdot\rho)_{id}$ being

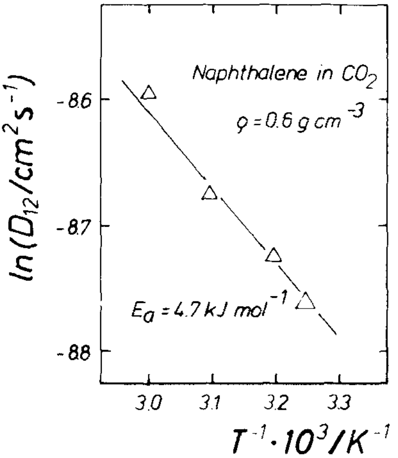

FIGURE 4. Effect of temperature on D_{12} at constant density. ln D_{12} versus reciprocal absolute temperature for naphthalene in supercritical CO_2 at ρ = 0.6 g/cm^3.

calculated on the basis of the low density theory for a gas at the same temperature.

D_{12} as a Function of Temperature at Constant Density

Previous investigations (see e.g. (8)) have shown that binary diffusion coefficients in dense gases exhibit a strong dependence on temperature if the pressure of the system is kept constant. This is mainly caused by the resulting density change of the medium. At constant density, however, the effect of temperature on D_{12} should be distinctly smaller.

Fig.4 shows the results which have been obtained for naphthalene in CO_2 between 35 and 60°C at a constant density of 0.6 g/cm^3. From the Arrhenius plot the energy of activation for the diffusion process was found to be 4.7 kJ/mol which is about half the value that is found in the case of typical organic solvents.

ACKNOWLEDGEMENTS

The authors thank Dipl.Chem. I. Swaid for his help during the experiment. Financial support of the Fonds der Chemischen Industrie e.V. is gratefully acknowledged.

REFERENCES

1. U. van Wasen, I. Swaid, and G. M. Schneider, Angew. Chem. Int. Ed. Engl., 19, 575 (1980).
2. R. Feist, Diploma Thesis, University of Bochum (1980).
3. G. Taylor, Proc. R. Soc. London, Ser. A, 219, 186 (1953); 223, 446 (1954); 225, 473 (1954).
4. R. Aris, Proc. R. Soc. London, Ser. A, 235, 67 (1956).

5. J. C. Giddings and S. L. Seager, J. Chem. Phys., 33, 1579 (1960).

6. J. Bohemen and J.H. Purnell, J. Chem. Soc., 360, 2630 (1961).

7. Z. Balenovic, M. N. Myers, and J.C. Giddings, J. Chem. Phys., 52, 915 (1970).

8. I. Swaid and G. M. Schneider, Ber. Bunsenges. Phys. Chem., 83, 969 (1979).

9. A. C. Ouano, Ind. Eng. Chem. Fundam., 11, 268 (1972).

10. E. Grushka and E. J. Kikta, Jr., J. Phys. Chem., 78, 2297 (1974).

11. T. R. Marrero and E. A. Mason, J. Phys. Chem. Ref. Data, 1, 3 (1972).

12. V. R. Maynard and E. Grushka, Adv. Chromatogr., 12, 99 (1975).

13. O. Levenspiel and K. Smith, Chem. Eng. Sci., 6, 227 (1957).

14. R. J. Laub and R. L. Pecsok, Physicochemical Applications of Gas Chromatography, Wiley, New York, 1978, p. 255.

15. J. C. Giddings and S. L. Seager, Ind. Eng. Chem. Fundam., 1, 277 (1962).

16. C. E. Cloete, T. W. Smuts, and K. De Clerk, J. Chromatogr., 120, 1 (1976).

17. IUPAC, International Thermodynamic Tables of the Fluid State, Carbon Dioxide, Pergamon Press, Oxford, 1976.

18. C. F. Beaton, Eng. Sci. Data Item, 76021 (1976).

19. W. Hayduk and S. C. Cheng, Chem. Eng. Sci., 26, 635 (1971).

20. S. Chapman and T. G. Cowling, The Mathematical Theory of Nonuniform Gases, Cambridge University Press, Cambridge, England, 1939.

Received by editor November, 1980