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DIFFUSION COEFFICIENTS IN WATER-ACETONITRILE MIXTURES

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SUMMARY

The open-tube elution method was utilized to determine diffusion coefficients in binary or ternary mixtures of solvents. Large variations occur with the relative proportions of the components and these variations are highly correlated with the viscosity. Some predictive equations were tested and it was found that none of the published equations is able to fit the experimental data.

INTRODUCTION

Whatever the chromatographic theory of band broadening, molecular diffusion plays a crucial role. For packed columns, the reduced plate height h can be represented as a function of the reduced velocity v by the equation proposed by Knox¹:

$$h = Av^{1/3} + B/v + Cv \quad (1)$$

where $h = H/d_p$, H is the plate height, d_p is the particle diameter and the reduced velocity is defined by $v = ud_p/D_m$, where u is the linear eluent velocity and D_m is the diffusion coefficient of solute in eluent.

The axial diffusion factor B can be given as $B = 2[\gamma_m + k'(D_s/D_m)]$, where k' is the phase capacity ratio, γ_m the obstructive factor in the mobile phase and D_s the diffusion coefficient of the solute in stationary phase. The mass transfer factor, C , is given by $C = (1/30)[k''/(1+k'')^2](D_{sz}/D_m)$, where k'' is the zone capacity ratio and D_{sz} is the diffusion coefficient of the solute within the particles (or stationary zone).

Likewise, the plate height for a straight open tube is given by the Golay equation², which has the form (in reduced parameters)

$$h = \frac{2}{v} + \frac{1 + 6k' + 11k'^2}{96(1 + k')^2} \cdot v + \frac{2}{3} \cdot \frac{k'}{(1+k')^2} \cdot \frac{d_f^2}{d_c} \cdot \frac{D_m}{D_s} \quad (2)$$

where d_f is the depth of the stationary phase.

It has also been demonstrated that the diffusion process is the main source of band broadening in high-performance thin-layer chromatography³. In spite of the well established role of D_m , available data are scarce. Some data on one solute diffusing in

one single solvent can be found but the use of a single solvent is very rare in chromatography as complex mixtures are required to achieve fine selectivity tuning.

Measurement of diffusion coefficients can be carried out with steady-state or dynamic methods. Among the former, the diaphragm cell method derived from the early work of Northrop and Anson⁴ and the interferometric Gouy diffusimeter⁵ are considered to be suitable and reliable. From the critical study of Cussler and Dunlop⁶, the Gouy diffusimeter yields more precise data; the diaphragm cell necessitates a calibration with a standard diffusing species. However, the diffusimeter cannot be used when the solute concentration is too low, which is exactly what occurs in chromatography.

In 1953, Taylor⁷ developed a dynamic method based on the dispersion of a solute in a solvent flowing in a coiled capillary tubing and Ouano⁸ extended the procedure for measuring diffusivities in liquid systems.

According to Poiseuille's law, the velocity profile in a laminar flow is parabolic and the diffusion equation is

$$\frac{\partial^2 C}{\partial z^2} + \frac{1}{z} \cdot \frac{\partial C}{\partial z} + r_c^2 \cdot \frac{\partial^2 C}{\partial x^2} = \frac{r_c^2}{D_m} \cdot \frac{\partial C}{\partial t} + \frac{r_c^2 u}{D_m} (1 - 2z^2) \frac{\partial C}{\partial x} \quad (3)$$

where $z = y/r_c$, r_c is the tube radius and y is the molecule position with respect to the tube axis (Fig. 1). At very low flow-rates, the mass transfer by molecular diffusion along the tube can be neglected and

$$r_c^2 \cdot \frac{\partial^2 C}{\partial x^2} \ll \frac{\partial^2 C}{\partial x^2} + \frac{1}{2} \cdot \frac{\partial C}{\partial x} \quad (4)$$

and we can write

$$\frac{\partial^2 C}{\partial z^2} + \frac{1}{2} \cdot \frac{\partial C}{\partial z} = \frac{r_c^2}{D_m} \cdot \frac{\partial C}{\partial t} + \frac{r_c^2 u}{D_m} (1 - 2z^2) \frac{\partial C}{\partial x} \quad (5)$$

The Taylor axial dispersion coefficient E is related to D_m by

$$E = \frac{(ur_c)^2}{48D_m} \quad \text{and} \quad \frac{\partial C}{\partial t} = E \cdot \frac{\partial^2 C}{\partial x^2} \quad (6)$$

The condition for validity of the above equations is that the reciprocal of the Peclet number, ur_c/D_m is very small, as it is in the case of a long tube. When the Peclet number

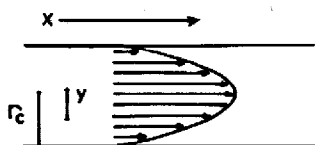


Fig. 1. Schematic diagram of the parabolic profile in a capillary tube and significance of y , x and r_c .

tends to zero, the dispersion coefficient is the molecular diffusion, D_m . When the axial dispersion is not neglected, following Aris⁹, then

$$E = D_m + \frac{r_c^2 u^2}{48 D_m} = D_m \left(1 + \frac{Pe^2}{192} \right) \quad (7)$$

where Pe is the Peclet number.

Ouano⁸ was the first to utilize the chromatographic broadening technique for determining the diffusion coefficients of organic solutes. The concentration *versus* time curve is well approximated by the gaussian distribution and

$$D_m = \frac{ur_c^2}{24L\sigma^2} \quad \text{or} \quad D_m = \frac{F}{24\pi L\sigma^2} \quad (8)$$

where σ^2 is the variance of the distribution and F is the flow-rate. The method has been extensively used by many workers and Table I compiles the published data obtained with the chromatographic broadening technique. The discrepancies between the advocated equations for D_m calculations are only slight. The most striking feature is the scarcity of data with solvent mixtures.

The data published by Knox and Scott¹⁰ deal only with a narrow range of methanol-water proportions. Komiyama and Smith¹¹ gave results for the diffusivity of benzaldehyde in the whole range of methanol-water mixtures. Surprisingly, no data are available on acetonitrile-water mixtures or ternary mixtures. Further, from recent relevant literature¹², there is no method for predicting the diffusivity of a solute infinitely diluted in a multi-component solvent. The purpose of this work was to investigate the behaviour of a solute in solvents of chromatographic interest. It is demonstrated that published equations are not suitable for predicting diffusivity.

EXPERIMENTAL

The measurement system (Fig. 2a) is of a classical design very similar to that published by Grushka and Kikta¹⁴. A Model 655 A liquid chromatographic pumping system (Merck-Hitachi, Tokyo, Japan) is equipped with a packed liquid chromatographic column (125 × 4 mm I.D. of 5- μ m silica), which ensures proper working of the pump and a coiled round pipe (1000 × 0.250 mm I.D.) acts as a pulse damper. The injection device (in Fig. 2b) was designed in order that the syringe needle would be positioned at the exact centre of the capillary tube. The septum is made of Viton (DuPont, Wilmington, DE, U.S.A.). The diffusion tubing is a stainless-steel pipe (1000 × 0.476 mm I.D.). Its diameter was found from the weights of the tube empty and full of water. It is coiled to a diameter of 110 mm. The whole tubing is immersed in a water-bath at 22°C, controlled with a Haake (Karlsruhe, F.R.G.) thermostat. The room is air conditioned at 22°C. Fused-silica capillary columns could also be used but dipping in the water-bath is tedious as the fittings may be damaged. A Knauer 6000 variable-wavelength UV detector (Knauer, Berlin, F.R.G.) is used. The recorder is a J. J. Instruments (Southampton, U.K.), the inlet voltage is 100 mV and the chart speed is 0.5 cm/min.

TABLE I
MEASUREMENT OF DIFFUSION COEFFICIENTS BY THE OPEN-TUBE ELUTION METHOD

D_m calculation	Column		Retention time	Solvent velocity (cm/s)	Solute and solvent	Ref.
	Length (cm)	I.D. (mm)				
$E = \frac{r_c^2 u^2}{48 D_m}$	152 ^a	0.5	3 h	0.014	KMnO ₄ in water	7
$E = \frac{r_c^2 u^2}{48 D_m}$	85 ^a	5	3 h	0.031		13
$D_m = 0.212 \cdot \frac{E}{L} \left(\frac{t_R}{\omega} \right)^2$	168 ^b	0.5	82 min	0.35 5 h	Acetone Benzene in chloroform	8
$D_m = \frac{0.231 r_c^2 u t_R^2}{L \omega_{\frac{1}{2}}^2}$	9189 ^b	0.39	>2.5 h	<1.0	Alkyl aromatics alkylphenones in heptane, cyclohexane, chloroform	14
$D_m = \frac{F}{24\pi L \sigma^2}$	830 ^b	0.936	15 min 2.5 h	0.096 0.96	Benzene in methanol Benzaldehyde in water- methanol	11
$\sigma = \frac{r_c^2 t_R}{24 D_m}$	1364 ^b	0.381	>50 min	<0.435	Mutual diffusion, water-methanol	15
$\sigma^2 = \frac{F}{24\pi L D_m}$	366 ^a	0.38	1.34-4 min	1.5-4.5	Sodium benzoate in water Benzene in hexane	16
$\omega_{\frac{1}{2}} = \frac{35.4}{D_m^{0.36}} \cdot r_c^2 \left(\frac{L}{F} \right)^{0.64}$	300 500	0.5-1	0; 5-10 min	0.85-10.5	K ₃ Fe(CN) ₆ in KCl solution	17
$D_m = \frac{r_c^2 t_R}{24 \sigma}$	5044 ^b	0.264	1-11 h	0.12-1.3	No experimental values	18
$D_m = \frac{1}{24} \left(\frac{r_c u}{\sigma} \right)^2 t_R$	100 ^a	0.86	2 min	1.44	KMnO ₄ in water, ethanol, acetone	19
$D_m = \frac{r_c^2 u}{24h} \left(h = \frac{L}{4} \cdot \frac{\omega \cdot 0.6}{t_R} \right)$	365.4 ^a	0.184	0.77 min	7.7	Benzyl acetate in alkanes	20
$D_m = 0.231 r_c^2 \cdot \frac{t_R}{(\omega_{\frac{1}{2}})^2}$	8570 ^b	0.98	5.5-7 h	0.22-0.44	Aromatics in hexane-ethyl acetate	21
$\sigma^{2c} = \frac{d_c^2 L^2}{96 t_R D_m}$	1090 ^b	0.412		0.2-0.5	Methylene chloride in acetone, methanol	10
$D_m = \frac{F t_R^2}{24\pi L \sigma^2}$	2700 ^b	0.213	10 min	4.76	Many solutes in hexane- ethyl acetate	22

^a Straight tube.

^b Coiled tube.

^c σ = Standard deviation of the peak.

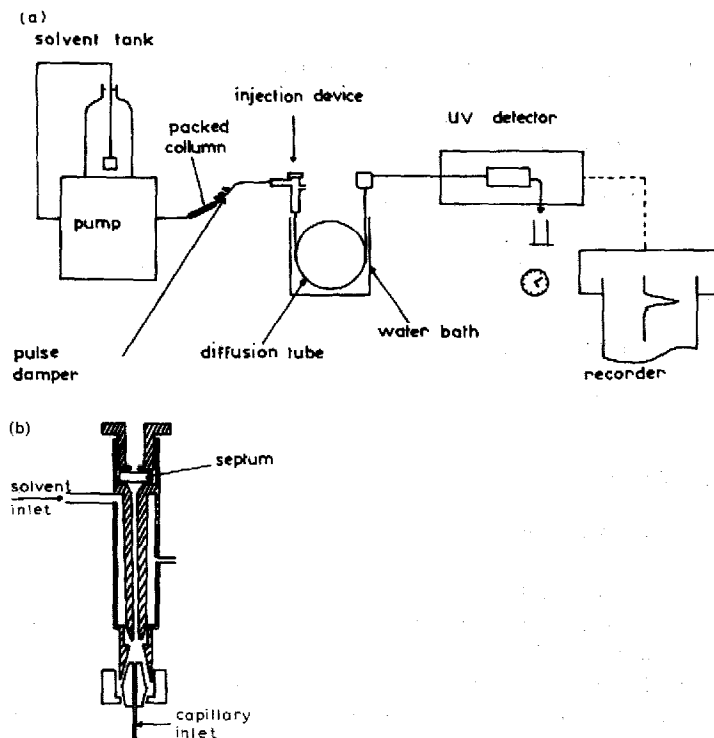


Fig. 2. Design of (a) the whole system and (b) the injector device.

All solvents are of LiChrosolv grade (Merck, Darmstadt, F.R.G.) and were carefully degassed by sonication prior to use. The solutes (benzene, toluene and benzaldehyde) are chromatographically pure (>99.9%). Injections are carried out with an HP305 N syringe (Hamilton, Bonaduz, Switzerland); $2 \mu\text{l}$ of a 2 g/l solution are injected. The flow-rate of the pump is fixed at 0.1 ml/min and carefully checked throughout the runs. In this mode the reciprocal of the Peclet number is very small and $r_c^2/D_m \cdot L = 0.0125 \ll 1$ and the retention times still acceptable (*ca.* 3 h). The measured peak variance is the sum of the peak variance due to the open-tubular column and that due to the various external peak-broadening processes. To determine the extra-column contribution, the diffusion tube was disconnected and the solute injected. It was observed that the resulting peak was symmetrical at half-height and the width was determined. For measurement of actual peaks, the width at half-height was considered as the peaks were wide and errors from those measurements were less than 1.5%. Viscosities of the eluents were either compiled from the International Critical Tables or determined with an Ubbelohde (Lauda, Austria) KPG viscosimeter.

RESULTS AND DISCUSSION

Calibration of the system was carried out with the determination of the diffusion coefficients of toluene in cyclohexane and heptane. The observed values ($1.65 \cdot 10^{-5}$

TABLE II
DIFFUSION OF BENZENE IN CYCLOHEXANE-HEXANE MIXTURES

Component ^a	Molar fraction	Volume fraction	Viscosity (cP)	$D_m \cdot 10^5$ (cm ² /s)	$D_m \cdot 10^5$ (lit.) (cm ² /s)
H	0.0	0	0.900	1.90	1.95 ¹⁴
C	1.0	100			1.89 ²⁸
H	0.254	30	0.689	2.75	2.77 ¹⁴
C	0.746	70			
H	0.502	55	0.531	3.43	3.42 ¹⁴
C	0.498	45			
H	0.733	77	0.417	4.19	4.16 ¹⁴
C	0.267	23			
H	1.00	100	0.315	4.76	4.79 ¹⁴
C	0.00	0			

^a H = hexane; C = cyclohexane.

and $3.23 \cdot 10^{-5}$ cm²/s) agree well with the values from the literature¹⁴ ($1.63 \cdot 10^{-5}$ and $3.24 \cdot 10^{-5}$ cm²/s).

Since it represents a non-associating system, we measured the diffusivity of benzaldehyde in methanol-water mixtures and our data are consistent with those of Komiyama and Smith¹¹. The method is reliable and we carried out two types of experiments: first, diffusion of benzene in hexane-cyclohexane mixtures, which do not exhibit association and can be considered close to the ideality; conversely, strong association between methanol and water is well known and in a recent paper²³ it was argued that methanol-water mixtures contain three distinct chemical species. Simi-

TABLE III
DIFFUSION OF BENZALDEHYDE IN WATER-METHANOL MIXTURES

Component ^a	Molar fraction	Volume fraction	Viscosity (cP)	$D_m \cdot 10^5$ (cm ² /s)	Data from Komiyama and Smith ¹¹ (cm ² /s)
M	0.00	0	0.958	0.860	0.873
W	1.00	100			
M	0.047	10	1.2	0.749	0.755
W	0.953	90			
M	0.100	20	1.425	0.691	0.685
W	0.900	80			
M	0.308	50	1.725	0.624	0.619
W	0.692	50			
M	0.572	75	1.315	0.865	0.845
W	0.428	25			
M	0.800	90	0.890	1.250	1.280
W	0.200	10			
M	1.00	100	0.585	1.790	1.830
W	0.00	0			

^a M = methanol; W = water.

larly, a paper²⁴ on the surface tension of acetonitrile-water mixtures indicated strong association.

Data are given in Tables II and III, together with values for benzene in cyclohexane-hexane and benzaldehyde in water-methanol taken from the literature. No discrepancy is observed between our values and those from the literature for the whole range of water-methanol proportions. A decrease in diffusivity of benzaldehyde is observed with a 20-40% proportion of methanol. These results are also consistent with what was observed by Knox and Scott¹⁰ with 60-45% methanol content in a methanol-water mixture. The most striking is the water-acetonitrile mixture and the variations with percentage of acetonitrile (as shown in Fig. 5). Eleven water-acetonitrile mixtures were selected and runs were performed four times with each mixture (observed relative standard deviation 1%) (Table IV). Dealing with ternary mixtures, a statistical mixture design was drawn and seven experiments were selected to represent the best coverage of the experimental domain. The data in Table V show a two-fold increase in D_m , on going from point 2 to point 4. This explains in part the differences in

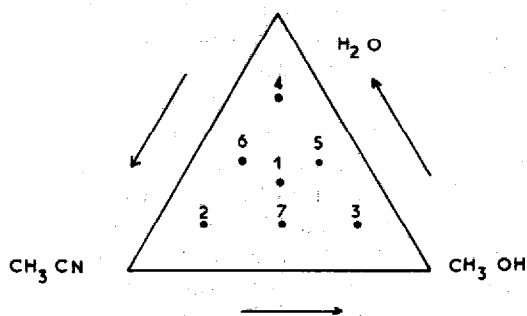
TABLE IV
EXPERIMENTAL DIFFUSION COEFFICIENTS OF BENZALDEHYDE IN WATER-ACETONITRILE

Component ^a	Molar fraction	Volume fraction	Viscosity (cP)	$D_m \cdot 10^5$ (cm ² /s)
W	1.00	100	0.900	0.860
A	0.00	0		
W	0.963	90	0.973	0.819
A	0.037	10		
W	0.921	80	0.909	0.835
A	0.079	20		
W	0.872	70	0.800	0.937
A	0.128	30		
W	0.814	60	0.727	0.964
A	0.186	40		
W	0.745	50	0.636	1.113
A	0.255	50		
W	0.660	40	0.545	1.359
A	0.340	60		
W	0.556	30	0.436	1.600
A	0.354	70		
W	0.422	20	0.400	1.750
A	0.578	80		
W	0.245	10	0.427	1.740
A	0.755	90		
W	0.00	0	0.354	2.42
A	1.00	100		

^a W = water; A = acetonitrile.

TABLE V

EXPERIMENTAL VALUES OF THE DIFFUSION COEFFICIENTS OF BENZALDEHYDE IN WATER-METHANOL-ACETONITRILE MIXTURES



Component ^a	Molar fraction ^b	Volume fraction	Viscosity (cP)	$D_m \cdot 10^5$ (cm ² /s)
W	1/3	23.9	0.994	1.10
M	1/3 (1)	33.6		
A	1/3	42.5		
W	2/3	55.7	1.269	0.93
M	1/6 (2)	19.5		
A	1/6	24.8		
W	1/6	11.9	0.898	1.61
M	2/3 (3)	66.9		
A	1/6	21.2		
W	1/6	10.5	0.625	1.98
M	1/6 (4)	14.7		
A	2/3	74.8		
W	1/6	3.6	0.719	1.72
M	5/12 (5)	36.3		
A	5/12	60.1		
W	5/12	10.8	0.844	1.41
M	1/6 (6)	17.3		
A	5/12	71.9		
W	5/12	13.1	1.204	1.05
M	5/12 (7)	52.2		
A	1/6	34.7		

^a W = water; M = methanol; A = acetonitrile.^b Number in brackets refer to points inside the above triangle.

observed plate count in the preliminary experiments with optimization methods in LC (e.g., the ORM technique).

It is striking from the plots in Figs. 3–5 that viscosity and diffusion coefficients are highly correlated; the more viscous the solvent, the lower is the diffusion coefficient. A proposed relationship¹² between diffusion coefficient and viscosity is

$$D_m = a\eta^q$$

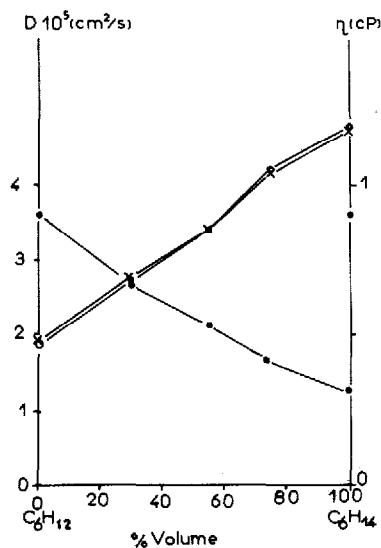


Fig. 3. Plot of diffusion coefficient ($D \cdot 10^5$) of benzene and viscosity (cP) versus the volume percentage in cyclohexane-hexane mixtures. ● = Viscosity; × = diffusion coefficients from ref. 14; ○ = experimental diffusion coefficients.

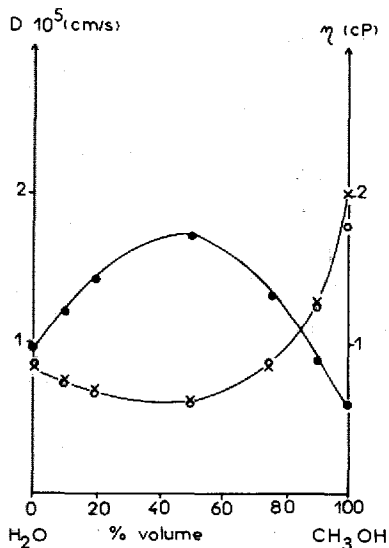


Fig. 4. Plot of diffusion coefficient of benzaldehyde and viscosity versus the volume percentage in water-methanol mixtures. ● = Viscosity; × = diffusion coefficients; ○ = experimental diffusion coefficients.

which is linearized as

$$\log D_m = q \log \eta + \log a \tag{9}$$

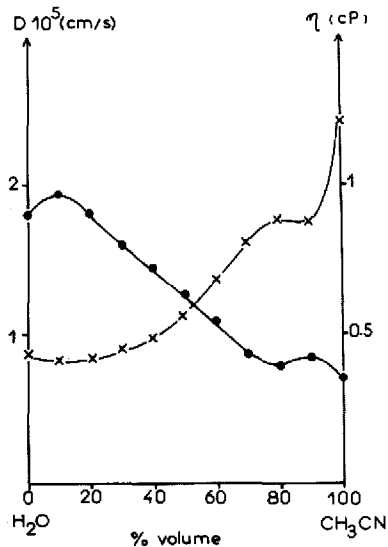


Fig. 5. Plot of diffusion coefficient of benzaldehyde and viscosity versus the volume percentage in water-acetonitrile mixtures. ● = Viscosity; × = diffusion coefficients.

TABLE VI

 a AND q PARAMETERS OF THE EQUATION $D = a\eta^q$

System	$a \cdot 10^5$	q	r
Benzene in cyclohexane-hexane	1.878	-0.867	0.963
Benzaldehyde in methanol-water	1.003	-0.976	0.897
Benzaldehyde in acetonitrile-water	0.751	-0.988	0.971
Benzaldehyde in acetonitrile-methanol-water	1.226	-1.008	0.912

a and q were determined by linear regression and the values are displayed in Table VI. Plots of $\log D_m$ versus $\log \eta$ for the diffusion of benzaldehyde are displayed in Fig. 6. The correlation coefficients are fairly good and no discrepancy over 10% between the experimental and calculated values is observed.

Eqn. 9 is valid but further refinement is required. The fit is not improved when the non-associating benzene in cyclohexane-hexane is considered. From the plots for the diffusion of benzaldehyde in associated systems, three parallel lines are observed and the q parameters are similar, which may indicate that q represents a physical constant of the diffusing species. This is supported by the different value of q for benzene. From the Einstein equation the ratio D_m/η should be constant, which implies that $q = 1$. This relationship was tested with all four solvent systems. It was found that D_m/η is far from constant as the percentage composition of the binary or ternary mixture varies (e.g., 2.1-15.1 with benzene in cyclohexane-hexane and 0.8-4.3 with

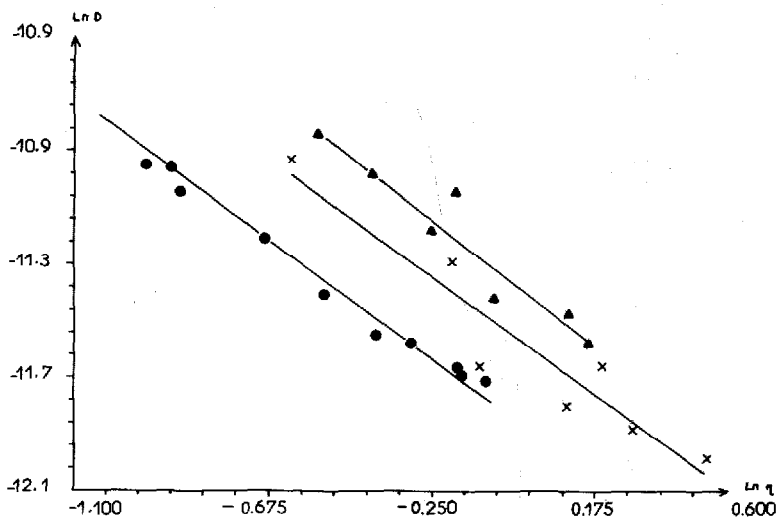


Fig. 6. Plots of $\log D_m$ versus $\log \eta$. Solute, benzaldehyde. \times = Water-methanol mixture; \bullet = water-acetonitrile mixture; \blacktriangle = water-methanol-acetonitrile mixtures.

benzaldehyde in water-acetonitrile). It must be pointed out that the Einstein equation is valid for spherical species diffusing in solvent molecules of similar or smaller size. The parameter a does not seem to be related to the solute and may be related to the type of solvent mixture.

Prediction of diffusion coefficient in a multi-component system

Many theories have been published to account for the diffusion process. The hydrodynamic theory is considered to be satisfactory for spherical molecules diffusing in small molecules of non-associating solvents. From the theory of absolute velocity, predictive equations have been derived.

We first tested the application of the simplest relationship:

$$D_m = \left(\frac{\sum Y_i}{D_{1i}} \right)^{-1}$$

where Y_i is the molar fraction and D_{1i} is the diffusion coefficient of solute 1 in solvent i . It was developed for diffusion in the gas phase and can be extended to non-associating systems. With our values the discrepancies are about 20% for toluene in cyclohexane-hexane and more than 68% for benzaldehyde in binary and ternary mixtures. In fact, this equation does not correlate D_m with viscosity as was previously shown, and must be discarded.

The Wilke-Chang²⁵ equation is most often used and can be written as

$$D_m = \frac{7.4 \cdot 10^{-8} (\bar{\varphi} \bar{M})^{\frac{1}{2}} T}{\eta_{\text{mix}} (V_i)^{0.6}}$$

where V_i is the molal volume of solute i (cm^3/mol), η is viscosity (cP) and $\bar{\varphi} \bar{M} = \sum_i \varphi_i M_i x_i$, where φ_i is the association constant, M_i the molecular weight of solvent i and X_i the volume fraction of solvent i . Calculations require the knowledge of φ and V_i , which are given in the literature¹² as $\varphi_{\text{water}} = 2.6$, $\varphi_{\text{methanol}} = 1.9$, $\varphi_{\text{acetonitrile}} = 1.2$, $V_{\text{benzene}} = 96 \text{ cm}^3/\text{mol}$ and $V_{\text{benzaldehyde}} = 112 \text{ cm}^3/\text{mol}$. Large deviations between the calculated and experimental values are observed (33% with the ternary mixture). Changes in the φ value of water from 2.6 to 2.26 and the exponent of V from 0.6 to 0.7 do not markedly change the overall features.

Eyring²⁶ proposed the relationship

$$\log(D_{1m} \eta_m^{1-\varepsilon}) = x_2 \log(D_{12} \eta_2^{1-\varepsilon}) + x_3 \log(D_{13} \eta_3^{1-\varepsilon})$$

where D_{1i} is the diffusion coefficient of solute 1 in the pure solvent i and η_m is the viscosity of the mixture. It was modified by Tang and Himmelbrau²⁷ to

$$D_{1m} \eta_m^{\frac{1}{2}} V_m^{-1/6} = x_2 D_{12} \eta_2^{\frac{1}{2}} V_2^{-1/6} + x_3 D_{13} \eta_3^{\frac{1}{2}} V_3^{-1/6}$$

The parameter ε has a value of 0.5 in systems close to ideality and 0.2 in associated mixtures. The calculated values are different from the experimental values. In fact, it

TABLE VII

COMPARISON OF DIFFUSION COEFFICIENTS CALCULATED USING DIFFERENT EQUATIONS

Solute: benzene in cyclohexane-hexane.

Component ^a	Volume fraction	$D \cdot 10^5$ (exptl.) (cm ² /s)	$D_m =$ ($\sum y_i/D_i$) ⁻¹	Tang and Himmelbrau ²⁷		Wilke- Chang ²⁵	Cullinan and Cusick ²⁸
				$\epsilon = 0.5$	$\epsilon = 0$		
C	100	1.90	—	—	—	1.45	—
H	0						
C	70	2.75	2.24	2.54	2.63	1.90	2.93
H	30						
C	45	3.43	2.72	3.12	3.33	2.47	3.21
H	55						
C	23	4.19	3.40	3.85	4.00	3.15	3.91
H	77						
C	0	4.76				4.19	—
H	100						

^a C = cyclohexane; H = hexane.

appears that the Eyring equation does not predict the diffusion coefficient but permits a correlation between viscosity and diffusion following optimization of ϵ .

In this mode we attempted to optimize ϵ . The best fit was obtained but a 4–9% deviation still occurred and hence the Eyring equation cannot be considered as satisfactory. The question arises of whether ϵ is a parameter of the mixture of solvents or not.

Cullinan and Cusick²⁸ proposed a relationship based on the linear additivity of the frictional activation energy:

$$D_{lm} = \left[\frac{x_1}{(D_{12})^{x_2} (\alpha_{12}^3 D_{23})^{x_3}} + \frac{x_3}{(D_{13})^{x_3} (\alpha_{13}^3 D_{32})^{x_2}} \right]^{-1}$$

where 1 represents the diffusing species in a mixture of solvents 2 and 3 and α is a thermodynamic parameter:

$$\alpha_{ij}^k = \frac{V_k \left(1 - \frac{D_{ik}}{D_{jk}} \right)}{(V_i - V_j)}$$

where V_i is the molal volume. Leffler and Cullinan²⁹ produced some experimental dilute diffusion coefficients for one species in a binary system. Testing the Cullinan and Cusick relationship yielded two types of results: (i) with a non-associating system (benzene in cyclohexane-heptane) a 6% discrepancy is observed, which is better than was observed with the Wilke and Chang equation (Table VII); and (ii) conversely, with

TABLE VIII

COMPARISON BETWEEN EXPERIMENTAL AND CALCULATED DIFFUSION COEFFICIENTS

Solutes: benzaldehyde in water-methanol and acetonitrile-water.

Component ^a	Volume fraction	$D \cdot 10^5$ (exptl.) (cm^2/s)	$D_m =$ ($\sum y_i/D_i$) ⁻¹	Tang and Himmelbrau ²⁷		Eyring ²⁶		Wilke- Chang ²⁵	Cullinan and Cusick ²⁸
				$\epsilon=0.2$	$\epsilon=0.6$	$\epsilon=0.2$	$\epsilon=0.3$		
W M	100 0	0.86	—	—	—	—	—	—	—
W M	90 10	0.75	0.89	0.75	0.75	0.70	0.75	0.74	0.65
W M	80 20	0.69	0.92	0.67	0.68	0.64	0.67	0.62	0.54
W M	50 50	0.62	1.04	0.65	0.65	0.62	0.64	0.53	0.44
W M	25 75	0.86	1.24	0.92	0.87	0.90	0.86	0.71	0.53
W M	10 90	1.25	1.50	1.38	1.25	1.37	1.23	1.10	0.80
W M	0 100	1.79	—	—	—	—	—	—	—
W A	100 0	0.86	—	—	—	—	—	0.98	—
W A	90 10	0.82	0.88	0.81	—	0.81	—	0.91	0.88
W A	80 20	0.85	0.91	0.87	—	0.86	—	0.97	0.90
W A	70 30	0.94	1.05	0.98	—	0.98	—	1.10	0.92
W A	60 40	1.05	0.98	1.06	—	1.06	—	1.22	0.94
W A	50 50	0.98	1.03	1.19	—	1.19	—	1.31	0.96
W A	40 60	1.03	1.10	1.37	—	1.37	—	1.63	0.98
W A	30 70	1.60	1.26	1.67	—	1.67	—	2.05	0.99
W A	20 80	1.75	1.37	1.84	—	1.83	—	2.23	0.99
W A	10 90	1.37	1.67	1.80	—	1.79	—	2.10	1.01
W A	0 100	2.42	—	—	—	—	—	2.55	—

^a W = water; M = méthanol; A = acetonitrile.

TABLE IX

COMPARISON BETWEEN EXPERIMENTAL AND CALCULATED DIFFUSION COEFFICIENTS

Solute: benzaldehyde in water-methanol-acetonitrile.

Component ^a	Volume fraction	$D \cdot 10^5$ (exptl.) (cm ² /s)	$D_m =$ ($\sum y_i/D_i$) ⁻¹ (cm ² /s)	Tang and Himmelbrau ²⁷		Eyring ²⁶ $\epsilon=0.6$	Wilke- Chang ²⁵
				$\epsilon=0.2$	$\epsilon=0.6$		
W	23.9						
M	33.6	1.10	1.40	1.02	1.29	1.25	0.94
A	42.5						
W	55.7						
M	19.5	0.93	1.07	0.80	0.97	0.93	0.94
A	24.8						
W	11.9						
M	66.9	1.61	1.57	1.19	1.43	1.40	0.71
A	21.2						
W	10.5						
M	14.7	1.98	1.78	1.51	1.75	1.70	1.47
A	74.8						
W	3.6						
M	36.3	1.72	1.67	1.38	1.60	1.52	1.38
A	60.1						
W	10.8						
M	17.3	1.41	1.33	1.12	1.34	1.29	1.08
A	71.9						
W	13.1						
M	52.2	1.05	1.27	0.87	1.13	1.09	0.77
A	34.7						

^a W = water; M = methanol; A = acetonitrile.

benzaldehyde in water-methanol the discrepancies are as important as was observed with the Wilke-Chang equation (Tables VIII and IX).

CONCLUSION

At present, no published relationship permit an accurate determination of the diffusivity of one species in a mixture of solvents. Such a relationship would be very useful. A method of group contributions has been developed³⁰ to evaluate the viscosity of mixtures of liquids, but it has not yet been developed to account for association with water.

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