J. Chem. Eng. Data 1993, 38, 407–409

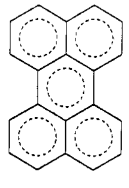
Diffusion Coefficients of Some Large Organic Molecules in Acetone, Cyclohexane, and Toluene

Vladimír Hejtmánek and Petr Schneider*

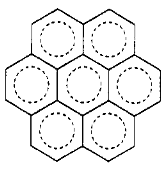
Institute of Chemical Process Fundamentals, Czechoslovak Academy of Sciences, 165 02 Praha 6, Czechoslovakia

Binary diffusion coefficients of perylene, coronene, 12-crown-4 ether, 18-crown-6 ether, and (5,10,15,20-tetraphenyl-21*H*,23*H*-porphine)vanadium(IV) oxide in acetone, cyclohexane, and toluene were determined by the Taylor dispersion technique at 25 °C. The obtained diffusivities correspond to infinite dilution conditions.

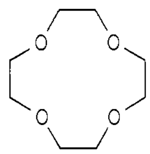
The knowledge of diffusion coefficients of large organic molecules in low molecular weight solvents is significant for the research and design of new processes. Quite often diffusion of these molecules occurs in pores of catalysts, carriers, or membranes (e.g., processing of heavy crude oil fractions, containing large metalloorganic molecules in petrochemistry; biotechnological processes with anchored enzymes; membrane separations, etc.). For the study of pore transport of large molecules the diffusion coefficients form the necessary reference basis; however, experimental diffusion coefficients of these molecules are very rare in the literature. Also the empirical and semiempirical prediction methods are not very reliable. The need for experimental diffusivities is, thus, evident.



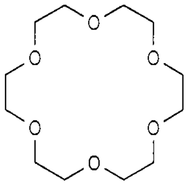
I.



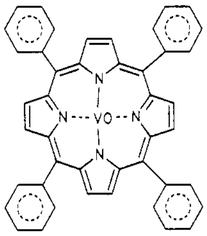
II.



III.



IV.



V

In connection with the study of pore diffusion of large organic molecules, we have determined binary diffusion coefficients, $\mathcal{D}_{AB}$, of perylene (I), coronene (II), 12-crown-4 ether (III), 18-crown-6 ether (IV), and (5,10,15,20-tetraphenyl-21*H*,23*H*-porphine)vanadium(IV) oxide (V) in acetone, cyclohexane, and toluene for low concentrations of tracer components at 25 °C using the Taylor dispersion method (*1, 2*). In this technique the binary diffusion coefficient, $\mathcal{D}_{AB}$, of a tracer (solute A), injected in the form of a short (Dirac) impulse, into a steady stream of carrier liquid (solvent B) flowing through a long narrow capillary (column), is evaluated from the shape of the tracer concentration peak detected at the column outlet, $c(t)$, which is described as (*3, 4*)

$$c(t) = \frac{m}{F_B t_c}\left(\frac{(\mathrm{Pe})t_c}{4\pi t}\right)^{1/2} \exp\left[-\frac{(\mathrm{Pe})t_c}{4t}\left(1-\frac{t}{t_c}\right)^2\right] \qquad (1)$$

Equation 1 contains two parameters, viz., the solute (A) peak residence time, t_c, and Peclet number, Pe, defined as

$$t_c = L/v_B \qquad \mathrm{Pe} = v_B L/E_{AB} \qquad (2)$$

E_{AB} is the axial dispersion coefficient (*5*) which includes the binary diffusion coefficient, $\mathcal{D}_{AB}$:

$$E_{AB} = \mathcal{D}_{AB} + v_B^2(d/2)^2/48\mathcal{D}_{AB} \qquad (3)$$

Equation 1 is valid provided the following condition is fulfilled (*1*):

$$t_c \gg t_{crit} = 8.66 \times 10^{-3} d^2/\mathcal{D}_{AB} \qquad (4)$$

Equation 1 contains two parameters (t_c (or V_c) and Pe) which can be obtained by fitting of the experimental column response signal to eq 1. Fitting of experimental response peaks, normalized to unity at the peak maximum, was accomplished by the Marquard–Levenberg technique (*6*); the objective function, Q, was the integral of squared deviations between experimental and calculated solute response peaks normalized by the square of the experimental peak integral; i.e.

$$Q \equiv \int_{t_{min}}^{t_{max}} [c^{exp}(t) - c(t)]^2 dt \Big/ \int_{t_{min}}^{t_{max}} [c^{exp}(t)]^2 dt \qquad (5)$$

where t_{min} and t_{max} are the shortest and longest times on the response peak for which a sensible solute signal from the detector was obtained.

Experimental Section

Standard HPLC components were used in the experimental setup: positive displacement high-pressure syringe pump (type HPP5001, Laboratorní přístroje Praha, flow range 20–1000 μL/min); six-port injection valve (Rheodyne 7125; 5-μL sampling loop); minimized length of connecting capillaries (i.d. 0.2 mm; approximate volume 19 μL). A continuous flow UV–vis detector (LCD2563, Laboratorní přístroje Praha, seven discrete wave lengths, cell volume 8 μL) or refractometric detector (RIDK101, Laboratorní přístroje Praha, cell volume 10 μL) was used for detecting the solute concentration in the column outflow. The detector signal, proportional to the solute concentration, was digitized and transmitted into a personal computer for further processing.

The coiled stainless steel column (i.d. 0.89 mm, length 206 cm, volume 1.28 cm^3, coil diameter 28 cm) was mounted horizontally. Because the volumes of the sampling loop and connecting capillaries were much lower than the column volume (5, 19, and 1280 μL, respectively), no corrections for the sampling time and time delay were necessary.

The solvents (acetone, cyclohexane, toluene) were of analytical grade. The employed solutes were purchased from

0021-9568/93/1738-0407$04.00/0

Table I. Initial Tracer Concentrations, c_0, in Carrier Liquids

tracer (A)	M_B/(g mol^{-1})	c_0/(μmol L^{-1}) acetone	c_0/(μmol L^{-1}) cyclohexane	c_0/(μmol L^{-1}) toluene
12-crown-4 ether	176.2	562	1289	1000
18-crown-6 ether	264.3	965	779	1347
perylene	252.3	111	128	49
coronene	300.4	160	133	130
(5,10,15,20-tetraphenyl-21*H*,23*H*-porphine) vanadium(IV) oxide	679.7	79	41	129

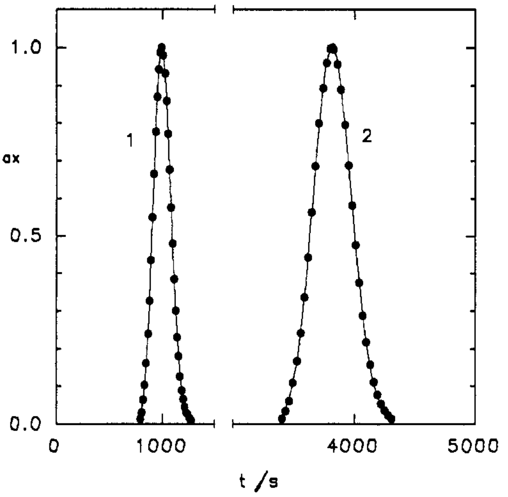


Figure 1. Comparison of experimental (points) and calculated (eq 1, lines) response peaks for the perylene (A)–toluene (B) binary: (1) F_B = 77 μL/min, (2) F_B = 20 μL/min.

Table II. Fitted Parameter for the Perylene (A)–Toluene (B) Binary (t_{crit} = 5.3 s)

F_B/(μL s^{-1})	v_B/(mm s^{-1})	t_c/s	Pe	E_{AB}/(cm^2 s^{-1})	$10^5 \mathcal{D}_{AB}{}^a$/(cm^2 s^{-1})	Q/%
4.97	8.00	257.6	80.0	2.059	1.28	2.52
4.95	7.96	258.8	81.6	2.011	1.30	2.30
4.94	7.95	259.4	82.5	1.983	1.31	2.23
3.32	5.34	385.9	122.0	0.902	1.30	2.38
3.29	5.30	390.5	123.9	0.880	1.30	2.98
2.80	4.51	456.6	138.2	0.673	1.25	1.64
2.79	4.49	458.5	136.5	0.678	1.23	1.54
2.80	4.50	458.1	139.1	0.666	1.25	1.89
2.13	3.43	600.2	180.5	0.392	1.24	1.40
2.13	3.43	600.2	179.1	0.395	1.23	1.50
2.12	3.42	602.7	179.3	0.393	1.23	1.32
1.61	2.59	795.2	243.2	0.220	1.26	1.48
1.61	2.59	796.3	245.6	0.217	1.27	1.16
1.28	2.07	996.5	296.4	0.144	1.23	0.67
1.28	2.07	997.1	301.8	0.141	1.25	0.54
1.28	2.06	1000.2	303.7	0.140	1.25	1.01
0.80	1.29	1595.1	743.9	0.056	1.22	0.67
0.80	1.29	1598.3	477.3	0.056	1.23	1.23
0.80	1.29	1608.3	480.9	0.055	1.23	0.71
0.34	0.54	3813.6	1190.7	0.009	1.29	0.74

[a] Mean, 1.293; standard deviation, 0.036.

Table III. Binary Diffusion Coefficients, $\mathcal{D}_{AB}$

tracer (A)	$10^5 \mathcal{D}_{AB}$/(cm^2 s^{-1}) for each carrier (B) cyclohexane	toluene	acetone
12-crown-4 ether	1.89 ± 0.06[a]	2.41 ± 0.04	10.30 ± 0.82
18-crown-6 ether	1.90 ± 0.05	2.48 ± 0.05	7.82 ± 0.04
perylene	0.98 ± 0.02	1.29 ± 0.04	2.02 ± 0.06
coronene	0.77 ± 0.02	2.43 ± 0.07	3.95 ± 0.11
(5,10,15,20-tetraphenyl-21*H*,23*H*-porphine) vanadium(IV) oxide	1.98 ● 0.06	0.64 ● 0.01	1.16 ● 0.04

[a] Standard deviation.

Aldrich [perylene (99+%), vanadylporphine (99%)], Fluka [coronene (97%)], and Merck [12-crown-4 ether (>98%), 18-crown-6 ether (>99%)] and used without further purification. The absence of ionic impurities in crown ethers was checked by an atomic absorption technique (Na, 3 ppm; K and heavy metals, <10^{-2} ppm). Concentrations of solutes in solvents used for injection into solvent streams, c_0, are shown in Table I; these values represent the upper solute concentration limits for which the diffusion coefficients were determined.

Three to five repeated measurements of response peaks at five to seven solvent flow rates, F_B, were performed for each solute–solvent pair at 25 ± 1 °C.

Results

The quality of fitting experimental tracer responses by eq 1 can be judged from Figure 1. The reproducibility of diffusion coefficients, $\mathcal{D}_{AB}$, obtained from Peclet numbers, Pe, via the axial dispersion coefficients, E_{AB} (eqs 2 and 3), is illustrated in Table II, which summarizes, in addition, the fitted parameters t_c and Pe for the system perylene (A)–toluene (B). The objective function, Q, was always less than 3% which indicates good fit by eq 1 in all cases. Because for the perylene–toluene binary the critical value of the convection time, t_{crit}, equals 5.3 s, also the condition (4) is always satisfied; the same applies for all binary systems studied. From the comparison of E_{AB} with $\mathcal{D}_{AB}$ it follows that the peak dispersion is nearly exclusively due to the second term on the right-hand side of eq 3. As expected, the diffusion coefficients are independent of the solvent flow rate and their standard deviation amounts to 2.8% of the mean value.

To verify the correctness of the employed procedure, the diffusion coefficient for the acetone (A)–water (B) binary was also determined. The obtained value $\mathcal{D}_{AB} = 1.33 \times 10^{-5}$ cm^2/s (standard deviation 0.03 cm^2/s) compares well with the results of Hančil et al. (*2*) ($\mathcal{D}_{AB}$(25 °C) = 1.32×10^{-5} cm^2/s), Anderson et al. (*7*) ($\mathcal{D}_{AB}$(25 °C) = 1.28×10^{-5} cm^2/s), and Tyn et al. (*8*) ($\mathcal{D}_{AB}$(25 °C) = 1.30×10^{-5} cm^2/s).

Binary diffusion coefficients of all solutes in all solvents are summarized in Table III. Standard deviations of the determined diffusion coefficients are less than 3.5% of the mean; a higher deviation (8%) was found only for the 12-crown-4 ether–acetone system which exhibits also the highest $\mathcal{D}_{AB}$. The solute concentrations for which the binary diffusivities are valid are not strictly defined in the Taylor dispersion technique. However, it was shown (*9*) that the maximum concentration in the solute band decreases sharply as the band moves through the column. Because the solute concentration even in the injected sample was very low (see Table I), it appears that the found diffusivities correspond essentially to infinite dilution of the solute. It follows from the data that, except for systems containing vanadylporphine, the diffusion coefficients increase when passing from cyclohexane to toluene and acetone. At the same time the diffusivities of crown ethers in a solvent are higher than the diffusivities of aromatic solutes in the same solvent.

Comparison with Some Estimates

The obtained diffusion coefficients were compared with the values found by three prediction methods recommended by Reid et al. (*10*). These methods are based on the viscosity, μ_B, of solvent B (mPa s), molar volumes (at normal boiling temperature), $\mathcal{V}_A$ and $\mathcal{V}_B$, of solute A and solvent B (cm^3/mol), and parachors P_A and P_B (cm^3 g$^{1/4}$/s$^{1/2}$).

Table IV. Comparison of Diffusion Coefficients for Various Estimation Methods

	$100[\mathcal{D}_{AB}(\text{calc}) - \mathcal{D}_{AB}(\text{exp})]/\mathcal{D}_{AB}(\text{exp})$			
tracer (A)	cyclohexane (B)	toluene (B)	acetone (B)	method[a]
12-crown-4 ether	−53	−37	−76	W–CH
	−8	−27	75	H–M
	−41	−25	−73	T–C
18-crown-6 ether	−63	−52	−75	W–CH
	−49	−40	−72	H–M
	−50	−39	−70	T–C
perylene	−20	1	8	W–CH
	21	41	34	H–M
	26	53	51	T–C
coronene	−4	−50	−48	W–CH
	47	−28	−35	H–M
	53	−22	−26	T–C
(5,10,15,20-tetraphenyl-21*H*,23*H*-porphine) vanadium(IV) oxide	−79	10	2	W–CH
	−66	64	34	H–M
	−66	67	42	T–C

[a] Key: W–CH, Wilke–Chang (*11*); H–M, Hayduk–Minhas (*12*); T–C, Tyn–Calus (*8*).

In the Wilke–Chang method (*11*) $\mathcal{D}_{AB}$ is estimated as

$$\mathcal{D}_{AB}/(\text{cm}^2\ \text{s}^{-1}) = 7.4 \times 10^{-8}(T(\phi_B M)^{0.5}/\mu_B \mathcal{V}_A{}^{0.6}) \quad (6)$$

where ϕ is a dimensionless association factor for solvent B (ϕ = 1 for unassociated solvents).

Hayduk and Minhas (*12*) recommend for nonelectrolyte solutions the following formula:

$$\mathcal{D}_{AB}/(\text{cm}^2\ \text{s}^{-1}) = 1.55 \times 10^{-8} \frac{T^{1.29}}{\mu_B^{0.92} \mathcal{V}_B^{0.23}} \frac{P_B{}^{0.5}}{P_A{}^{0.42}} \quad (7)$$

Similarly, Tyn and Calus (*8*) recommend

$$\mathcal{D}_{AB}/(\text{cm}^2\ \text{s}^{-1}) = 8.93 \times 10^{-8} \left(\frac{\mathcal{V}_A}{\mathcal{V}_B^2}\right)^{1/6} \left(\frac{\text{P}_B}{\text{P}_A}\right)^{0.6} \frac{T}{\mu_B} \quad (8)$$

The results of comparison between experimental and predicted values are summarized in Table IV. As can be seen, in the majority of cases the estimates are too low; this is true for all systems with crown ethers (with the exception of 12-crown-4 ether–acetone estimated by the Hayduk–Minhas method) and all coronene systems (an exception is the coronene–cyclohexane binary with the Hayduk–Minhas and Wilke–Change equations). On the other hand, the diffusivity for perylene is systematically overestimated (an exception is the perylene–cyclohexane system with the Wilke–Chang method).

Only for six binary systems the diffusion coefficients are predicted within 10%; interestingly enough, in five of these cases the prediction is based on the simplest Wilke–Change equation (6).

Thus, it appears that the three compared prediction methods are, in general, not very reliable for the large organic molecules.

Summary

Binary diffusion coefficients $\mathcal{D}_{AB}$, of five large organic solutes (I–V) in acetone, cyclohexane, and toluene were determined by the Taylor dispersion technique at nearly infinite dilution of the solute. With one exception the standard deviations of $\mathcal{D}_{AB}$ were less than 3.5%. Comparison of experimental diffusivities with three prediction methods has shown that the predictions are not very reliable.

Glossary

c	tracer molar concentration
c_0	inlet tracer molar concentration
$c_{\max}$	tracer molar concentration in the peak maximum
d	column diameter
$\mathcal{D}_{AB}$	binary diffusion coefficient, tracer (A)–carrier (B)
E_{AB}	axial dispersion coefficient, tracer (A)–carrier (B)
F_B	volumetric carrier flow rate
L	column length
m	amount of tracer injected
M_B	carrier molecular weight
P_i	parachor for the tracer (i = A) and carrier (i = B)
Pe	Peclet number
Q	objective function
t	time
t_c	convection time
t_{crit}	critical convection time
T	absolute temperature
v_B	linear velocity of carrier liquid
$\mathcal{V}_i$	molar volume of the tracer (i = A) and carrier (i = B) at normal boiling temperature
μ_B	viscosity of the carrier liquid

Literature Cited

(1) Taylor, G. *Proc. R. Soc. London* **1953**, *A219*, 186.
(2) Hančil, V.; Rod, V.; Rosenbaum, M. *Chem. Eng. Commun.* **1979**, *3*, 155.
(3) Levenspiel, O.; Smith, W. K. *Chem. Eng. Sci.* **1982**, *37*, 18.
(4) Van der Laan, E. T. *Chem. Eng. Sci.* **1957**, *6*, 227.
(5) Aris, R. *Proc. R. Soc. London* **1956**, *A235*, 67.
(6) Press, W. H.; Flannery, B. P.; Poling, B. E.; Vetterling, W. T. *Numerical Recipes*; Wiley: New York, 1986.
(7) Anderson, D. K.; Hall, J. R.; Babb, A. L. *J. Phys. Chem.* **1958**, *62*, 404.
(8) Tyn, M. T.; Calus, W. F. *J. Chem. Eng. Data* **1975**, *20*, 5106.
(9) Schneider, P.; Smith, J. M. *AIChE J* **1968**, *14*, 886.
(10) Reid, R. C.; Prausnitz, J. M.; Poling, B. E. *The Properties of Gases and Liquids*, 4th ed.; McGraw-Hill: New York, 1986.
(11) Wilke, C. R.; Chang, P. *AIChE J.* **1955**, *1*, 264.
(12) Hayduk, W.; Minhas, B. S. *Can. J. Chem. Eng.* **1982**, *60*, 295.

Received for review September 4, 1992. Revised February 3, 1993. Accepted February 23, 1993.