Diffusion Coefficient of Water in Some Organic Liquids

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The diffusion coefficient of water in organic liquids close to infinite dilution and at 25°C was measured using the diaphragm cell method in the following solvents, for which measurements have not previously been made: n-butyl acetate, n-butyric acid, toluene, methylene chloride, 1,1,1-trichloroethane, trichloroethylene, 1,1,2,2-tetrachloroethane, 2-bromo-2-chloro-1,1,1-trifluoroethane, nitrobenzene, and pyridine. The first two liquids fit the Olander equation and the next seven the original Wilke-Chang equation, while the last is intermediate between the two. For pyridine, the effect of dissolved nitrogen has been found to reduce the diffusion coefficient of water by about 30%.

A knowledge of the diffusion coefficient of water in organic liquids is often required in chemical engineering. However, the shortage of experimental data makes it difficult to check the validity of methods of prediction based on fundamental principles or empirical correlations.

A number of fundamental methods for the prediction of liquid-phase diffusion coefficients have been presented in recent years, but in most cases the authors have not considered water as a solute. An exception is the work of Gainer and Metzner (5), who presented a method which they show to be successful in predicting the diffusion coefficient of water in two alcohols (ethylene glycol and glycerol).

One of the most widely used empirical equations for liquid diffusion coefficients is the Wilke-Chang equation (22).

$$D = \frac{7.4 \times 10^{-8} (\chi M_b)^{1/2} T}{\eta V_a^{0.6}} \qquad (1)$$

Olander (13) has shown, however, that this equation is not valid for water as the solute. He found that experimental diffusion coefficients for water in organic liquids are lower than those predicted by the Wilke-Chang equation by a factor of 2.3. This is equivalent to increasing the molar volume of the solute, V_a, used in the equation by a factor of 4 and Olander suggested that water in solution might be present in associated form as $(H_2O)_4$. Whether this is so or not, the modification proposed by Olander is at present the main empirical method for the prediction of the diffusion coefficient of water in solvents.

Another equation for the diffusion coefficient of water in organic liquids (17) appears to give values similar to those predicted by Olander.

The experimental data quoted by Olander were limited, consisting of four alcohols, a ketone, an aldehyde, an ester, an amine, and ethylene chlorohydrin. Although some additional data are available, these are predominantly for alcohols and there is a total lack of data on certain classes of compound, such as halogenated hydrocarbons, organic acids, and nitro compounds, while other classes, such as hydrocarbons, are poorly represented.

The work described in this paper was undertaken to provide experimental data for a wider range of compounds.

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EXPERIMENTAL APPARATUS, METHOD, AND RESULTS

The diffusion coefficient of water in organic liquids close to zero concentration has been measured for ten compounds which have not apparently been investigated previously and also for ethanol as a check on the experimental technique (15).

The apparatus used was the diaphragm cell as described by Stokes (19, 20). The cell consists of two glass compartments placed vertically one above the other and separated by a sintered glass diaphragm. The liquid in the two compartments is kept perfectly mixed and the diffusion through the diaphragm is measured.

In the cell used by Stokes large-bore liquid connections with rubber stoppers were used on the two compartments, whereas in the present cell these connections consisted of capillary tubes, as described by Dullien and Shemilt (3). The diaphragm was a sintered glass disk (supplied by Gallenkamp, London), 40 mm in diameter and 2.2 mm thick, porosity 4 and average pore size 15 microns. The volumes of the upper and lower compartments and of the pores were 55.8, 55.9, and 0.33 cm³, respectively. The cell was used with the diaphragm horizontal and stirring was effected using small glass rods with iron wire sealed in, which were rotated by a horseshoe magnet. These stirring rods were designed so that the rod in the upper compartment sank, while that in the lower compartment floated and both, when rotated, swept the surface of the diaphragm. The whole apparatus was held in a thermostatic bath maintained at 25° ± 0.1°C. The time required for a single run varied between about 24 and 72 hours.

The diffusion coefficient in this type of cell is obtained by determining the concentrations of the liquids in the two compartments before and after a run. The diffusion coefficient measured is the integral diffusion coefficient, $\bar{D}$, defined by the equation

$$\bar{D} = \frac{1}{\beta t} \ln \frac{\Delta c_o}{\Delta c_f} \qquad (2)$$

The definition of this diffusion coefficient has been discussed by Stokes (20).

The cell was calibrated using a 0.1N solution of KCl in water, for which the diffusion coefficient, as given by Stokes (19), is 1.87×10^{-5} cm² per second, and the cell constant, β, was calculated from Equation 2. Since the stirrers caused wear of the diaphragm, the cell constant was determined again at intervals and values required for runs with organic-water systems were obtained by interpola-

Table I. Experimental Diffusion Coefficients of Water in Organic Liquids at 25° C

Liquid	Water concn (max value), wt %	Experimental diffusion coefficient, cm²/sec	No. of measurements	Scatter of measurements, %
Ethanol	2.3	1.24×10^{-5}	4	± 2.5
Toluene	0.04	6.19	2	± 0.8
Methylene chloride	0.13	6.53	3	± 0.5
1,1,1-Trichloroethane	0.05	4.64	1	...
Trichloroethylene	0.02	8.82	2	± 2.0
1,1,2,2-Tetrachloroethane	0.04	3.82	3	± 0.5
2-Bromo-2-chloro-				
1,1,1-trifluoroethane	0.03	8.85	2	± 1.3
Nitrobenzene	0.20	2.80	3	± 0.4
n-Butyl acetate	0.60	2.87	2	± 2.2
n-Butyric acid	0.51	0.79	4	± 3.0
Pyridine	0.52	2.73	3	± 0.7

tion. The change in the cell constant between the first and the last experiments was about 8%.

The concentration of water in the organic liquid was determined by the Karl Fischer method. Concentrations were measured in both the upper and lower compartments before and after a run and a mass balance check was carried out. Run times were chosen so as to give a value of the ratio $\Delta c_o / \Delta c_f$ in excess of 1.2.

Distilled water and analytical grade chemicals were used without further purification. The liquids were degassed using vacuum from the tap and care was taken to prevent pickup of moisture from the atmosphere.

For a given cell, there is a critical stirring rate below which the liquid in the two compartments is not completely mixed and inaccurate values of the diffusion coefficient are obtained. For the cell used, this stirring rate was 35 r.p.m. and the experiments were done using a rate in excess of this.

Surface diffusion in the diaphragm is a possible source of error in this type of apparatus. This was investigated for electrolyte systems by Stokes (19). For the system in which the error was greatest, the potassium bromide-water system, he observed a maximum error of about 5% at the minimum concentration used, which was 0.0025N.

As a check on the experimental method, the diffusion coefficient of water in ethanol was determined. The value is 1.24×10^{-5} cm² per second, which agrees closely with that obtained by Dullien and Shemilt (3). This system was used to determine the critical stirring rate.

The experimental diffusion coefficients for the other systems are given in Table I. The value quoted for 1,1,1-trichloroethane is based on only one measurement and should be treated with reserve. The theoretical probable error of the determination, calculated from the assumed accuracy of the analytical method, depends on the water concentrations used and thus on the solubility of water in the liquids. This error was estimated to be $\pm 12\%$ for toluene and trichloroethylene, $\pm 7\%$ for 1,1,2,2-tetrachloroethane and 2-bromo-2-chloro-1,1,1-trifluoroethane, and less than $\pm 2\%$ for the other liquids, but since the

observed scatter is mostly less than this, the accuracy of the analyses may have been better than that assumed.

EFFECT OF DISSOLVED INERT GAS

Gross (7) has shown that the diffusion coefficient of water in an organic liquid is reduced if the liquid is saturated with inert gas. He investigated the diffusion of water in Shell oil K8, both degassed and saturated with nitrogen, and in paraffin oil, both degassed and saturated in one case with nitrogen and in another with argon. The partial pressure of the saturating gas was 740 mm Hg. The experimental results are given in Table II.

Also shown in this table are the results of an experiment by the authors in which the diffusion coefficient of water in pyridine saturated with nitrogen at atmospheric pressure was measured. Two measurements were made on the saturated liquid and the deviation was $\pm 0.13\%$.

The reduction in the diffusion coefficient of water due to the presence of dissolved gas for the four cases given in the table is 69, 40, 40, and 31%, respectively.

This effect cannot be attributed simply to disengagement of gas in the diaphragm pores, because Gross did not use a diaphragm cell, but an unsteady-state method in which the diffusion of water in a bulk liquid is measured.

DISCUSSION AND CONCLUSIONS

The experimental values of the diffusion coefficient of water in organic liquids measured by the present and by previous authors are shown in Table III. The first value given for each compound is that believed by the present authors to be most accurate and for this case the values predicted by the Wilke-Chang and Olander equations are also given.

In using the Wilke-Chang equation it is necessary to know the association parameter, χ, but for many liquids values of this parameter are not available. In the present case the value has been taken as 1.9 for methanol and

Table II. Effect of Dissolved Inert Gas on Diffusion Coefficient of Water in Organic Liquids

Liquid	Temp, ° C	Water concn, wt % (max value)	Dissolved gas	Experimental diffusion coefficient, cm²/sec	Reference
Shell oil K8	20	≈ 0	None	7.8×10^{-5}	(7)
		≈ 0	Nitrogen	2.4	(7)
Paraffin oil	20	≈ 0	None	15	(7)
		≈ 0	Nitrogen	9	(7)
		≈ 0	Argon	9	(7)
Pyridine	25	0.52	None	2.73	This work
		0.85	Nitrogen	1.88	This work

Table III. Comparison of Experimental and Predicted Diffusion Coefficients of Water in Organic Liquids at 25°C and Infinite Dilution

Liquid	Temp, °C	Water concn (max value), vol %	Liquid viscosity, cp	Experimental cm²/sec × 10⁵	Diffusion coefficient Reference	Wilke-Chang, cm²/sec × 10⁵	Olander, cm²/sec × 10⁵
Methanol	15	0.5	0.66	1.75	(10)	4.35	1.89
	20	≈0	...	2.2	(21)	...	...
Ethanol	25	0ᵃ	1.15	1.22	(3)	2.75	1.20
	15	0.5	...	1.02ᵇ	(10)	...	...
	20	≈0	...	0.85	(21)	...	...
	25	0ᵃ	...	2.3	(18)	...	...
	25	0ᵃ	...	1.13	(8)	...	...
	25	2.3 wt %	...	1.24	This work	...	...
1-Propanol	15	0.5	2.70	0.61	(10)	1.61	0.50
	20	≈0	...	0.5	(21)	...	...
2-Propanol	15	0.5	2.65	0.38ᵇ	(10)	1.18	0.51
	20	≈0	...	0.5	(21)	...	...
1-Butanol	25	≈0	2.60	0.56	(4)	1.26	0.55
	30	3.5 wt %	...	1.24ᵇ	(14)	...	...
Isobutanol	15	0.5	4.7	0.30ᶜ	(10)	0.67	0.29
	20	6	...	0.36	(11)	...	...
Benzyl alcohol	20	0ᵃ	6.5	0.372	(6)	0.60	0.26
Ethylene glycol	20	0ᵃ	21	0.180	(6)	0.14	0.061
	25	0.8 wt %	...	0.243	(2)	...	...
Triethylene glycol	30	0.5 wt %	30	0.191	(12)	0.352	0.153ᶜ
Propane-1,2-diol	20	0ᵃ	56	0.075	(6)	0.058	0.025
2-Ethylhexane-1,3-diol	20	0ᵃ	320	0.019	(6)	0.014	0.0061
Glycerol	20	0ᵃ	1500	0.0083	(6)	0.0024	0.0010
Acetone	25	3 molar %	0.33	4.56ᵇ	(1)	8.80	3.72
Furfuraldehyde	20	3	1.64	0.90ᶜ	(11)	2.24	0.97
Ethyl acetate	20	3	0.47	3.20ᵇ	(11)	7.48	3.25
Aniline	20	2	4.4	0.70ᵇ	(11)	0.82	0.36
n-Hexadecane	20	≈0	3.45	3.76ᵈ	(16)	1.63	0.71
n-Butyl acetate	25	0.6 wt %	0.67	2.87	This work	6.12	2.66
n-Butyric acid	25	0.51 wt %	1.41	0.79	This work	2.53	1.10
Toluene	25	0.04 wt %	0.55	6.19	This work	6.63	2.88
Methylene chloride	25	0.13 wt %	0.41	6.53	This work	8.64	3.75
1,1,1-Trichloroethane	25	0.05 wt %	0.78	4.64	This work	5.65	2.46
Trichloroethylene	25	0.02 wt %	0.55	8.82	This work	7.87	3.42
1,1,2,2-Tetrachloroethane	25	0.04 wt %	1.63	3.82	This work	3.04	1.32
2-Bromo-2-chloro-1,1,1-trifluoroethane	25	0.03 wt %	0.61	8.85	This work	8.71	3.79
Nitrobenzene	25	0.20 wt %	1.84	2.80	This work	2.29	1.00
Pyridine	25	0.52 wt %	0.88	2.73	This work	3.83	1.6

ᵃ Value obtained by extrapolation to zero concentration. ᵇ Value quoted by Olander. ᶜ Value quoted by original authors. ᵈ Value calculated by extrapolation from original author's data at 25° and 30° C.

1.5 for ethanol, as given by Wilke and Chang, as 1.2 for 1- and 2-propanol, and as 1.0 for all the other liquids.

Some of the data are fitted by the Wilke-Chang equation, some by the Olander equation and some by neither. If a compound of a particular type tends to fit one of the equations, other compounds of the same type tend to fit the same equation. The data for the higher viscosity alcohols are an exception to this, in that the experimental values start off intermediate between those predicted by the two equations and rise to values greater than those predicted by the Wilke-Chang equation, suggesting that at high viscosities the viscosity correction overcompensates.

The compounds which fit the Wilke-Chang equation are broadly those in which water is very insoluble, while those which fit the Olander equation are those in which it is somewhat more soluble. However, the solubility of water in aniline is relatively high, but it is fitted by the Wilke-Chang equation.

The self-diffusion coefficient for water fits the Wilke-Chang rather than the Olander equation. The experimental value given by Jones et al. (9) is 2.22×10^{-5} cm² per second at 25° C and that predicted by the Wilke-Chang equation, using a value of 2.6 for the association parameter, is 2.98×10^{-5} cm² per second.

No explanation is offered for the experimental results obtained, but it is hoped that these additional data will be useful in the development of methods for the prediction of the diffusion of water in organic liquids.

NOMENCLATURE

D = diffusion coefficient, cm² per second
$\bar{D}$ = integral diffusion coefficient, defined by Equation 2, cm² per second
M = molecular weight
t = time, seconds

T = temperature, °K
V = molar volume of liquid at normal boiling point, cm³ per gram mole
β = cell constant, cm⁻²
Δc = difference in concentration between cell compartments, grams/liter
η = viscosity of solution, centipoises
χ = association parameter of solvent

Subscripts

a = solute
b = solvent
o = initial
f = final

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Surface Tension of Aqueous Solutions of Some Glycols

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The surface tensions of aqueous solutions of ethylene glycol, 1,2-propanediol, 1,3-propanediol, 1,3-butanediol, and 1,4-butanediol were measured at 30° C. A correlation between the surface tension of pure glycols and the volume contraction in an aqueous solution is presented.

As part of a thermodynamic study on aqueous solutions of alcohols and glycols (4, 5), the surface tensions of aqueous solutions of five glycols were measured at 30.00° C and are reported. This paper also calls attention to the fact that the surface tension of a pure glycol parallels the volume contraction of the same glycol in aqueous solution reported previously (5).

EXPERIMENTAL

The samples used were of G. R. grade JIS (Japan Industrial Standard) guaranteed reagent and were purified further by dehydrating over anhydrous salts such as Na₂SO₄ and distilling repeatedly with a fractionating column until their gas chromatogram (polyethylene glycol as column and H₂ as carrier gas) showed minimum impurities (probably isomeric glycols). Estimated purity was 99.8%. The densities of the final purified liquids were practically the same as those given in our previous report (4, 5).

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The capillary height method (2) was used throughout the surface tension measurements. The uniformity in the inner diameter of capillaries was checked by measuring the length of a known amount of mercury in the capillary. Since by the conventional single capillary method it is difficult to determine the position of meniscus of free surface accurately, we adopted the two-capillary method, a modification credited to Sugden (7) and Richards et al. (6). The diameters of capillaries were 0.50 and 0.27 mm. The height of capillary rise was determined with a traveling microscope. All the measurements were made in a thermostat controlled to ±0.01° C. The accuracy of surface tension determination was estimated to be ±0.3 dyn/cm.

RESULTS AND DISCUSSION

In Table I are given the data for the surface tension of aqueous solutions of five glycols: ethylene glycol (12ED), 1,2-propanediol (12PD), 1,3-propanediol (13PD), 1,3-butanediol (13BD), and 1,4-butanediol (14BD).