A CORRELATION OF DIFFUSIVITIES OF GASES IN LIQUIDS

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Using existing correlations of limited range of validity and an expanded set of experimental data a new correlation of diffusivities of gases in liquids is proposed. The new correlation has a broader validity. The liquids are divided into three groups: water, organic liquids with approximately spherical molecules and liquids with linear molecules. The diffusivity in each group is determined by molar volume of the diffusing gas and viscosity of the liquid.

Diffusivities in liquids are estimated from semi- and empirical relations as there exists to date no theory of liquids enabling an accurate and generally applicable description of diffusion. Until the previous decade the experiments concerned mostly diffusion of gases in water; older correlations for organic liquids are therefore poorly founded by experimental data and inaccurate, albeit data for diffusion in water are reliable.

A first author to have dealt with the correlations of diffusivities in liquids was Wilke[1]. Together with Chang[2] they proposed the today well known and for estimation of diffusivities widely used relation written as

$$D = 7{\cdot}4 \,.\, 10^{-8}(x_L M_L)^{1/2}/V_G^{0.6} \,.\, T/\mu_L \,. \qquad (1)$$

The value of the association parameter x_L amounts for water to 2·6, for methanol 1·9, for ethanol 1·5 and for nonassociated liquids to 1. For diffusion in water the Wilke–Chang correlation yields

$$D = 5{\cdot}06 \,.\, 10^{-7}/V_G^{0.6} \,.\, T/\mu_L \,. \qquad (2)$$

The mean relative deviation estimated by the authors for their set of experimental data was 6% for diffusion in water and 11% for diffusion in methanol. As follows from more recent experimental studies the relation between the parameter x_L and the degree of association of the molecules of liquid is not quite clear. Other authors[3–5] therefore replaced x_L in Eq. (*1*) by expressions depending only on the known properties of the diffusing solute and/or liquid. Yet, the agreement of such correlations with experimental diffusivities in organic liquids remains unsatisfactory.

Also the correlation due to Othmer and Thakar[6] can be recommended for estimation of diffusivities in water only for which the authors estimated the average relative error to be 5%. In the relation

$$D = 14 \,.\, 10^{-5}/V_G^{0.6} \,.\, 1/\mu_L^{1.1} \,, \qquad (3)$$

which is approximately equivalent to the correlation of Wilke and Chang[2] (*2*), the temperature dependence of diffusivity is implicitly contained in the viscosity of water.

A starting point of Akgerman's and Gainer's[7] relation

$$D = \frac{kT}{6\mu_L}\left(\frac{V_L}{V_G}\right)^{1/6}\left(\frac{M_L}{M_G}\right)^{1/2}\exp\left(\frac{E_{\mu L} - E_D}{RT}\right) \tag{4}$$

has been the Eyring theory of diffusion. The last correlation contains no empirical constants; the activation energies are also calculated from theoretical relationships. In spite of this the agreement with experimental data is very good, at least as far as the diffusion in water is concerned.

Only in the last decade do we have sufficient experimental evidence available in the scientific literature enabling correlation of diffusivities in organic liquids. Hayduk and Cheng[8] published a hypothesis according to which the diffusivity of each solute dissolved in a liquid is a unique function of liquid viscosity. Evaluating diffusivities in liquids whose viscosity ranged between 0·25 and 4 cP the authors found the correlation

$$D = A \,.\, \mu_L^B\,, \tag{5}$$

where *A* and *B* are constants taking specific values for each diffusing substance. In a log–log plot of diffusivity *versus* viscosity the experimental points for each diffusing solute fall, according to

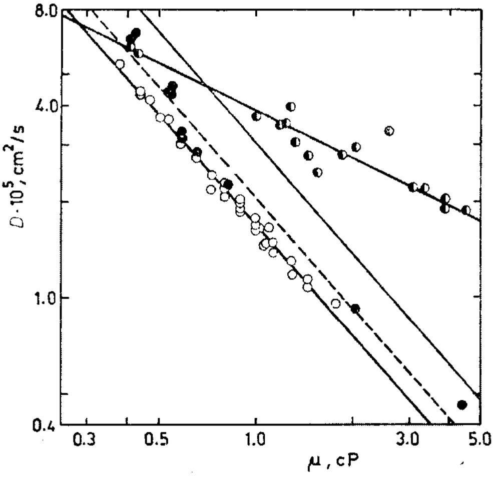

FIG. 1

Diffusivity of CO_2 as a Function of Viscosity of Liquid

Experimental points in Figs 1—8: ○ Diffusion in water, ● diffusion in liquids of the first group, ◐ diffusion in liquids of the second group.

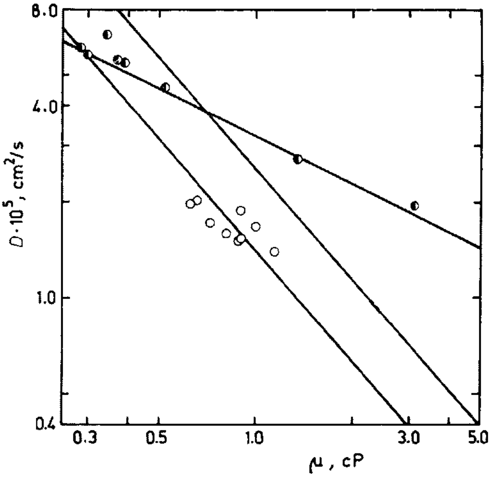

FIG. 2

Diffusivity of C_2H_6 as a Function of Viscosity of Liquid the correlation (*5*), onto a straight line with a slope B. Although the dependence of A and B on the properties of the diffusing solute has been examined[8] no unambiguous conclusions have been reached. The values found for carbon dioxide were: $A = 3{\cdot}6 \,.\, 10^{-5}$, $B = -0{\cdot}44$; for ethane: $A = 3{\cdot}3 \,.\, 10^{-5}$, $B = -0{\cdot}49$.

The diffusivities in water were not incorporated into this work[8]. It was only concluded that as a consequence of formation of complexes in water solutions the diffusivity in water, in comparison with tetrachloromethane of equal viscosity, is lower.

The basis for setting up a new correlation was an extensive set of experimentally determined diffusivities of gases in water (365 data) and organic liquids (126 data) compilled in the previous paper[9]. In order to evaluate these data we have applied the approach proposed by Hayduk and Cheng[8]. The data were plotted in a log D *versus* log μ_L plot separately for each diffusing gas. Figs 1–8 show some of these plots. As may be apparent the data can be mostly correlated by three straight lines the position of which differs only by a vertical displacement. One of these straight lines corresponds to diffusion in water, the other two to diffusion in organic liquids which for this purpose were divided into two groups. The first group contains, among others, aromatic hydrocarbons and their derivatives and the second aliphatic hydrocarbons and alcohols. More specifically, the examined liquids were divided into these two groups as follows:

1-st group – benzene, toluene, chlorobenzene, nitrobenzene, aniline, tetrachloromethane, acetone, 4-methyl-2-pentanone, methanol.

2-nd group – n-paraffins C_6—C_{16}, alcohols of n-paraffins C_2—C_8, cyclohexane, cyclohexene.

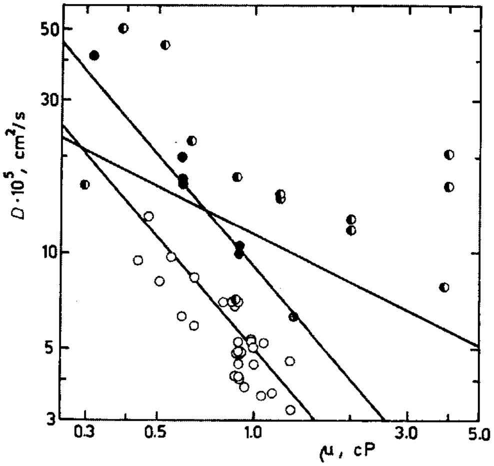

FIG. 3

Diffusivity of H_2 as a Function of Viscosity of Liquid

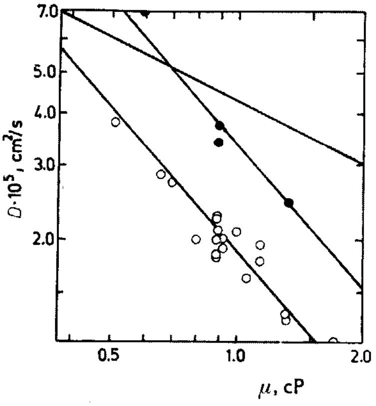

FIG. 4

Diffusivity of N_2 as a Function of Viscosity of Liquid

Experimental data for diffusion in water are correlated in the graph by a straight line with a slope −1·15. Expressed mathematically

$$D = A_0 \cdot \mu_L^{-1.15} . \qquad (6)$$

The agreement of this relation with experimental data can be best observed for oxygen and carbon dioxide where the diffusivity was measured over a broad interval of temperatures and the experimental error is small (probably due to the fact that for these gases there are accurate analytical methods available).

The data for the first group form a straight line with the same slope as those for water but displaced in the graph upward (see Figs 3, 4, 6, 8). Thus

$$D = A_1 \cdot \mu_L^{-1.15} = A_0 \cdot f_1 \cdot \mu_L^{-1.15} . \qquad (7)$$

An exception to this rule are the diffusivities of carbon dioxide in liquids of the first group which do not fall onto a straight line – see Fig. 1. Also two data for diffusion of oxygen deviate from the proposed correlation but this is probably due to experimental error.

Data for diffusion in liquids of the second group give a straight line of the slope −0·50.

$$D = A_2 \cdot \mu_L^{-0.50} = A_0 \cdot f_2 \cdot \mu_L^{-0.50} . \qquad (8)$$

Greater number of experimental data are available only for carbon dioxide, for ethane and hydrogen. As has been mentioned above the diffusivities of the first two

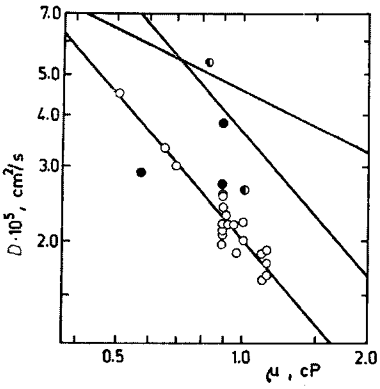

FIG. 5

Diffusivity of O_2 as a Function of Viscosity of Liquid

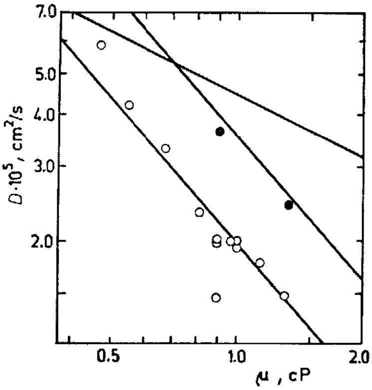

FIG. 6

Diffusivity of Ar as a Function of Viscosity of Liquid gases have been correlated by Hayduk and Cheng. The data for hydrogen considerably deviate from correlation (*8*) – see Fig. 3.

The value of the constant A_0 in Eq. (*6*) for diffusion in water can be derived from the verified correlation of Wilke and Chang (*2*) at 20°C when $\mu_L = 1$ cP:

$$D \approx 5{\cdot}06 \,.\, 10^{-7}/V_G^{0.6}\, 293/\mu_L^{1.15}\,, \qquad (9)$$

$$A_0 = 14{\cdot}8 \,.\, 10^{-5}/V_L^{0.6}\,. \qquad (10)$$

The molar volume of a gas is computed in an additive fashion from the contributions of individual atoms in the molecule of the gas or is determined experimentally at the normal boiling point. As may be seen from comparison of tables published in ref.[2,10-12], these values for some gases considerably differ; for hydrogen Arnold[12] gives $V_G = 7{\cdot}4\ \mathrm{cm^3\ mol^{-1}}$ while Wilke and Chang[2] indicate $V_G = 14{\cdot}3\ \mathrm{cm^3\ mol^{-1}}$ and according to Himmelblau[10] $V_G = 28-29\ \mathrm{cm^3\ mol^{-1}}$.

Table I compares the values of molar volumes for a total of 21 gases recommended by the author of this work (see the second line of this table) with the values used for the calculation by Akgerman and Gainer[7]. In those cases where we had enough experimental data V_G was computed from diffusivities according to the modified relation (*9*); in the remaining cases we took for V_G values used by Akgerman and Gainer. The table shows also the values of A_0 corresponding to the recommended molar volumes.

By substituting the values A_0 into correlations (*7*) and (*8*) and by comparison with the experimental data the factors f_1 and f_2 were determined with the result $f_1 = 1{\cdot}8$

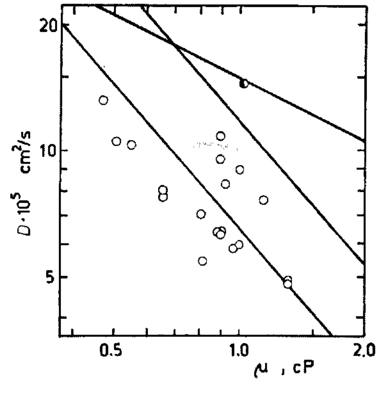

FIG. 7

Diffusivity of He as a Function of Viscosity of Liquid

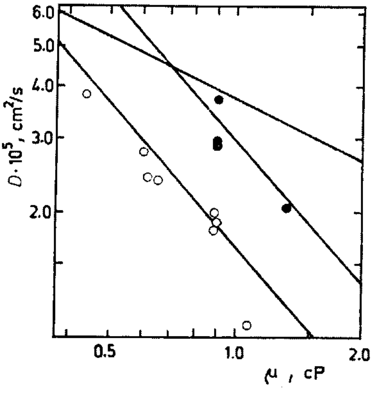

FIG. 8

Diffusivity of CH_4 as a Function of Viscosity of Liquid

TABLE I

Molar Volumes of Gases, $cm^3\,mol^{-1}$

Gas	O_2	CO_2	N_2	H_2	Cl_2	CO	NO	N_2O	SO_2	He	Ne
V_G	27·9	37·3	31·6	6·0	53·0	29·2	23·0	36·0	43·1	3·9	15·6
V_G(A—G)	25·6	33·7	30·8	13·9	48·0	29·2	23·0	36·0	43·1	1·0	15·6
$A_0 \,.\, 10^5$	2·01	1·69	1·87	5·05	1·37	1·95	2·26	1·72	1·55	6·54	2·85

Gas	Ar	Kr	Xe	CH_4	C_2H_6	C_3H_8	N_2O_4	H_2S	C_2H_2	$n\text{-}C_4H_{10}$
V_G	29·0	33·4	43·1	38·6	50·2	72·0	63·0	39·6	32·5	93·0
V_G(A—G)	27·3	33·4	43·1	28·8	50·2	72·0	31·4	32·9	32·5	93·0
$A_0 \,.\, 10^5$	1·96	1·80	1·55	1·64	1·41	1·14	1·23	1·63	1·83	0·98

and $f_2 = 2{\cdot}28$. The intersects of the correlation straight lines can be obtained by a simple calculation. From Eqs (*6*) and (*8*) it follows for the intersect of the diffusivities in water and the liquids of the second group that

$$\mu_L = f_2^{-1/0.65} = 0{\cdot}281\,. \tag{11}$$

Similarly for the intersect of the diffusivities in the liquids of the first and the second group we get from Eqs (*7*) and (*8*)

$$\mu_L = (f_1/f_2)^{1/0.65} = 0{\cdot}695\,. \tag{12}$$

The resulting form of the correlation reads

$$\begin{aligned} D = 14{\cdot}8\,.\,10^{-5}/V_G^{0.6}\,.\,f_i\,.\,\mu_L^{B_i}\,; \quad & f_0 = 1{\cdot}00 \quad B_0 = -1{\cdot}15\,;\\ & f_1 = 1{\cdot}80 \quad B_1 = -1{\cdot}15\,;\\ & f_2 = 2{\cdot}28 \quad B_2 = -0{\cdot}50\,, \end{aligned} \tag{13}$$

where the subscript i takes the values of 0, 1 and 2 for diffusion in water, the liquids of the first and the second group respectively.

For clarity we adherred in this paper to the CGS system of units which is traditionally used in the field of correlation of diffusivities. An equivalent correlation in terms of the internationally adopted SI unit system ($(D) = m^2\,s^{-1}$, $(V_G) = m^3\,mol^{-1}$, $(\mu_L) = kg\,m^{-1}\,s^{-1}$) is:

$$\begin{aligned} D = 1{\cdot}32\,.\,10^{-15}/V_G^{0.6}\,.\,f_i\,.\,\mu_L^{B_i}\,; \quad & f_0 = 1{\cdot}0 \quad\;\;\, B_0 = -1{\cdot}15\,;\\ & f_1 = 1{\cdot}8 \quad\;\;\, B_1 = -1{\cdot}15\,;\\ & f_2 = 203{\cdot}2 \quad B_2 = -0{\cdot}50\,. \end{aligned} \tag{14}$$

DISCUSSION

A reliable criterion of accuracy of a correlation is its mean relative deviation from experimental data. In its evaluation we used the paper listed as ref.[7] presenting an extensive table of experimentally determined diffusivities of gases in liquids and their relative deviations from five correlations, among these the correlation of Wilke and Chang (*1*), Othmer and Thakar (*3*) and Akgerman and Gainer (*4*). This material was supplemented with the deviations from the proposed correlation (*13*) and the mean relative deviation of individual correlations was determined and it is given in Table II. It is seen that the accuracy of the proposed correlation is comparable with the accuracy of the correlation of Akgerman and Gainer for diffusion in water and markedly better for diffusion in organic liquids. In view of the good agreement of the correlation with experimental data, because the correlation is simple and requires only a small number of information about the diffusing species, the Eq. (*13*) or (*14*) appear convenient for estimating diffusivities of gases in liquids.

More significant deviations of experimental data from the correlation can be observed in case of diffusivities of hydrogen in liquids of the second group and diffusivities of CO_2 in liquids of the first group. Owing to its low solubility the measurement of diffusivity of hydrogen is difficult. Some experimental data carry a considerable error as can be seen from comparison of diffusivity of hydrogen in cyclohexane and n-hexane at 25°C measured by Akgerman[13] ($7{\cdot}08 \,.\, 10^{-5}\,cm^2/s$ and $16{\cdot}36 \,.\, 10^{-5}\,cm^2/s$) and the data of Sporka and coworkers[14] ($17{\cdot}32 \,.\, 10^{-5}\,cm^2/s$ and $62{\cdot}38 \,.\, 10^{-5}\,cm^2/s$). The so far known data do not permit to ascertain whether the diffusivity of hydrogen deviates from the proposed correlation.

The diffusivities of CO_2 in liquids of the second group exhibit small scatter and were thus obtained with considerable precision. These values are lower than those predicted by the correlation (*13*) and do not form a straight line in the log D *versus* log μ_L plot but rather a curve with the ends bent upwards – see Fig. 1. Broken line in this

TABLE II

A Comparison of Correlations

Correlation	Mean relative deviation		
	total	water	org. liquids
Wilke–Chang (*1*)	26·9	24·4	40·9
Othmer–Thakar (*3*)	37·0	34·2	52·0
Akgerman–Gainer (*4*)	17·4	13·8	37·4
This work (*13*)	16·6	14·9	26·0

figure indicates the fitted straight line (*7*) with a constant $A_1 = 2{\cdot}06 \,.\, 10^{-5}$ correlating the experimental data better than Eq. (*13*). The explanation for this behaviour was not found.

Classification of liquids into two groups, which stemmed in this work from the character of the dependence of diffusivity of gases in liquids on the viscosity of liquids, is similar to the classification introduced by Panchenkov, Borisenko and Yerchenkov[15]. These authors compared experimental values of the coefficient of self-diffusion in liquids with the theoretical values computed from the modified equation of Stokes and Einstein and found positive deviations from the theoretical value for the group of n-paraffins and negative deviations for aromates and additional compounds. Their finding that the assignment of a liquid into the group is determined by the shape of the molecule is valid also for diffusion of gases in liquids. The molecules of the liquids belonging to the first group are approximately spherical. The dependence of diffusivities on viscosity for these liquids and water corresponds to the Stokes–Einstein equation. The reason for the slower diffusion in water is probably formation of complexes of the diffusing solute with water. The molecules of the liquids of the second group have a linear shape (from this standpoint it is proper to put cyclohexane and cyclohexene into the first group although the effect on the estimate of diffusivity at current temperatures is rather small because viscosity for both substances fall into the region near the intersect of the correlating straight lines for the first and the second group). The different character of the dependence of diffusivities on viscosity for the liquids of the second group stems probably from the various possible spatial configurations of linear molecules.

LIST OF SYMBOLS

A	correlation constant
B	correlation exponent
D	diffusion coefficient, $cm^2\ s^{-1}$
E_D	activation energy for diffusion, $erg\ mol^{-1}$
E_u	activation energy for viscosity, $erg\ mol^{-1}$
f	correlation factor
k	Boltzmann constant, $erg\ grad^{-1}$
M	molecular weight, $g\ mol^{-1}$
R	gas constant, $erg\ grad^{-1}\ mol^{-1}$
T	Kelvin temperature, grad
V	molar volume, $cm^3\ mol^{-1}$
x	association parameter
μ	viscosity, cP

Subscripts

G	gas
L	liquid

0	diffusion in water
1	diffusion in liquids of the first group
2	diffusion in liquids of the second group

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