A Generalized Equation for Diffusion in Liquids

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The association parameter in the diffusion equation due to Wilke and Chang has been interpreted in determinable properties, thus permitting easily the calculation of the same for unknown systems. The proposed equation also holds good for water as solute in organic solvents. The over-all percentage error remains the same as that of the original equation.

THE IMPORTANCE of diffusion coefficients in mass transfer operations have been well recognized. However, an exact theoretical equation for the evaluation of diffusion coefficients is still not available since the kinetic theory of liquids is incompletely developed. The theories of Einstein (*1*) Eyring (*7*), and Hirschfelder, Curtiss, and Bird (*8*) are definitely helpful in understanding the mechanism of diffusion, but by their use it is not possible to predict diffusivity with confidence. Hence, empirical correlations are relied on for the prediction of diffusivity in cases where experimental data are not available.

A wide variety of correlations are available for this purpose. For the diffusion in dilute solutions, the correlations of Othmer and Thakar (*13*), Arnold (*2*), Scheibel (*15*), Wilke and Chang (*16*), and Ibrahim and Kuloor (*9*) seem to be useful. Every correlation has its own drawbacks. As first pointed out by Olander (*12*), the one drawback of all the correlations is the inapplicability of these equations when water is a solute in different organic solvents. Whereas all the correlations hold good for the diffusion of organic solutes into water they do not hold good when water diffuses into organic solvents. Olander (*12*) postulates that this may be due to the polymerization of water molecules. Apart from this, all correlations deviate in cases where association of either solute or solvent molecules takes place, when the internal pressure becomes higher due to association, when the polymerization of solute molecules occurs, or the solvation of solute molecules takes place. Hence a correction factor has to be introduced for all these cases. It was considered desirable to have a single equation of universal application with no extra correction factor. The earlier correlation due to Ibrahim and Kuloor (*9*) is simple in application but requires different equations for different solvents. We have critically examined all the available correlations to arrive at a generalized equation. As a first attempt, we have chosen the following equation of Wilke and Chang (*16*), for further analysis

$$D = \frac{7.4 \times 10^{-8}\,(XM_s)^{1/2}T}{\eta\, V_m^{0.6}} \qquad (1)$$

This correlates most of the experimental values within an average deviation of ±13%. But the trouble comes when one must find the association parameter (X) for unknown systems. The association parameter was introduced in the above equation to define the effective molecular weight of the solvent with respect to the diffusion process. Apart from the difficulty of getting this parameter for an unknown system, the value of 1.0 for organic unassociated solvents and 2.6 for water may probably lead to errors in the diffusion values as pointed out by Garner and Marchant (*6*). According to them, for alcohols diffusing into water, the parameter of 2.6 is approximately correct but requires gradual reduction to about 2.35 for glycerol or C_2 alcohols diffusing into water. This shows that the abnormality may be due to the lack of understanding of intermolecular forces in liquids.

The highly associated molecules may have high viscosities and hence the size and structure of the molecules are different. Instead of arriving at this parameter in an arbitrary manner we feel it would be better to reach the goal through some readily determinable physical property which has direct relation to association and the consequent internal pressure.

PROPOSED CORRELATION

As the heat required to vaporize a substance consists of energy absorbed in overcoming the intermolecular forces of attraction in the liquid and work performed by the vapors in expanding against the external pressure, we believe the latent heat of vaporization of the solute and the solvent should be an effective property to assess association. To check this assumption, we have taken the correlation of Wilke and Chang and eliminated X and introduced the latent heat factor. To arrive at the best equation, we must modify the exponent V_m of Wilke and Chang from 0.6 to 0.5. The final equation thus obtained is

$$D = 5.4 \times 10^{-8}\left(\frac{M_s^{1/2}\, L_s^{1/3}\, T}{\eta\, V_m^{0.5}\, L_s^{0.3}}\right)^{0.93} \qquad (2)$$

From this equation, the diffusion coefficient was calculated for nearly 120 systems. All the calculated values of diffusion coefficient (D_T) are comparable with values (D_W) of Wilke and Chang. The complete analysis is given in Table I and Figure 1. In cases like aniline in ethanol, benzoic acid in toulene, and acetic acid in carbon tetrachloride, there seem to be some arithmetical errors in the reported values (D_W) of Wilke and Chang. We have recalculated these and given the values in the Table I, and the recalculated values agree with D_T.

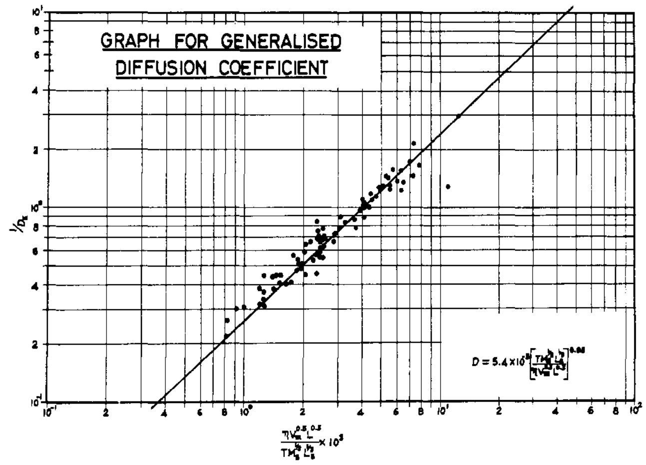

Figure 1. Graph for generalized diffusion coefficient

Table I. Diffusion Coefficients in Various Solvents

Solute	Solvent	Temp., ° C.	D_E	Ref.	D_T	Dev. from Exptl., %	D_W	Ref.	Dev. from Exptl., %
n-Propyl alcohol	Benzene	15	1.60	*(14)*	1.41	12	1.92	*(14)*	20
Ethyl ether	Benzene	15	2.21	*(14)*	1.50	32	2.24	*(14)*	1
Chloroform	Benzene	15	2.11	*(14)*	1.85	12	1.90	*(14)*	10
Chlorobenzene	Benzene	15	1.42	*(14)*	1.48	4	1.57	*(14)*	11
Bromobenzene	Benzene	15	1.86	*(14)*	1.59	15	1.54	*(14)*	17
Nitrobenzene	Benzene	15	1.84	*(14)*	1.41	23	1.50	*(14)*	19
Ethylene bromide	Benzene	15	1.97	*(14)*	1.84	7	1.72	*(14)*	13
Isoamyl alcohol	Benzene	15	1.48	*(14)*	1.26	15	1.47	*(14)*	1
Phenol	Benzene	15	1.27	*(14)*	1.42	12	1.37	*(14)*	8
Bromobenzene	Benzene	7.3	1.41	*(16)*	1.39	1	1.29	*(16)*	9
Carbon tetrachloride	Benzene	25	2.00	*(14)*	1.89	6	2.02	*(14)*	1
Bromine	Benzene	12	2.00	*(9)*	2.40	20	2.36	Calcd.^{a}	18
Iodine	Benzene	20	1.95	*(9)*	2.39	23	2.28	Calcd.^{a}	17
Formic Acid	Benzene	6.2	1.991	*(16)*	1.715	14	1.480	*(16)*	26
Formic Acid	Benzene	13.9	2.306	*(16)*	2.00	13	1.76	*(16)*	24
Benzene	Benzene	15	1.885	*(10)*	1.53	19	1.795	Calcd.^{a}	5
Aniline	Methyl alcohol	15	1.49	*(14)*	1.425	4	1.61	*(14)*	8
Allyl alcohol	Methyl alcohol	15	1.80	*(14)*	1.46	19	2.04	*(14)*	13
Carbon tetrachloride	Methyl alcohol	15	1.70	*(14)*	1.72	1	1.69	*(14)*	1
Chloroform	Methyl alcohol	15	2.07	*(14)*	1.80	13	1.90	*(14)*	9
Ethyl bromide	Methyl alcohol	15	2.40	*(14)*	1.99	17	2.02	*(14)*	16
Ethylene bromide	Methyl alcohol	15	1.95	*(14)*	1.82	7	1.72	*(14)*	12
Furfural	Methyl alcohol	15	1.70	*(14)*	1.455	14	1.75	*(14)*	3
Isoamyl alcohol	Methyl alcohol	15	1.34	*(14)*	1.24	7	1.43	*(14)*	7
Phenol	Methyl alcohol	15	1.40	*(14)*	1.39	1	1.62	*(14)*	15
Acetone	Methyl alcohol	18.8	2.22	*(5)*	1.70	23	2.12	Calcd.^{a}	4
Nitromethane	Methyl alcohol	16	2.23	*(5)*	1.735	21	2.27	Calcd.^{a}	3
Ethyl acetate	Methyl alcohol	17.8	1.72	*(5)*	1.46	15	1.73	Calcd.^{a}	0
Nitrobenzene	Methyl alcohol	16.8	1.48	*(5)*	1.44	3	1.47	Calcd.^{a}	0
Ethyl benzoate	Methyl alcohol	16	1.28	*(5)*	1.19	7	1.085	Calcd.^{a}	15
Methyl alcohol	Methyl alcohol	25	2.27	*(10)*	2.24	1	3.84	Calcd.^{a}	70
Acetone	Water	20	1.16	*(11)*	1.01	13	1.115	Calcd.^{a}	4
Acetic acid	Water	12.5	0.91	*(14)*	0.91	0	0.99	*(14)*	9
Acetic acid	Water	20	1.19	*(11)*	1.12	6	1.15	Calcd.^{a}	3
Aniline	Water	20	0.92 ±0.04	*(11)*	0.913	0	0.875	Calcd.^{a}	1
Allyl alcohol	Water	15	0.90	*(14)*	0.823	9	0.97	*(14)*	8
Glycerol	Water	10	0.63	*(14)*	0.654	4	0.70	*(14)*	11
Isoamyl alcohol	Water	15	0.69	*(14)*	0.70	2	0.70	*(14)*	2
Isobutyl alcohol	Water	20	0.84 ±0.10	*(11)*	0.833	0	0.90	Calcd.^{a}	0
Diethylamine	Water	20	0.97	*(11)*	0.90	7	0.867	Calcd.^{a}	11
Ethyl acetate	Water	20	1.00 ±0.07	*(11)*	0.89	4	0.895	Calcd.^{a}	4
Furfural	Water	20	1.04 ±0.08	*(11)*	0.94	2	0.96	Calcd.^{a}	0
Ethyl alcohol	Water	15	1.00	*(14)*	0.845	16	1.11	*(14)*	11
Methyl alcohol	Water	15	1.28	*(14)*	0.985	34	1.38	*(14)*	8
n-Propyl alcohol	Water	15	0.87	*(14)*	*0.785*	*12*	*0.91*	*(14)*	5
n-Butyl alcohol	Water	15	0.77	*(14)*	0.725	6	0.79	*(14)*	3
Nitrogen	Water	22	2.02	*(14)*	2.07	3	1.97	*(14)*	3
Bromine	Water	12	0.90	*(14)*	0.695	22	1.08	*(14)*	20
Iodine	Water	25	1.25	*(14)*	1.56	25	1.24	*(14)*	1
Carbon dioxide	Water	18	1.71	*(14)*	1.51	12	1.68	*(14)*	2
Hydrogen	Water	25	3.36	*(14)*	3.54	5	3.25	*(14)*	3
Nitrous oxide	Water	16	1.54	*(14)*	1.38	10	1.60	*(14)*	4
Oxygen	Water	25	2.60	*(14)*	2.40	8	2.29	*(14)*	12
Chlorine	Water	12	1.40	*(14)*	1.67	16	1.14	*(14)*	21
Hydrogen Chloride	Water	20	2.64	*(4)*	1.73	34	2.12	Calcd^a	20
Hydrogen iodide	Water	20	1.51	*(9)*	2.08	38	1.59	Calcd.^{a}	5
Ethyl benzoate	Ethylacetate	20	1.85	*(16)*	1.86	0	2.01	*(16)*	9
Nitrobenzene	Ethyl acetate	20	2.25	*(16)*	2.34	4	2.48	*(16)*	10
Acetone	Ethyl acetate	20	3.18 ±0.04	*(11)*	2.64	16	3.41	Calcd.^{a}	6
Acetic acid	Ethyl acetate	20	2.18	*(11)*	2.94	29	3.62	Calcd.^{a}	60
Nitrobenzene	Ethyl benzoate	20	0.73	*(16)*	0.58	21	0.66	*(16)*	10
Acetone	Ethyl benzoate	17	0.83	*(5)*	0.605	27	0.815	Calcd.^{a}	2
Ethyl acetate	Ethyl benzoate	15.7	0.68	*(5)*	0.516	24	0.63	Calcd.^{a}	7
Nitromethane	Ethyl benzoate	14.9	0.73	*(5)*	0.623	15	0.881	Calcd.^{a}	21
Ethyl benzoate	Nitrobenzene	20	0.60	*(16)*	0.497	17	0.51	*(16)*	15
Acetone	Nitrobenzene	17.8	0.79	*(5)*	0.69	13	0.87	Calcd.^{a}	10
Ethyl acetate	Nitrobenzene	16.8	0.64	*(5)*	0.595	7	0.684	Calcd.^{a}	7
Nitromethane	Nitrobenzene	18.6	0.81	*(5)*	0.765	6	1.02	Calcd.^{a}	26

Table I. Diffusion Coefficients in Various Solvents (*Continued*)

Solute	Solvent	Temp., °C.	D_E	Ref.	D_T	Dev. from Exptl., %	D_W	Ref.	Dev. from Exptl., %
Isoamyl alcohol	Ethyl alcohol	20	0.78	(*16*)	0.77	1	0.85	(*16*)	9
Aniline	Ethyl alcohol	18.5	2.7	(*16*)	0.804	70	0.75	Calcd.[a]	70
Bromoform	Ethyl alcohol	20	0.97	(*16*)	0.865	11	0.96	(*16*)	0
Bromonaphthalene	Ethyl alcohol	20	0.76	(*16*)	0.68	11	0.72	(*16*)	5
Pyridine	Ethyl alcohol	20	1.12	(*16*)	0.91	19	1.00	(*16*)	12
Ethyl alcohol	Ethyl alcohol	25	1.05	(*10*)	1.04	1	1.445	Calcd.[a]	38
Iodine	Ethyl alcohol	40	1.772	(*16*)	1.96	11	1.72	(*16*)	3
Acetone	Isobutyl alcohol	20	0.74 ±0.05	(*11*)	0.354	50	0.36	Calcd.[a]	48
Acetic acid	Isobutyl alcohol	20	0.34 ±0.04	(*11*)	0.396	4	0.382	Calcd.[a]	0
Diethylamine	Isobutyl alcohol	20	0.34 ±0.06	(*11*)	0.32	0	0.28	Calcd.[a]	0
Nitrobenzene	Acetone	20	2.94	(*16*)	2.71	8	2.83	(*16*)	3
Formic acid	Acetone	25	3.768	(*16*)	4.07	8	3.59	(*16*)	5
Ethyl benzoate	Acetone	20	2.47	(*16*)	2.15	13	2.29	(*16*)	7
Cinnamic acid	Acetone	25	2.41	(*16*)	2.27	6	2.51	(*16*)	4
Acetic acid	Acetone	25	3.309	(*16*)	3.630	10	2.850	(*16*)	14
Benzoic acid	Acetone	25	2.622	(*16*)	2.44	7	1.89	(*16*)	28
Acetic acid	Toluene	25	2.265	(*16*)	2.38	5	2.00	(*16*)	12
Benzoic acid	Toluene	25	1.493	(*16*)	1.62	9	2.06	(*16*)	38
Benzoic acid	Toluene	20	1.74	(*11*)	1.535	12	1.87	Calcd.[a]	7
m-Bromotoluene	Toluene	7.4	1.52	(*16*)	1.7	12	1.48	(*16*)	3
Carbon tetrachloride	Toluene	25	2.19	(*16*)	2.26	3	2.22	(*16*)	1
Cinnamic acid	Toluene	25	1.18	(*16*)	1.51	22	1.14	(*16*)	3
Formic acid	Toluene	25	2.646	(*16*)	2.70	2	2.54	(*16*)	4
Methyl iodide	Toluene	7.4	2.23	(*16*)	2.66	19	2.40	(*16*)	8
Diethylamine	Toluene	20	2.36 ±0.30	(*11*)	1.79	13	2.06	Calcd.[a]	0
Acetone	Toluene	20	2.93 ±0.03	(*11*)	1.99	31	2.66	Calcd.[a]	5
Acetone	Butyl Acetate	20	2.66 ±0.06	(*11*)	1.63	37	2.42	Calcd.[a]	7
Acetic acid	Butyl acetate	20	1.64 ±0.07	(*11*)	1.93	13	2.56	Calcd.[a]	50
Acetone	Carbon tetrachloride	20	1.86 ±0.10	(*11*)	1.49	15	2.11	Calcd.[a]	13
Acetic acid	Carbon tetrachloride	25	1.49	(*16*)	1.64	10	2.43	Calcd.[a]	63
Formic acid	Carbon tetrachloride	25	1.888	(*16*)	1.86	1	2.01	(*16*)	6
Iodine	Carbon tetrachloride	25	1.50	(*16*)	2.06	37	2.3	(*16*)	53
Carbon tetrachloride	Carbon tetrachloride	25	1.41	(*16*)	1.545	10	1.74	(*16*)	23
Bromobenzene	Ethylbenzene	7.3	1.44	(*16*)	1.52	6	1.55	(*16*)	8
Bromobenzene	Mesitylene	7.3	1.31	(*16*)	1.49	14	1.54	(*16*)	18
Bromobenzene	*m*-Xylene	7.3	1.52	(*16*)	1.66	9	1.69	(*16*)	11
Bromobenzene	*n*-Hexane	7.3	2.6	(*16*)	2.82	8	3.02	(*16*)	16
Iodine	Heptane	25	3.42	(*16*)	4.15	21	4.60	(*16*)	35
Iodine	Cyclohexane	15	1.54	(*16*)	1.49	3	1.19	(*16*)	23
n-Propyl alcohol	*n*-Propyl alcohol	25	0.646	(*10*)	0.806	25	0.885	Calcd.[a]	37
Water	Acetone	25	4.56	(*12*)	4.1	10	8.7	(*12*)	91
Water	Furfural	20	0.9 ±0.1	(*11*)	1.08	8	2.14	(*12*)	114
Water	Ethylene chlorohydrin	21.5	0.46	(*12*)	0.515	12	1.20	(*12*)	160
Water	Aniline	20	0.7 ±0.1	(*11*)	0.41	32	0.83	(*12*)	19
Water	Isobutyl alcohol	20	0.36 ±0.03	(*11*)	0.45	15	0.81	(*12*)	107
Water	Ethyl alcohol	18	1.1	(*12*)	1.17	6	2.58	(*12*)	125
Water	Ethyl acetate	20	3.2 ±0.15	(*11*)	3.33	0	7.52	(*12*)	124

[a] Calculated by the authors using Equation 1.

CONCLUSION

The proposed equation holds good even for systems in which water is a solute in different organic solvents whereas the Wilke and Chang equation does not hold good for them. By explaining the association, arriving at the association parameter in a rational way, and obtaining an equation which has general applicability for systems in which water is solute where the Wilke and Chang correlation does not hold good, we believe that the equation proposed here should have wider applicability. However, the interaction of solute-solvent is not taken into account in either of these correlations. This has certain obvious disadvantages. For example, in the system Methyl alcohol-benzene (*3*), even a slight change in concentration causes considerable decrease in diffusion coefficient. In such cases, if the correlations are used, they will tend to give wrong values. Perhaps this sort of abnormal behavior exists in systems with iodine or bromine as solutes. Therefore, one must be cautious in using these correlations meant for infinite dilution and be assured that such abnormal behavior as found in methyl alcohol–benzene is not present in the system for which diffusion coefficient is required. We would also like to point out that we have taken viscosity of solvent which is easily available, whereas Wilke and Chang have used viscosity of solution in their equation.

The average percentage error remains within ±13% for the proposed equation which is the same for Wilke and Chang equation. In the latter case, the diffsuion values for water as solute were not included in calculating the average because the Wilke and Chang equation does not hold good.

NOMENCLATURE

D = diffusion coefficient, sq. cm./sec.
η = viscosity of solvent in Equation 2 and viscosity of solution in Equation 1, cp.
V_m = molecular volume, cc./gram mole
M_s = molecular weight of solvent
X = association parameter
L_s = latent heat of vaporization of solvent, at normal boiling point, cal./gram
L = latent heat of vaporization of solute, at normal boiling point, cal./gram
D_T = diffusion coefficient calculated by Equation 2
D_E = experimental diffusion coefficient
D_W = diffusion coefficient calculated by Equation 1

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Specific Heat Measurements of Complex Saturated Hydrocarbons

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Specific heats of complex saturated hydrocarbons were measured from 100° to 400° F. Major hydrocarbon groups investigated were cyclohexanes, bicyclohexyls, tercyclohexyls, decalins, and hydrindans. A differential heating method employing twin thermal cells was used. The cells were charged with 25 ml. of test fluid and 25 ml. reference fluid (diphenyl ether), respectively, and suspended in air in identical bronze cylinders. These cylinders were, in turn, welded in place to the circular metallic cover of a silicone fluid bath regulated to ±0.02° F. from 80 to 420° F. The samples were stirred magnetically and the rate of heating of each was followed using Chromel-Alumel thermocouples connected to a precision potentiometer. Calorimetric cell constants were previously obtained with fluids of known specific heats. The over-all accuracy of the method at two temperatures, 104° and 212° F., was determined by measuring fluids of known specific heats. Density and viscosity data obtained by standard techniques are included for each fluid.

RECENTLY, greater emphasis has been placed on the physical properties of complex saturated hydrocarbons as potential fuels for supersonic aircraft and advanced missile power plants. In addition to density-temperature, viscosity-temperature, and vapor pressure–temperature relationships, and heat of combustion, boiling range, freezing point, and thermal stability data, the heat transfer properties of these organics have been examined more closely in the past several years. It is increasingly evident that heat capacity and thermal conductivity information at higher temperatures is of paramount importance in fully evaluating the potential of any hydrocarbon as a fuel in high performance aircraft and missile vehicles.

This article summarized experimentally determined specific heat results for many new complex saturated hydrocarbons.

EXPERIMENTAL

A differential heating method was chosen for determining the specific heats of hydrocarbon fuels over a wide temperature range. In recent years, more emphasis has been placed on differential heating techniques. For evaluating the specific heat of hydrocarbon fuels over the desired 100° to 400° F. temperature range, a small-sample calorimeter using twin tubes was selected. The apparatus constructed for this fuels program is very similar to that described in the literature by Porter *et. al.* (*7*), Spear (*8*), and Thompson

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