Diffusivity of Water in Organic Solvents

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Recently Olander (*2*) has rightly pointed out that all available correlations for liquid diffusivities fail when one needs diffusivity of water in organic solvents. Both Wilke-Chang (*4*) correlation and the correlation proposed by Ibrahim and Kuloor (*1*) are in error only in the case of diffusion of water in organic solvents by factors ranging from 1.5 to 2.5. In an attempt to explain this discrepancy Olander (*2*) proposed a polymerisation hypothesis of the nature $4\,H_2O \rightleftharpoons (H_2O)_4$, assuming a constancy factor of 2.3 for the correlated diffusion coefficients owing to Wilke-Chang and experimental diffusion coefficients of water in organic solvents.

Ibrahim and Kuloor (*1*) have proposed a modified Schmidt group $N'_{Sc}\left(=\frac{\mu V_m}{D}\right)$ for evaluating liquid and gaseous diffusion coefficients. Making use of N'_{Sc} one can correlate the diffusion coefficients of water in organic solvents with reasonable accuracy. In this proposed correlation the use of the Olander constancy factor of 2.3 for correcting the correlation owing to Wilke-Chang method is avoided. This method differs from the earlier method of Ibrahim and Kuloor (*1*) inasmuch as it takes into consideration viscosity of solvents instead of molecular weight-surface tension factors. The method proposed here is exclusively for water in organic solvents. For other systems our earlier correlation (*1*) can be employed.

As pointed out by Olander (*2*) a specific treatment is needed for the diffusion of water into organic solvents. In cases of similar nature the present approach may help to evaluate the diffusion coefficients, and it is hoped that this method may throw some light on the theory of diffusion.

METHOD

N'_{Sc} for water in different solvents are plotted against viscosity (centipoise) of solvents (Figure 1). A perfect straight line is obtained, from which the following equation is derived:

$$D_w = \frac{\mu\, V_m}{131.5\, \eta} \qquad (1)$$

Substituting the values for viscosity of water vapor (9.6×10^{-5} poise) and molecular volume (18.8 cc./g. mole) for the same in Equation (1) one gets for this particular case

$$D_w = \frac{1.37 \times 10^{-5}}{\eta} \qquad (2)$$

which gives the value of D_w fairly accurately for most of the systems given by Olander (*2*). There are deviations in four cases for which the following explanations are given.

n-BUTANOL

The experimental values of D_w in isobutanol and *n*-butanol are 0.36×10^{-5} and 1.24×10^{-5}, respectively (*2*). This large difference in diffusivity of water in the isomers is inexplicable, since both have the same physical properties except viscosity. Wilke-Chang (*4*) method gives the value 0.81×10^{-5} and 1.43×10^{-5} respectively. The relative proportion or difference seems reasonable in view of the difference in viscosity. Applying Olander's correlation factor 2.3 one gets $1.43/2.3 \times 10^{-5} = 0.62 \times 10^{-5}$ which compares well with the value by the proposed correlation, which is 0.53×10^{-5}. This casts doubt in the reported experimental value of D_w in *n*-butanol. Olander (*3*) also expresses the view that the experimental value of *n*-butanol may be wrong.

ANILINE

By a similar reasoning the deviation of D_w in aniline can be explained. By applying 2.3 factor to Wilke-Chang value one gets $0.83/2.3 \times 10^{-5} = 0.36 \times 10^{-5}$ which compares well with the value by the proposed correlation, which is 0.37×10^{-5}. In the above two cases Olander's hypothesis also fails. This clearly points out that the experi-

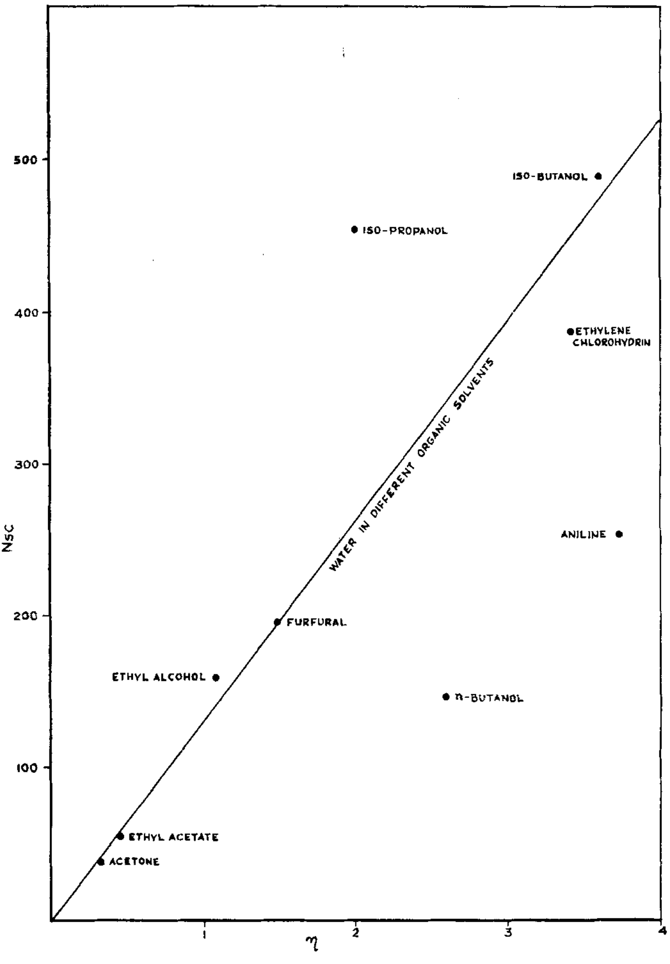

Fig. 1. Diffusivities of water in different organic solvents.

TABLE 1. D_w IN ORGANIC SOLVENTS

No.	Solvent	Diffusion coefficient × 10^5, 25°C. (exptl)*	N'_{Sc}	Viscosity of solvent at 25°C., centipoise	$D \times 10^5$ (4)	$D_o \times 10^5$	$D_w \times 10^5$ (present work)	Deviation, % †	Deviation, % ††
1.	Acetone	4.56	39.5	0.32	8.50	3.70	4.30	5.7	18.8
2.	Ethyl acetate	3.26	55.4	0.45	7.52	3.27	3.06	6.1	3.1
3.	Ethyl alcohol	1.13	160.0	1.10	2.58	1.12	1.24	9.7	0.8
4.	Furfural	0.92	197.0	1.49	2.14	0.93	0.92	0.0	1.1
5.	Iso propanol	0.39	457.0	2.00	0.99	0.43	0.68	—	10.3
6.	n-butanol	1.22	147.5	2.60	1.43	0.62	0.53	—	—
7.	Ethylene chlorhydrin	0.46	388.0	3.43	1.20	0.52	0.40	13.0	13.0
8.	Iso-butanol	0.37	492.0	3.60	0.81	0.35	0.38	2.7	5.4
9.	Aniline	0.71	253.0	3.75	0.83	0.36	0.36	—	—
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10.	Methanol	—	72.0	0.56	5.27	2.30	2.50	8.7	
11.	Diethyl ether	—	27.0	0.23	14.17	6.16	6.60	7.1	
12.	Benzene	—	79.0	0.61	5.48	2.38	2.28	4.2	

* The experimental values of diffusion coefficients were taken from (2). All the values were corrected to 25°C.

** Deviation of D_w from the D_o values.

† Deviation of D_w from the experimental values.

† † Deviation of D_o from the experimental values.

mental values in the cited cases may not be reliable.

ETHYLENE CHLORHYDRIN

The deviation for ethylene chlorhydrin is explained by the fact that the reported experimental value is for 80% water and not for infinite dilution. Hence the deviation is due to the concentration effect. If one considers the viscosity of solution (2.95) instead of viscosity of solvent, one gets $D_w = 0.46 \times 10^{-5}$ which is exactly the experimental value.

ISO PROPANOL

Applying Olander's correction to Wilke-Chang value for this case one gets $0.99/2.3 \times 10^{-5} = 0.43 \times 10^{-5}$ which differs from the value calculated from the proposed correlation by 36% (0.68×10^{-5}). The reported experimental value is 0.38×10^{-5} with 0.5% water as solute.

The calculated values from Equation (2) are given in Table 1. They agree fairly well with the experimental values except in the cases discussed above. For comparison three more systems which were not given by Olander were chosen. The values in respect of these were calculated by the present method and compared with the method of Wilke-Chang and Wilke-Chang method corrected by Olander's constant. The values calculated from present correlation are in agreement with the values obtained by the Wilke-Chang correlation with the correction factor of Olander (D_o).

NOTATION

μ = viscosity of solute (water) vapor, poise

V_m = molecular volume of solute

D_w = diffusivity of water in organic solvents

η = viscosity of solution, centipoise

D_o = diffusion coefficient of Reference 4 as corrected by Olander

D = diffusion coefficient as calculated by Wilke-Pin Chang equation

N'_{Sc} = modified Schmidt group $[= (\mu V_m)/(D)]$

LITERATURE CITED

1. Ibrahim, S. H., and N. R. Kuloor, *Brit. Chem. Eng.*, **5**, 795 (1960).
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Isothermal Diffusion with a Variable Density

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For ordinary isothermal binary diffusion with composition dependent density, the diffusion equation can be written for two-dimensional flow as (*1*)

$$\rho\left[\frac{\partial w}{\partial \theta} + u\frac{\partial w}{\partial x} + v\frac{\partial w}{\partial y}\right] = D\left[\frac{\partial}{\partial y}\left(\rho\frac{\partial w}{\partial y}\right) + \frac{\partial}{\partial x}\left(\rho\frac{\partial w}{\partial x}\right)\right] \tag{1}$$

This equation is valid for ideal solutions (that is perfect gas mixtures) for both laminar and turbulent flow, and the diffusivity D is essentially independent of composition. When one considers a perfect gas mixture, the density is given by

$$\rho = \frac{pM}{Rt} \tag{2}$$

and M is related to w by

$$\frac{1}{M} = Bw + \frac{1}{M_2} \tag{3}$$

where $B = 1/M_1 - 1/M_2$. Thus, using Equations (2) and (3), one may write

$$\rho\frac{\partial w}{\partial i} = \frac{pM}{Rt}\left(-\frac{1}{BM^2}\right)\frac{\partial M}{\partial i} = -\frac{p}{BRt}\frac{\partial \ln M}{\partial i} \tag{4}$$

By using Equation (4) with t constant, Equation (1) can be rewritten as

$$p\left[\frac{\partial \ln M}{\partial \theta} + u\frac{\partial \ln M}{\partial x} + v\frac{\partial \ln M}{\partial y}\right] = D\left[p\frac{\partial^2 \ln M}{\partial y^2} + \frac{\partial}{\partial x}\left(p\frac{\partial \ln M}{\partial x}\right)\right] \tag{5}$$

since p is independent of y. Except when the pressure gradient $\partial p/\partial x$ is a significant part of the absolute pressure in systems where longitudinal diffusion is important, Equation (5)can be reduced to

$$\frac{\partial \ln M}{\partial \theta} + \bar{u} \cdot \nabla \ln M = D\nabla^2 \ln M \tag{6}$$

This equation is valid for laminar or turbulent flow with variable density, except for the unusual case of a strong pressure gradient coupled with longitudinal diffusion. Equation (6) was first derived, although somewhat differently, by Bedingfield and Drew (2). With $\ln M = r$, Equation (6) becomes

$$\frac{\partial r}{\partial \theta} + u\frac{\partial r}{\partial x} + v\frac{\partial r}{\partial y} = D\left[\frac{\partial^2 r}{\partial y^2} + \frac{\partial^2 r}{\partial x^2}\right] \tag{7}$$

To obtain exact solutions to isothermal, variable density mass transfer problems