Applications of holdup data to explain the effect of diffusivity on the vaporization of liquids in packings and to estimate effective interfacial areas for mass transfer have been outlined.

ACKNOWLEDGMENT

NOTATION

a = effective interfacial area, sq. ft./cu.ft.

c = constant in Equation (5)

D = diffusivity of solute in gas, sq. ft./hr.

D_p = diameter of sphere possessing the same surface area as a piece of packing, ft.

G = superficial gas rate, lb./(hr.)(sq.ft.)

h_o = operating holdup, cu.ft./cu.ft.

h_s = static holdup, cu.ft./cu.ft.

h_t = total holdup, cu.ft./cu.ft.

k_G = gas-phase mass transfer coefficient, lb. moles/(hr.)(sq. ft.)(atm.)

$k_G a$ = gas-phase mass transfer coefficient, lb. moles/(hr.)(cu. ft.)(atm.)

L = superficial liquid rate, lb./(hr.)(sq.ft.)

m = constant in Equation (5)

M_M = mean molecular weight of gas, lb./lb. mole

n = constant in Equation (5)

P_{BM} = mean partial pressure of inert gas in the gas phase, atm.

Greek Letters

μ = liquid viscosity, centipoises

= gas viscosity, lb./(hr.)(ft.)

ρ = liquid density, g./ml.

= gas density, lb./cu.ft.

σ = surface tension, dynes/cm.

ε = void fraction, cu. ft./cu.ft.

Subscripts

w = for water systems

abs = for absorption work without a chemical reaction

vap = for vaporization work

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Parts I and II presented at the A. I. Ch. E. Springfield meeting, Part III at the New York meeting.

CORRELATION OF DIFFUSION COEFFICIENTS IN DILUTE SOLUTIONS

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The diffusion coefficient is normally defined and assumed in this study to be the proportionality constant in the rate equation written for undirectional mass transfer as follows:

$$N_A = - D \frac{dC_A}{dz} \quad (1)$$

Equation (1) is strictly applicable in ideal dilute solutions in which convective transport due to volume changes on mixing is negligible, and in which other possible modes of mass transfer are not operative. This paper represents an attempt to generalize the relation of D to conveniently available properties of dilute solutions so as to permit estimation of diffusion coefficients for engineering purposes.

PREVIOUS CORRELATION

In the earlier paper by Wilke (10) a method of correlating diffusion coefficients was proposed on the basis of qualitative conclusions of the Eyring theory(3) and the Stokes-Einstein relation. It was shown that the group $T/D\eta$, designated as the diffusion factor F, was essentially independent of temperature for available systems. Furthermore F could be represented as a smooth function of molal volume for diffusion of various solutes in a given solvent. In general it was assumed that this function extrapolated into the Stokes-Einstein equation at very large solute molal volumes.

DEVELOPMENT OF NEW CORRELATION

Sources of Data. At the time of the previous work so few data were available for diffusion of single solutes in a variety of solvents that the effect of solvent properties, could not be brought into a general correlation. In a special effort to obtain suitable data of this kind a companion experimental study (2) was conducted involving the diffusion of iodine and toluene in a wide variety of hydrocarbon

FIG. 1. DIFFUSION IN WATER.
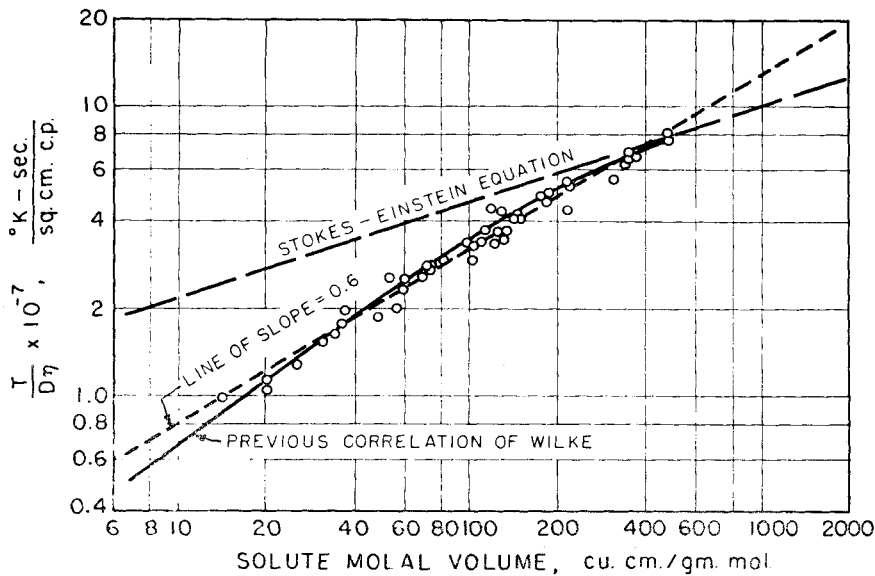
solvents ranging from hexane through tetradecane. Data were also obtained for diffusion of organic acids in several solvents. These new data were supplemented by certain other data from the literature, including all the data reported in the previous paper(*10*), to provide a basis for the present development. All data which supplement those presented in Tables 2 through 5 of reference(*10*) are presented in Table 1.
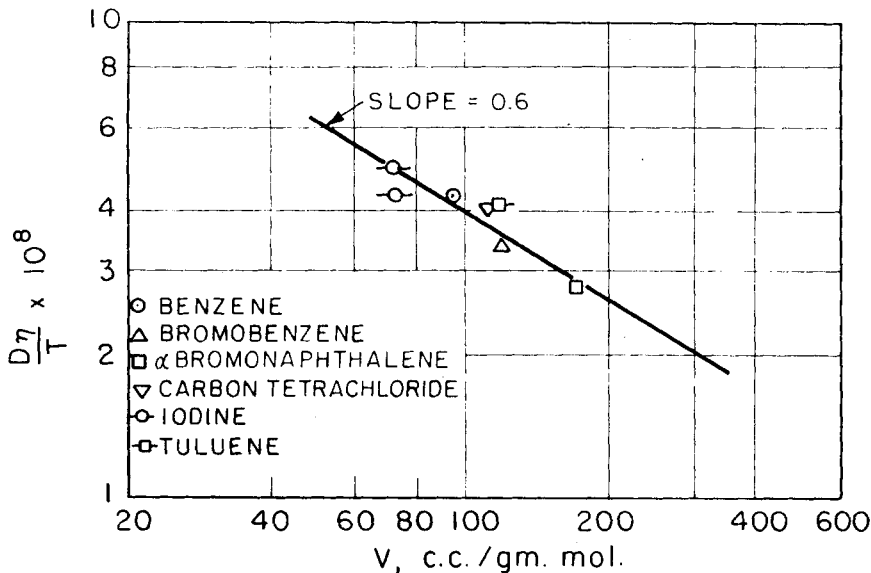

FIG. 2. DIFFUSION IN HEXANE.

Effect of Solute Molal Volume. Figure 1 shows the diffusion as a function of molal volume for various solutes in water based on data from Table 2 of reference *10*. Molal volumes used throughout this work are values at the normal boiling point estimated for complex molecules by the atomic contributions of LeBas(*1, 6*) as summarized in Table 2.

As indicated in Figure 1, F is a smooth function of molal volume having a log-log slope of about 0.7 at low molal volumes and apparently merging smoothly with the
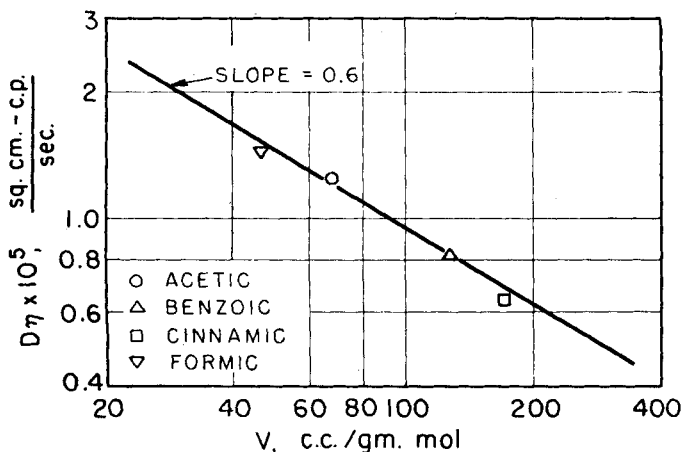

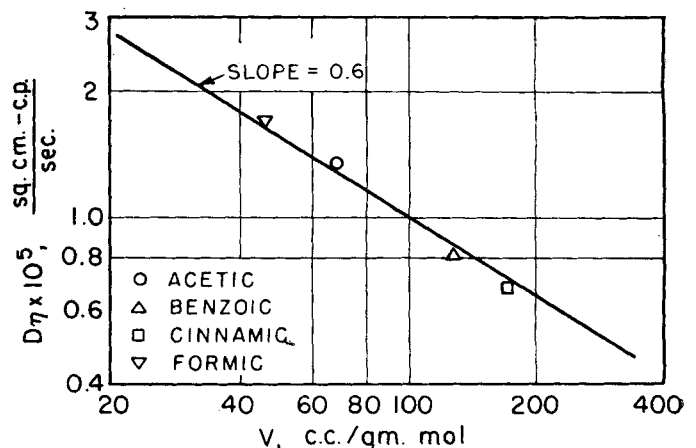FIG. 3. DIFFUSION OF ORGANIC ACIDS IN TOLUENE.

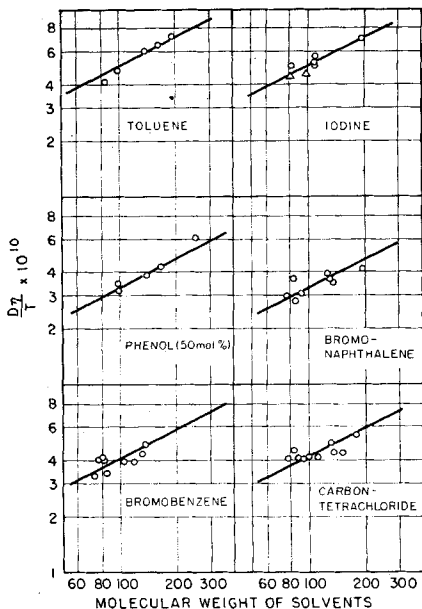FIG. 4. DIFFUSION OF ORGANIC ACIDS IN CARBONTETRACHLORIDE.

FIG. 5. EFFECT OF SOLVENT MOLECULAR WEIGHT.

Stokes-Einstein equation which requires a slope of 1/3 at high molal volumes. On the assumption that molecules are spherical with a radius equal to $(3V/4\pi N)^{1/3}$ the Stokes-Einstein equation may be written as follows:

$$\frac{T}{D\eta} = 1.004 \times 10^7 \, V^{1/3} \quad (2)$$

Equation (2) is shown as a dotted line on Figure 1. The general behavior of the curve of Figure 1 relative to the Stokes-Einstein equation constitutes reasonable evidence in favor of the proposed method of correlation.

Over the middle range of molal volumes the curve of Figure 1 may be satisfactorily represented by a line of slope 0.6. Bearing in mind the theoretical limitations of the assumption it is convenient to assume that the diffusion factor is proportional to $V^{0.6}$ over the middle range. The proportionality of $D\eta$ to $V^{0.6}$ was used by Thakar and Othmer (8) in their representation of the correlation for diffusion of substances in water.

To explore the molal volume effect in nonaqueous systems several solvents were studied as shown in Figures 2 through 4. The group $D\eta/T$ may be represented satisfactorily as proportional to $V^{0.6}$. It is therefore a fair generalization that $D\eta/T$ is proportional to $V^{0.6}$ in the medium molal volume

TABLE 1.—DIFFUSION DATA FOR VARIOUS SYSTEMS

(Supplementary to Tables 2 to 5 of reference 10)

Solute	Solvent	Temperature, °C.	$D\times10^5$ sq. cm./sec. (obs.)	$D\times10^5$ sq. cm./sec. (calc.)	Ref.
Acetic acid	Acetone	40.0	4.044	3.49	a
		25.0	3.309	2.85	
		15.0	2.916	2.51	
	Benzene	25.0	2.081	1.74	a
		5.9	1.587	1.22	
	Carbon tetrachloride	6.5	1.151	1.13	a
		14.8	1.267	1.32	
		25.0	1.490	1.58	
		40.0	1.780	2.04	
	Toluene	25.0	2.265	2.00	a
		15.0	1.905	1.72	
		6.8	1.661	1.48	
i-Amyl alcohol	Ethyl alcohol	20.0	0.78	0.85	b
Aniline	Ethyl alcohol	18.5	2.70	2.41	c
Benzene	Bromobenzene	7.5	1.02	1.20	d
	Chloroform	15.0	3.70	2.54	e
	n-Hexane	15.0	3.70	3.85	e
Benzoic acid	Acetone	13.2	2.368	1.66	a
		25.0	2.622	1.89	
		40.0	3.054	2.19	
	Benzene	15.0	1.170	0.95	a
		25.0	1.379	1.13	
		40.0	1.762	1.44	
	Carbon tetrachloride	14.8	0.776	0.87	a
		25.0	0.908	1.04	
		40.5	1.168	1.36	
	Toluene	16.0	1.289	1.16	a
		25.0	1.493	1.34	
		40.0	1.851	1.65	
Benzo-trichloride	Toluene	7.6	1.32	1.29	d
Bromobenzene	Benzene	7.3	1.41	1.29	d
	Cyclohexane	7.3	0.90	0.91	d
	m-Cymene	7.3	1.34	1.18	d
	Ethyl benzene	7.3	1.44	1.55	d
	Ethl ether	7.3	3.50	3.80	d
	n-Hexane	7.3	2.60	3.02	d
	Mesitylene	7.3	1.31	1.54	d
	Transdecalin	7.3	0.47	0.48	d
	m-Xylene	7.3	1.52	1.69	d
Bromform	Acetone	20.0	2.74	3.22	f
	Benzene	20.0	1.77	1.88	f
	Ethyl alcohol	20.0	0.97	0.96	b
Bromonaphthalene	Ethyl alcohol	20.0	0.76	0.72	b
a–Bromo-naphthalene	Benzene	7.3	1.04	1.05	d
	Cyclohexane	7.3	0.85	0.72	d
	Decalin	7.3	0.34	0.39	d
	Dibenzyl ether	7.3	0.149	0.17	d
	n-Hexane	7.3	2.15	2.44	d
	a–Methyl naphthalene	7.5	0.226	0.22	d
	Tetralin	7.5	0.36	0.38	d
	Toluene	7.5	1.24	1.31	d
m-Bromotoluene	Toluene	7.4	1.52	1.48	d
Carbon tetrabromide	Benzene	7.3	1.12	1.27	d
Carbon tetrachloride	Benzene	25.0	2.00	1.87	g
	Carbon tetrachloride	25.0	1.41	1.74	j
	Cyclohexane	25.0	1.49	1.32	g
	Decalin	25.0	0.776	0.733	g
	Dioxane	25.0	1.02	1.01	g
	n-Heptane	25.0	3.17	3.25	g
	n-Hextane	25.0	3.70	3.71	g
	Isooctane	25.0	2.57	2.86	g
	Kerosene	25.0	.961	1.03	g
	Tetralin	25.0	0.735	.735	g
	Toluene	25.0	2.19	2.22	g
Cinnamic acid	Acetone	25.0	2.41	2.51	a
	Benzene	25.0	1.21	0.99	a
	Carbon tetrachloride	25.0	0.755	0.91	a
	Toluene	25.0	1.18	1.14	a
Ethyl benzoate	Acetone	20.0	2.47	2.29	h
	Benzo trichloride	20.0	0.52	0.58	h
	Ethyl acetate	20.0	1.85	2.01	h
	Nitrobenzene	20.0	0.60	0.51	h

Ethylene bromide	Ethylene chloride	7.3	1.11	1.31	*d*
Formic acid	Acetone	25.0	3.768	3.59	*a*
		18.5	3.274	3.12	
		6.5	3.132	2.87	
	Benzene	6.2	1.991	1.48	*a*
		13.9	2.306	1.76	
		25.0	2.577	2.14	
	Carbon tetrachloride	8.5	1.612	1.48	*a*
		25.0	1.888	2.01	
		15.0	1.673	1.67	
	Toluene	6.2	2.285	1.90	*a*
		14.1	2.463	2.32	
		25.0	2.646	2.54	
n-Heptyl bromide	Heptane	7.4	1.52	1.48	*d*
n-Hexyl bromide	Hexane	7.6	2.31	2.54	*d*
Iodine					
	Carbon tetrachloride	25.0	1.50	2.30	*i*
	Cyclohexane	15.0	1.54	1.19	*a*
	Dioxane	25.0	1.07	1.31	*i*
	Ethyl alcohol	40.0	1.772	1.72	*a*
		25.0	1.316	1.32	*a*
	Heptane	25.0	3.42	4.60	*i*
	Hexane	25.0	4.05	4.96	*i*
	n-Hexane	25.0	4.24	4.37	*a*
Iodine	Methyl cyclohexane	40.0	2.71	2.74	*i*
		30.0	2.30	2.28	*i*
	n-Octane	15.0	2.43	3.04	*a*
	n-Tetradecane	25.0	0.96	1.14	*a*
Iodobenzene	Benzene	7.3	1.35	1.31	*d*
Methyl iodide	Toluene	7.4	2.23	2.40	*d*
	Methylene chloride	7.5	2.06	2.54	*d*
Nitrobenzene	Acetone	20.0	2.94	2.83	*h*
	Ethyl benzoate	20.0	0.73	0.66	*h*
	Ethyl acetate	20.0	2.25	2.48	*h*
n-Octyl bromide	Octane	7.5	1.46	1.42	*d*
Pyridine	Ethyl alcohol	20.0	1.12	1.00	*b*
1, 2, 4, 5–Tetra-chlorobenzene	Benzene	7.6	1.24	1.03	*d*
1, 2, 4–Trichloro-toluene	Benzene	7.6	1.34	1.12	*d*
Toluene	*n*-Decane	25.0	2.09	1.77	*a*
	n-Dodecane	25.0	1.38	1.19	*a*
	n-Heptane	40.0	4.33	4.08	*a*
		25.0	3.72	3.35	*a*
		6.9	2.95	2.56	*a*
	n-Hexane	25.0	4.21	4.13	*a*
	n-Tetradecane	25.0	1.02	0.86	*a*

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*b*International Critical Tables 5, 63-75 (1929).

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*h*Dummer, E., *Z. anorg. u. allgem. Chem.*, **109**, 49 (1919).

*i*Stokes, R. H., P. J. Dunlop, and J. R. Hall., *Trans. Faraday Soc.*, **49**, 886 (1953).

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range for both aqueous and non-aqueous solvents. However, it must be recognized that special structural features of molecules and other molecular interactions may be important in certain cases and that therefore the proposed relationship is at best an oversimplification utilized to obtain a practical result.

Effect of Solvent Properties. Study of the effect of solvent properties in addition to viscosity centered on the behavior of the group $D\eta/T$ for diffusion of single solutes in a variety of solvents. A wide variety of variables such as molal volume, heat of vaporization, molecular weight, etc., were examined. Of these the solvent molecular weight

appeared to correlate the data most successfully. Figure 5 shows the group $D\eta/T$ as a function of molecular weight for diffusion of given solutes in a number of solvents.

Although there is considerable scatter of the points a line of slope 1/2 on the log-log plots correlates each system moderately well. As in the case of the molal-volume effect there are obviously other factors involved so that use of solvent molecular weight is satisfactory only as a first approximation. The data of Trevoy and Drickamer[9] are for 0.50 mole fraction of phenol in various hydrocarbons so that the solvent molecular weight is used primarily to show the trend.

General Correlation for Unassociated Liquids. From the results of the preceding section it was concluded that an equation of the following form would express the effects of solute and solvent:

$$D = \text{const.} \ \frac{TM^{1/2}}{\eta V^{0.6}} \qquad (3)$$

Figure 6 shows a log-log plot of D/T vs. the group $\eta V^{0.6}/M^{1/2}$ for a wide variety of unassociated solvents embracing the data of Table 2 of this paper and Table 5 of reference *10*. The method of plotting was selected to spread the data and best illustrate the scope of the correlation. The line through the data has slope −1 as required in the assumptions of the correlation and may be expressed by the equation

$$D = 7.4 \times 10^{-8} \frac{TM^{1/2}}{\eta V^{0.6}} \qquad (4)$$

Data for 155 points among 123 different solute-solvent systems are expressed by the correlation with an average deviation of 12% between calculated and observed results.

Correlation of Associated Liquids. Associated liquids such as water and other hydrogen-bonding solvents might be expected to show deviation from the correlation of Figure 6. Figure 7 shows the plot of D/T vs. $\eta V^{0.6}/M^{1/2}$ for diffusion in water. The best line through the data falls clearly above the dotted line representing Figure 6. This deviation is in the direction corresponding to association of the solvent. By assigning a molecular weight to the solvent equal to 2.6 times the nominal molecular weight of water one can bring the data of

TABLE 2—ATOMIC VOLUMES FOR COMPLEX MOLECULES, MOLECULAR VOLUMES FOR SIMPLE SUBSTANCES

Atomic Volumes

Bromine	27.0	Nitrogen, in secondary amines	12.0
Carbon	14.8	Oxygen (except as noted below)	7.4
Chlorine	24.6	Oxygen, in methyl esters	9.1
Hydrogen	3.7	Oxygen, in methyl ethers	9.9
Iodine	37.0	Oxygen, in higher ethers and esters	11.0
Nitrogen, double bonded	15.6	Oxygen, in acids	12.0
Nitrogen, in primary amines	10.5	Sulfur	25.6

For three-membered ring, as in ethylene oxide, deduct	0.6
For four-membered ring, as in cyclobutane, deduct	8.5
For five-membered ring, as in furan, thiophene, deduct	11.5
For pyridine, deduct	15
For benzene ring, deduct	15
For naphthalene ring, deduct	30
For anthracene ring, deduct	47.5

Molecular Volumes

H_2	14.3	N_2O	36.4
O_2	25.6	NH_3	25.8
N_2	31.2	H_2O	18.9
Air	29.9	H_2S	32.9
CO	30.7	COS	51.5
CO_2	34.0	Cl_2	48.4
SO_2	44.8	Br_2	53.2
NO	23.6	I_2	71.5
D_2O*	20.0		

*Estimated value.

TABLE 3—COMPARISON OF ASSOCIATION PARAMETERS WITH ASSOCIATION NUMBERS OF JACOBSEN

Solvent	Association parameter, x	Association number*
Water	2.6	60
Methyl alcohol	1.9	3.5
Ethyl alcohol	1.5	2.7
Benzene	1.0	1.0
Ether	1.0	1.02
Heptane	1.0	1.0

*At 20°C.

hol, illustrated in Figure 9, x is found to be 1.5.

It is of interest to compare the values of x with the association numbers recommended by Jacobsen (4) from intermolecular free-length relationships as given in Table 3. Although Jacobsen's association numbers are larger than the present association parameters the agreement in order of the solvents suggests that the general concept of the association effect may be valid. The results further suggest that the methods of Jacobsen might be used to select an association parameter which normally would lie between the values of 2.6 for water and 1.0 for unassociated solvents.

By use of the given association parameters the data for diffusion in water are correlated by Equation (5) with an average deviation of about 6%. Data for methyl alcohol are predicted within 11%. It should be noted that the experimental data for methyl alcohol systems are known to be of rather low precision in the original source.

DISCUSSION

General Comment. The correlation represented by Equation (5) is satisfactory for estimation of diffusion coefficients in dilute solutions with sufficient precision for most engineering purposes, i.e., about 10% average error.* It must be emphasized that the diffusion process is extremely complex and that any rigorous treatment must consider solute-solvent interaction in a more detailed manner than the present relation could possibly imply.† Although the present functional relationship of diffusion coefficient to solute molal volume rests upon some qualitative theo-
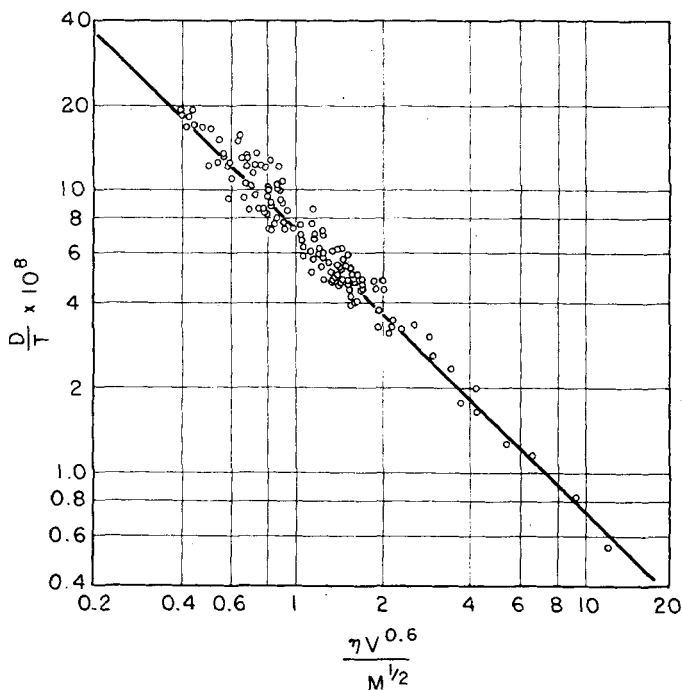

FIG. 6. DIFFUSION IN UNASSOCIATED LIQUIDS.

Figure 7 squarely onto the curve of Figure 6.

Thus the correlation for diffusion in water and also in nonassociated solvents may be expressed by the general equation

$$D = 7.4 \times 10^{-8} \frac{(xM)^{1/2}T}{\eta V^{0.6}} \quad (5)$$

The association parameter x is introduced to define the effective molecular weight of the solvent with respect to the diffusion process. For nonassociated solvents $x = 1$ and for water $x = 2.6$.

Diffusion in methyl alcohol is shown similarly in Figure 8, indicating an association parameter of 1.9, and for diffusion in ethyl alco-

*For 285 points among 251 solute-solvent systems of this study.
†Diffusion of iodine in aromatic hydrocarbons, for example, has been excluded from the present correlation because of known complex formation.

retical foundation, the relationship to solvent molecular weight is strictly empirical. Some theoretical basis for the latter relationship or some improved correlation would be highly desirable.

Only a tenfold range of viscosity is covered by the solvents presented here. Study of the correlation and deviations from constancy of the group $D\eta/T$ over more extensive temperature and viscosity ranges is especially needed. Although deviations in constancy of $D\eta/T$ have been observed and might well be expected for strongly interacting solute-solvent systems such as iodine in aromatic solvents and acetic acid in ethylene glycol, use of the group seems justified for prediction of the effect of temperature on D in absence of experimental data.

Comparison with Other Correlations. Olson and Walton[5] have proposed a general form of correlation of diffusion coefficients based on surface-tension lowering of the solvent by the solute. In view of the special data required no attempt will be made to compare their method quantitatively with the present correlation.

Scheibel[7] has fitted the correlation of Wilke to a general equation involving the molal volumes of solute and solvent based on the curves for water, methyl alcohol, and benzene. In view of the special distinction developed above between water and methyl alcohol as associated solvents and benzene as an unassociated solvent the basic assumptions used by Scheibel are believed to be in error.

Thakar and Othmer[8] have proposed the following general equation developed through the reference substance method:

$$D = \frac{14 \times 10^{-5}}{\eta_s{}^\circ V^{0.6} \eta_w{}^{1.1} L_s/L_w} \quad (6)$$

For diffusion in water only it was assumed that the group $D\eta^{1.1}$ fitted the temperature behavior better than did the Stokes-Einstein group $D\eta/T$. However since the ratio $[\eta^{1.1}]/[\eta/T]$ changes only 10% for water between 0° and 80°C. it is difficult to justify a choice between the two ways of representing the temperature dependence on the basis of the relatively limited data presently available.

Contrary to conclusions of the present study, for diffusion of a single solute in various solvents at 20°C. Equation (6) does not permit variation of $D\eta_s{}^\circ$ with solvent molecular weight. Application of Equation (6) to thirty-six representative systems involving diffusion of various solutes among twenty-one unassociated solvents gave rather unsatisfactory results, with an average deviation of over 30% between calculated and experimental diffusion coefficients.
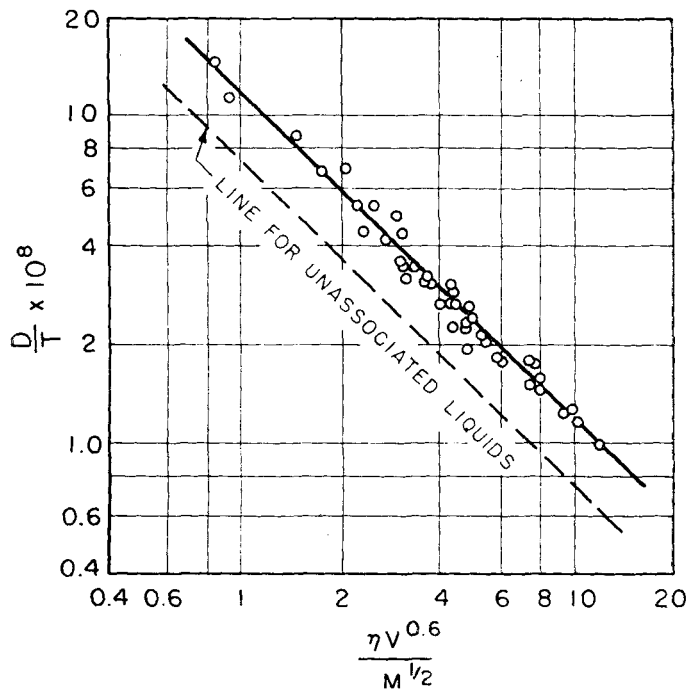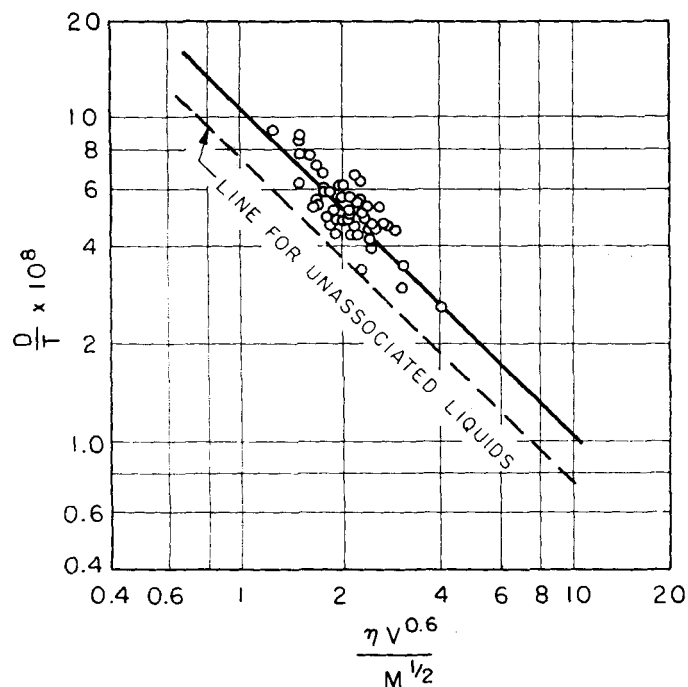

FIG. 7. DIFFUSION IN WATER.

FIG. 8. DIFFUSION IN METHYL ALCOHOL.

CONCLUSION

It is believed that Equation (5) represents an improvement over previous correlations of diffusion coefficients in dilute solutions. Due caution of course should be observed in extending the method far beyond the range of variables and types of systems included in the present development. To facilitate use of the method a revised diffusion-factor chart is given in Figure 10 to include the association parameter and molecular weight of the solvent.

NOTATION

C = concentration, g. moles/cc.

D = diffusion coefficient, sq.cm./sec.

F = diffusion factor, $T/D\eta$, $\dfrac{(°K.)\,(\text{sec.})}{(\text{sq.cm.})\,(\text{centipoise})}$

L_s = latent heat of vaporization of solvent

L_w = latent heat of vaporization of water

M = molecular weight of solvent

N = Avogadro's number, molecules per mole

N_A = diffusion rate of component A, g. moles/(sec.) (sq.cm.)

V = molal volume of solute at normal boiling point, cc./g. mole

t = temperature, °C.

T = temperature, °K.

x = association parameter, multiple of nominal molecular weight of solvent to give effective value

Z = distance in direction of diffusion

η = viscosity of solution, centipoise

η_w = viscosity of water, centipoise

η_s^o = viscosity of solvent at 20°C., centipoise
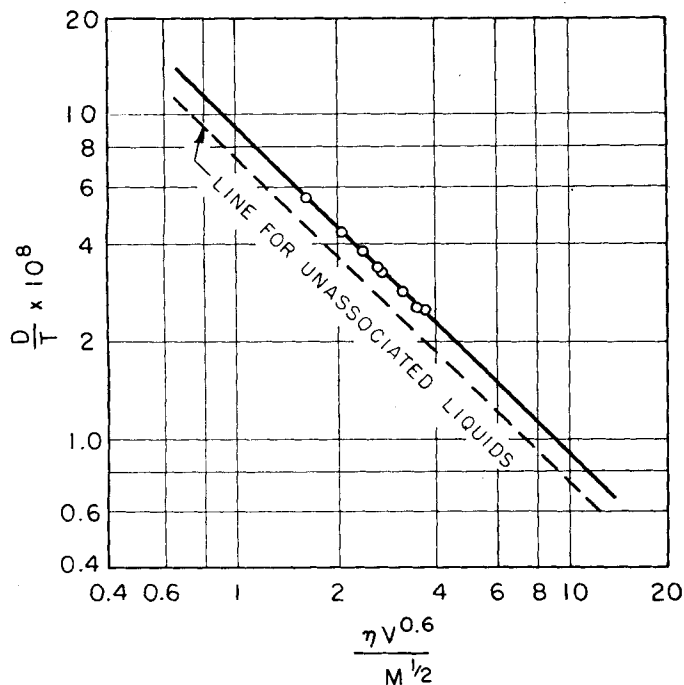

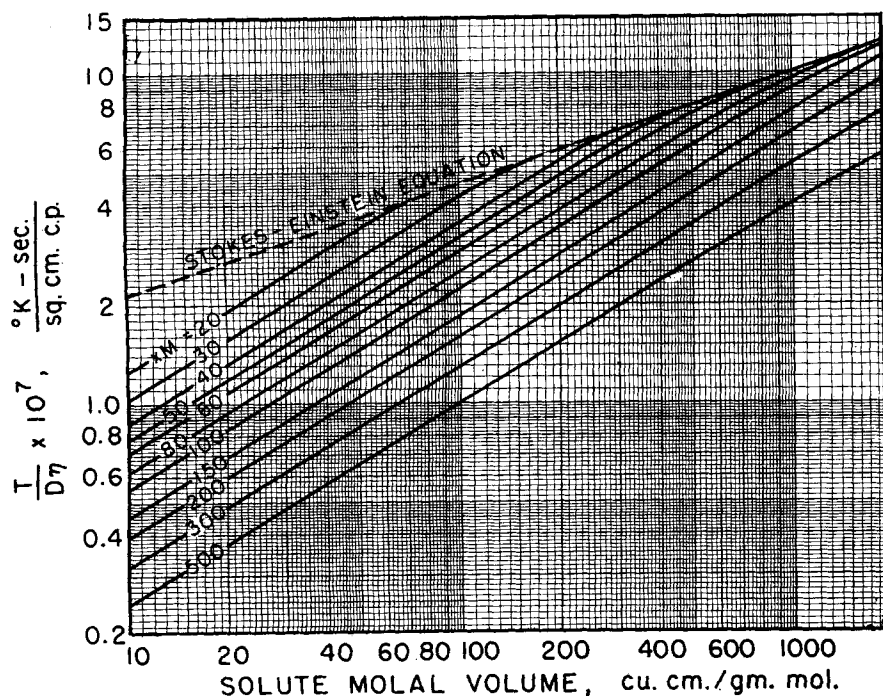FIG. 9. DIFFUSION IN ETHYL ALCOHOL.

FIG. 10. GENERALIZED DIFFUSION-FACTOR CHART.

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