critical point, the empirical methods based on Equations (1) and (2) appear to provide the best practical estimates of $k_{T,x}$ near the critical locus at this time.

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NOTATION

T = temperature
P = pressure
V = molar volume
$k_{T,x}$ = isothermal compressibility
σ = $(P - \hat{P})/\hat{P}$
θ = $(T - T_c)/T_c$
A, C = constants
λ = experimental exponent defining divergence of $k_{T,x}$ according to Equation (1) or (2)
σ_0 = an arbitrary reduced reference pressure ($\sigma = 0.1$)
$k^c{}_{T,x}$ = the (erroneous) value of $k_{T,x}$ predicted by an empirical equation of state upon substitution of the critical value for the independent variable
$k^m{}_{T,x}$ = the (erroneous) maximum value of $k_{T,x}$ calculated by an empirical equation of state when the pressure (and volume) are allowed to vary
P^m = pressure corresponding to $k^m{}_{T,x}$
k_1, k_2, k_3 = exponents in FOV equation
$\wedge$ = value of a given independent variable (P or V) at which $k_{T,x}$ shows a singularity
$_c$ = the critical value of a given independent variable

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Infinite Dilution Diffusion Coefficients in Liquids

The extension of the Enskog theory by Tham and Gubbins for the calculation of diffusivities is applied to the prediction of infinite dilution diffusion coefficients in binary organic systems. The resulting expression is a function only of the size and mass of the diffusing species. Excellent agreement is obtained for nonassociating *n*-alkane mixtures as well as for associated systems. Extension of the expression to alcohol and aqueous systems is shown to require only an empirical correction factor. It is also shown that the quantity $D_{ij}^{\infty}\ \eta_j\ M_j/\rho_j T$ is independent of temperature for all systems.

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SCOPE

The use of statistical mechanical approaches in the prediction of diffusion has provided much insight into the analysis of experimental data. Enskog and subsequent extensions to binary systems have analyzed the transport properties of dense fluids in terms of a rigid sphere model (Chapman and Cowling, 1952). Loflin and McLaughlin (1969), by an application of the Rice-Allnatt theory (1961), have described diffusion in a mixture of Lennard-Jones fluids. In these approaches the diffusion coefficient is described in terms of the size and mass of the diffusing species, as well as the interactions encountered by the species under study. However, these theories have been shown to provide only qualitative agreement with data and, as such, are of only limited value.

In this work the rigid sphere model of a dense fluid will be utilized as a basis for the development of a predictive equation for diffusion in binary systems at infinite dilution. The rigid sphere molecule exhibits infinite repulsion at collision and zero interaction at all other intermolecular distances. A description of diffusion in pure fluids exhibit-

ing this type of interaction was provided by Enskog. Thorne (Chapman and Cowling, 1952) extended this work to binary systems; Tham and Gubbins (1971) provided a description of diffusion in a multicomponent mixture. The primary dependent variables in the present treatment will be shown to be the size and mass of the diffusing species.

CONCLUSIONS AND SIGNIFICANCE

It is demonstrated that the results of statistical mechanical developments can be successfully applied to diffusion in liquid systems. In particular the rigid sphere Enskog approach may be modified to yield good results. Further the molecular length parameter may be characterized in terms of either the critical volume or the liquid volume at the melting point. It has also been shown that for a particular system the quantity $D_{ij}^{\infty}\ \eta_j\ M_j/\rho_j\ T$ is a constant when plotted as a function of temperature. Consequently, if the diffusivity is known at one temperature it may be calculated at any other temperature. For unassociated systems, such as *n*-alkanes, the mass of the diffusing species is an important factor, but for associated molecules the mass effect is overshadowed by molecular interactions.

An expression is derived, which is shown to closely represent both binary and self diffusion data for most organic, nonhydroxyl systems. Comparison with previous relationships of Wilke-Chang (1955) and Lusis-Ratcliff (1968) demonstrates the superiority of the proposed expression.

Finally, application of a correction coefficient to the proposed expression permits accurate prediction of diffusivities for binary alcohol and aqueous solvent solutions. An improvement in accuracy from 12% to less than 6.5% is achieved over the Wilke-Chang expression for all data tested.

EQUATION DEVELOPMENT

The general expression for diffusion in a mixture of rigid spheres has been presented by Tham and Gubbins (1971) as

$$D_{ij} = \frac{P_2\ E_{11} - P_1\ E_{22}}{n_1\ P_1 + n_2\ P_2} \left(\frac{n^0\ \mathcal{D}_{ij}^0}{g_{ij}} \right) \tag{1}$$

where $n^0\ \mathcal{D}_{ij}^0$ is the dilute gas value, g_{ij} is the radial distribution function, and the P's and E's describe the interactions of the species i and j as a function of composition with

$$E_{hl} = \delta_{hl} + 2\rho\ b_{lh}\ g_{hl} + \Sigma\ n_h\ \rho b_{hi} \frac{\partial g_{ik}}{\partial h_l} \tag{2}$$

and

$$P_m = \sum_i \delta_{im} + 2\rho\ b_{mi}\ g_{im} + \Sigma\ n_i\ \rho b_{ik} \frac{\partial g_{ik}}{\partial n_i} = \sum_i E_{im} \tag{3}$$

where δ is the Kronekker delta,

$$\rho b_{lh} = \zeta x_h\ (R_l + R_h)^3/2Y_3 \tag{4}$$

R is the reduced molecular diameter, and ζ is the reduced density of the mixture. An accurate expression for the radial distribution function of rigid sphere mixtures has been developed by Carnahan and Starling (1969) and is

$$g_{ij}\ (\sigma_{ij}) = \frac{1}{1-\zeta} + \frac{3}{(1-\zeta)^2} \left(\frac{R_i\ R_j}{R_i + R_j} \frac{\zeta Y_2}{Y_3} \right) + \frac{2}{(1-\zeta)^3} \left(\frac{R_i\ R_j}{R_i + R_j} \frac{\zeta Y_2}{Y_3} \right)^2 \tag{5}$$

where $Y_n = \Sigma x_i\ R_i^n$. These then are the general equations which describe diffusion in a rigid sphere mixture.

At infinite dilution the diffusion process is described by a single solute molecule, isolated from all other such molecules, in a medium of solvent molecules. For this condition the descriptive equations reduce to

$$D_{ij}^{\infty} = \lim_{n_i \to 0} D_{ij} = \frac{n^0\ \mathcal{D}_{ij}^0}{n_j\ g_{ij}^{\infty}} \tag{6}$$

The radial distribution function reduces to

$$g_{ij}^{\infty} = \frac{1}{1-\zeta} + \frac{3}{(1-\zeta)^2} \left(\frac{\sigma_{ii}}{\sigma_{ii} + \sigma_{jj}}\ \zeta \right) + \frac{2}{(1-\zeta)^3} \left(\frac{\sigma_{ii}}{\sigma_{ii} + \sigma_{jj}} \right)^2 \zeta \tag{7}$$

The dilute gas value for a binary mixture is given by

$$n^0\ \mathcal{D}_{ij}^0 = \frac{3}{2} \left(\frac{NkT}{2\pi} \right)^{1/2} \frac{1}{(\sigma_{ii} + \sigma_{jj})^2} \left(\frac{M_i + M_j}{M_i\ M_j} \right)^{1/2} \tag{8}$$

As can be seen by these equations, the infinite dilution diffusion coefficient of a rigid sphere fluid is described in terms of the size and mass of the diffusing species.

A particular application of these equations is for identical size and mass of solute and solvent species, as in the case of self-diffusion. Equations (6), (7), and (8) reduce to

$$D_{ij}^{\infty}\ (i = j) = D_{jj}^{\infty} \tag{9}$$

$$g_{jj}^{\infty} = \frac{1}{1-\zeta} + \frac{3}{(1-\zeta)^2} \frac{\zeta}{2} + \frac{2}{(1-\zeta)^3} \left(\frac{\zeta}{2} \right)^2 \tag{10}$$

and

$$n^0\ \mathcal{D}_{jj}^0 = \frac{3}{8} \left(\frac{NkT}{M_j \pi} \right)^{1/2} \frac{1}{\sigma_{jj}^2} \tag{11}$$

Thus, an expression for the deviation from the self-diffusion value due to a change in solute may be developed

$$\frac{D_{ij}^{\infty}}{D_{jj}^{\infty}} = \left(\frac{2\ \sigma_{jj}}{\sigma_{ii} + \sigma_{jj}} \right)^2 \left(\frac{M_i + M_j}{2\ M_i} \right)^{1/2} \frac{g_{jj}^{\infty}}{g_{ij}^{\infty}} \tag{12}$$

The diffusion ratio is seen to be dependent only on size, mass, and radial distribution functions of the species involved.

In order to provide a more tractable form, several simplifying assumptions for liquid systems may be made. In Figure 1 the radial distribution function ratio $g_{ij}^{\infty}/g_{jj}^{\infty}$ is plotted versus the length parameter ratio σ_{ii}/σ_{jj}. For most organic molecules the molecular diameter is in the range of 5 to 7 Angstroms. Assuming an average diameter of 6 Angstroms the length ratio should fall in the range of 0.8 to 1.2. In this region the radial distribution function may be represented by

$$\frac{g_{ij}^{\infty}}{g_{jj}^{\infty}} = \alpha \frac{\sigma_{ii}}{\sigma_{jj}} + \beta \tag{13}$$

However, it may be shown that

$$\frac{g_{ij}^{\infty}}{g_{jj}^{\infty}} = \frac{\sigma_{ii}}{\sigma_{jj}} \tag{14}$$

introduces an average error of less than 5% over the range $0.8 < \sigma_{ii}/\sigma_{jj} < 1.2$.

In Figure 2 the quantity $(2\sigma_{jj}/(\sigma_{ii} + \sigma_{jj}))^2$ is plotted versus the length ratio σ_{jj}/σ_{ii}. It is immediately apparent that in the range $0.8 < \sigma_{jj}/\sigma_{ii} < 1.2$, the length ratio $(2\sigma_{ii}/\sigma_{ii} + \sigma_{jj})^2$ is approximately a linear function of σ_{jj}/σ_{ii}. The use of the relation

$$\left(\frac{2\,\sigma_{ii}}{\sigma_{ii} + \sigma_{jj}}\right)^2 = \frac{\sigma_{jj}}{\sigma_{ii}} \tag{15}$$

introduces almost no error in the region in which most liquid mixtures occur. Thus Equation (12) may be rewritten as

$$\frac{D_{ij}^{\infty}}{D_{jj}^{\infty}} = \left(\frac{\sigma_{jj}}{\sigma_{ii}}\right)^2 \left(\frac{M_i + M_j}{2\,M_i}\right)^{1/2} \tag{16}$$

Here it is seen that the ratio of the coefficients of the infinite dilution to self-diffusion is reduced to simply a function of size and mass.

A major drawback in the use of Equation (16) is that the molecular lengths are not generally known. Numerous authors, including Ashcroft and Lekner (1966) and Vadovic and Colver (1970), have related the molecular length parameter to the volume at the melting point, or

$$\sigma_{ii} = \gamma\, V_{m_i}^{1/3} \tag{17}$$

where γ is a constant for a given class of compounds. Dullien has suggested that the critical volume be used to obtain the length parameter, that is

$$\sigma_{ii} = \epsilon\, V_{c_i}^{1/3} \tag{18}$$

It has further been shown by Vadovic and Colver (1972) that for most organic compounds, the following relationship holds

$$V_{m_i} = 0.310\, V_{c_i} \tag{19}$$

Thus the choice of V_m or V_c depends entirely on the availability of critical or melting point data.

Several accurate expressions for the self-diffusivity of liquids have recently been presented in the literature. For example, Dullien (1972) presented an expression which may be written as

$$\frac{D_{jj}^{\infty}\, \eta_j\, M_j}{\rho_j\, T} = 0.103 \times 10^{-6}\, V_{c_j}^{2/3} \tag{20}$$

Alternately, Vadovic and Colver (1972), from a consideration of the rigid sphere theory of Longuet-Higgins and Pople (1956), have presented the following equation:

$$\frac{D_{jj}^{\infty}\, \eta_j\, M_j}{\rho_j\, T} = 0.219 \times 10^{-6}\, V_{m_j}^{2/3} \tag{21}$$

Both these equations have been shown to accurately predict self-diffusion in liquids. It should be noted that the density dependence is a direct result of the theoretical analysis.

Substituting these results into Equation (16) yields

$$\frac{D_{ij}^{\infty}\, \eta_j\, M_j}{\rho_j\, T} = 0.103 \times 10^{-6} \left(\frac{V_{c_j}}{V_{c_i}}\right)^{2/3} \left(\frac{M_i + M_j}{2\,M_i}\right)^{1/2} V_{c_j}^{2/3} \tag{22}$$

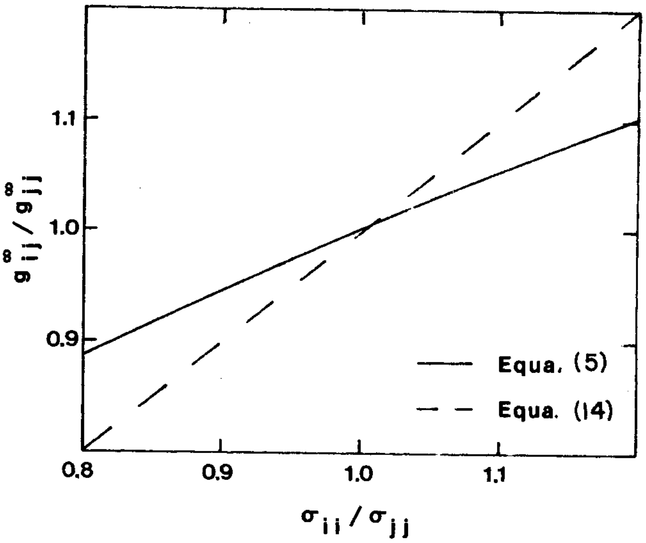

Fig. 1. Plot of radial distribution function ratio vs. length parameter ratio.

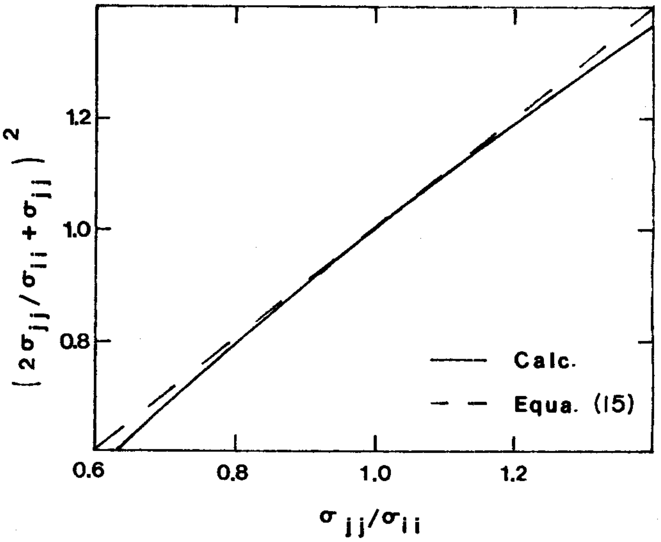

Fig. 2. Length function vs. length parameter ratio.

or

$$\frac{D_{ij}^{\infty}\, \eta_j\, M_j}{\rho_j\, T} = 0.219 \times 10^{-6} \left(\frac{V_{m_j}}{V_{m_i}}\right)^{2/3} \left(\frac{M_i + M_j}{2\,M_i}\right)^{1/2} V_{m_j}^{2/3} \tag{23}$$

It is immediately apparent that the quantity $\mathcal{D}_{ij}^{\infty}\, M_j\, \eta_j/\rho_j\, T$ should be a constant for a particular binary mixture. This is indeed the case as shown in Table 1 for the data of Haluska and Colver (1971) and that of Sanni, Fell, and Hutchinson (1971).

In order to test the developed relationship, Equation (22) was tested with the data for binary mixtures of n-alkanes at 25°C. The molecules in this series are normally considered to be nonassociated and undergo uniform interaction with other members of the series. These interactions are somewhat ideal, and as such a rigid sphere approach would be expected to yield at least qualitative results. In Table 2 the calculated results are compared to the literature values. The proposed equation reproduces both the infinite dilution diffusion coefficient and the ratio of diffusivities $\mathcal{D}_{ij}^{\infty}/\mathcal{D}_{jj}^{\infty}$ with good accuracy. Also pre-

Table 1. Diffusion Coefficient Group for Associated Systems

i	j	T	$D_{ij}^{\infty} \times 10^5$	$\frac{D_{ij}^{\infty} \eta_j}{M_j/\rho_j T} \times 10^6$	$D_{ji}^{\infty} \times 10^5$	$\frac{D_{ji}^{\infty} \eta_i}{M_i/\rho_i T} \times 10^6$	Reference
$C_6H_5CH_3$	$C_6H_{11}CH_3$	298	1.65	4.63	2.21	4.40	Haluska & Colver (1971)
		318	2.18	4.66	3.09	4.70	
		333	2.73	4.63	3.66	4.78	
$C_6H_5CH_3$	$C_6H_5NH_2$	298	0.478	5.45	2.10	4.22	Haluska & Colver (1971)
		318	0.880	5.30	2.78	4.50	
		333	1.27	5.24	3.60	4.68	
C_6H_{12}	$C_6H_5CH_3$	298	2.420	4.82	1.569	5.16	Sanni, Fell, & Hutchison (1971)
		313	3.069	4.73	1.913	4.75	
		328	3.800	5.04	2.409	4.76	
C_6H_6	C_6H_{12}	298	1.896	6.25	2.090	3.81	Sanni, Fell, & Hutchison (1971)
		313	2.450	6.09	2.650	3.78	
		333	3.285	6.14	3.445	3.33	
CCl_4	C_6H_{12}	298	1.486	4.90	1.275	3.78	Sanni, Fell, & Hutchison (1971)
		313	1.915	4.79	1.611	3.76	
		328	2.415	4.72	1.979	3.76	
n-C_7H_{14}	C_6H_6	298	1.785	3.26	3.915	7.60	Sanni, Fell, & Hutchison (1971)
		313	2.279	3.33	4.744	7.78	
		328	2.795	3.29	5.616	7.90	

Table 2. Diffusivities in Paraffinic Systems

		$(D_{ij}^{\infty})_{exp}$		$(D_{ij}^{\infty})_{calc.} \times 10^5$			$D_{ij}^{\infty}/D_{jj}^{\infty}$	
Solute	Solvent	$\times 10^5$	Ref.	This work	Wilke-Chang	Exp.	This work	Wilke-Chang
C_5	C_5	5.45	*a*	5.62	5.07	1	1	1
C_6	C_6	4.21	*b*	4.08	3.73	1	1	1
C_{12}		2.73	*e*	2.27	2.67	0.608	0.556	0.718
C_{16}		2.19	*d*	1.80	2.30	0.498	0.442	0.618
C_7	C_7	3.12	*a, b*	3.06	2.86	1	1	1
C_{16}		1.78	*e*	1.52	1.89	0.543	0.497	0.662
C_8	C_8	2.368	*c*	2.28	2.17	1	1	1
C_{16}		1.719	*c*	1.61	1.77	0.732	0.705	0.816
C_9	C_9	1.70	*b*	1.72	1.66	1	1	1
C_{10}	C_{10}	1.31	*b*	1.32	1.29	1	1	1
C_6	C_{12}	1.45	*e*	1.51	1.14	2.05	1.91	1.39
C_8		1.143	*c*	1.15	1.00	1.53	1.45	1.23
C_{12}		0.809	*c*	0.795	0.817	1	1	1
C_{16}		0.67	*f*	0.618	0.70	0.796	0.777	0.857
C_6	C_{16}	0.869	*d*	0.847	0.59	2.71	2.53	1.64
C_7		0.760	*e*	0.729	0.55	2.47	2.18	1.53
C_{12}		0.49	*f*	0.435	0.42	1.53	1.30	1.17
C_{16}		0.32	*g*	0.334	0.36	1	1	1
			Average error	5.85%	10.02%		4.43%	13.11%

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g. Extrapolated.

sented in the table are the results as calculated by the Wilke-Chang (1955) equation

$$D_{ij}^{\infty} = 7.4 \times 10^{-8} (\phi M_j)^{1/2} T/\eta_j V_i^{0.6} \qquad (24)$$

The average errors produced by Equations (22) and (24) are 5.86 and 10.02% respectively. Also it should be noticed that Equation (22) reproduces the data for the solvents dodecane and hexadecane with good agreement, whereas the Wilke-Chang equation does not. The Wilke-Chang result predicts a much lower dependence upon solute properties than that which is experimentally observed. It is interesting to note that the equation presented by Lusis-Ratcliff (1968) results in an average error of 13.96% for these binary pairs.

To further test the proposed equation the results were compared with the data given in Table 1. In these systems either one or both of the mixture constituents have associative properties. As such these molecules are nonideal and can be expected to exhibit irregular interactions. It should be noted that for these systems and similar systems the mass factor is expected to be negligible due to the small differences in mass between the solute and solvent species. As shown in Figure 3, the mass factor of the mixture is very nearly unity for mixtures with species of similar mass. As a further consideration, in associated systems the effect of association are most likely to be much greater than the effect of mass. Consequently, Equation (22) may be rewritten as

$$\frac{D_{ij}{}^{\infty}\,\eta_j\,M_j}{\rho_j\,T} = 0.103 \times 10^{-6}\left(\frac{V_{cj}}{V_{ci}}\right)^{2/3}\left(\frac{M_i+M_j}{2\,M_i}\right)^{N/2} V_{cj}{}^{2/3} \quad (25)$$

where $N = 1$ for nonassociated systems and $N = 0$ for a system where one or both of the species exhibits associative tendencies. Hence, for associative systems Equation (25) is rewritten as

$$\frac{D_{ij}{}^{\infty}\,\eta_j\,M_j}{\rho_j\,T} = 0.103 \times 10^{-6}\left(\frac{V_{cj}}{V_{ci}}\right)^{2/3} V_{cj}{}^{2/3} \quad (26)$$

The results of this equation when compared with the data given in Table 1 are plotted in Figure 4. As can be seen, good agreement with experiment is achieved over a wide range of variables. The average error resulting from the use of Equation (26) is less than 9%, whereas the use of Equation (25) with $N = 1$ results in an error of 12.8%. The Wilke-Chang and Lusis-Ratcliff expressions result in errors of 13 and 15% respectively. Equation (26) has been further compared to experimental diffusivities for over 50 binary systems made up of associating and nonassociating solvents and solutes. The overall average agreement [see the thesis by Vadovic (1972) for individual comparisons] is within 9%.

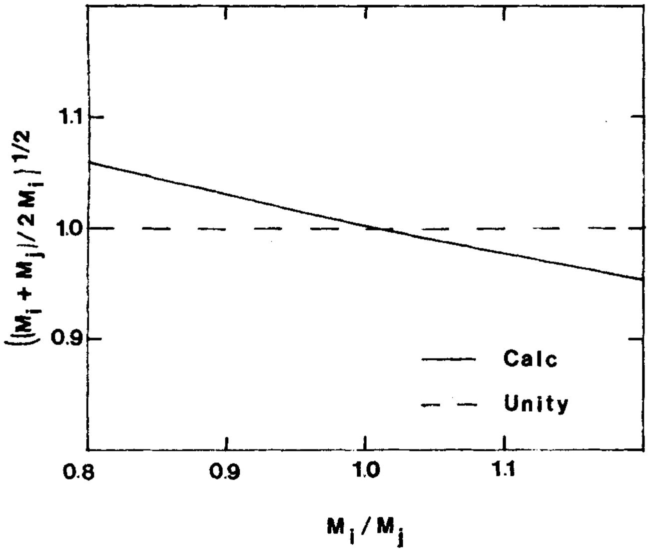


Fig. 3. Mass factor plot.

In some cases, most notably for alcohol and water as solvents, the predicted values of the diffusivities, as calculated by Equation (26), were found to be much lower than those observed experimentally. It was also found that the parameter $(V_{cj}/V_{ci})^{2/3}$ reproduced the qualitative trend of the data. Consequently, the following formulation was developed to aid in the prediction of diffusivities in these cases

$$D_{ij}{}^{\infty}/D_{jj}{}^{\infty} = F(V_{cj}/V_{ci})^{2/3} \quad (27)$$

where F is a constant characteristic of the class of compounds being considered.

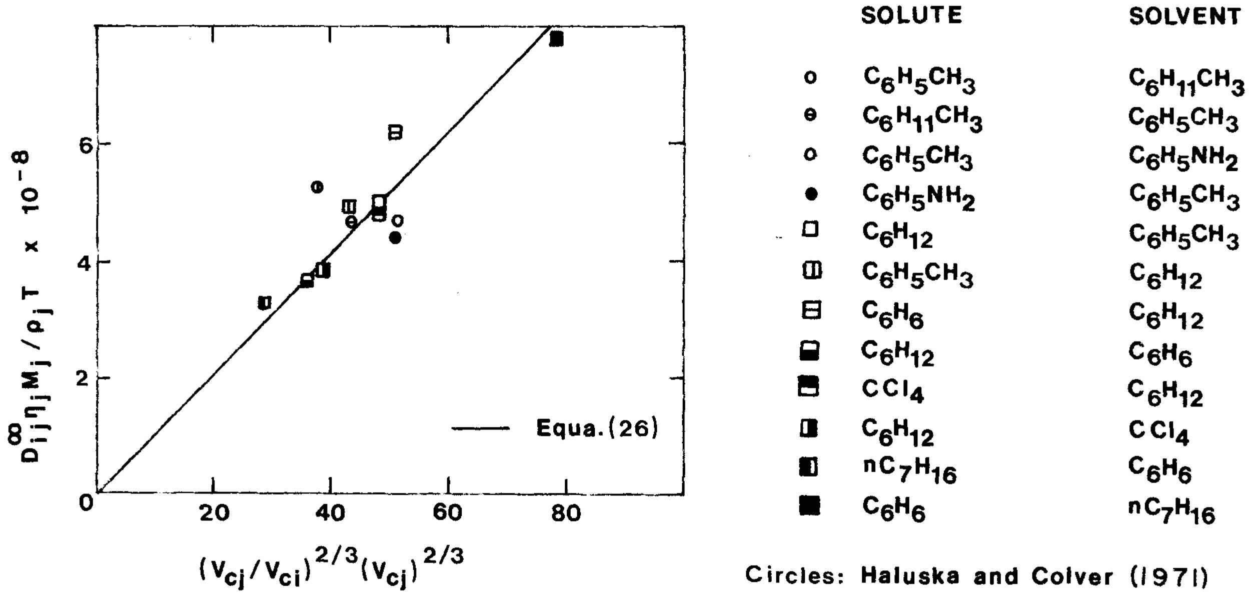
In the consideration of primary alcohols as solvents it was found that application of Equation (27) with $F = 1$ gave diffusivities for organic nonalcoholic solutes approximately 50% lower than the experimentally observed values. But the use of a value of $F = 2.08$ gave an average deviation of 10.8% when compared with the experimental data presented in Lusis and Ratcliff (1971).

A similar situation was found for water as a solvent. The predicted values, however, were consistently lower than those measured experimentally. The coefficient in Equation (26) was empirically adjusted to give

$$D_{ij}\,\eta_j\,M_j/\rho_j T = 1.08 \times 10^{-6}\,(V_{cj}/V_{ci})^{2/3}\,(V_{cj})^{2/3} \quad (28)$$

by best-fit with the aqueous data of Bonoli and Witherspoon (1968) and data cited in Reid and Sherwood (1966). The data of Bonoli and Witherspoon, for cyclic hydrocarbons in water in the temperature range of 2 to 60°C, were reproduced to within 5.5%; all of the aqueous data tested compared to within 6.5%. Table 3 gives individual comparisons. These deviations are significantly lower than those produced by previously published correlations; the Wilke-Chang equation, for example, yields an average error of 12%.

In the consideration of alcohol and water systems, it must be remembered that they exhibit conditions which



Circles: Haluska and Colver (1971)

Squares: Sanni, Fell and Hutchison (1971)

Fig. 4. Plot of diffusivity group for associative systems.

TABLE 3. DIFFUSIVITIES WITH WATER AS SOLVENT

Solute	T	$(D_{ij}^{\infty})_{\text{exp}} \times 10^5$	$(D_{ij}^{\infty})_{\text{calc.}} \times 10^5$
Data of Bonoli and Witherspoon (1968)			
Benzene	275	0.58	0.52
	283	0.75	0.70
	293	1.02	0.94
	313	1.60	1.47
	333	2.55	2.22
Toluene	275	0.45	0.45
	283	0.62	0.62
	293	0.85	0.83
	313	1.34	1.29
	333	2.15	1.95
Ethylbenzene	275	0.44	0.40
	283	0.61	0.55
	293	0.81	0.74
	313	1.30	1.15
	333	1.95	1.74
Cyclopentane	275	0.56	0.52
	283	0.64	0.70
	293	0.93	0.94
	313	1.41	1.46
	333	2.18	2.22
Methylcyclopentane	275	0.48	0.45
	283	0.59	0.61
	293	0.85	0.82
	313	1.32	1.28
	333	1.92	1.94
Cyclohexane	275	0.46	0.46
	283	0.57	0.63
	293	0.84	0.84
	313	1.31	1.31
	333	1.93	1.98
Data cited in Reid and Sherwood (1966)			
Methanol	288	1.26	1.40
Ethanol	283	0.84	0.94
	288	1.00	1.11
	298	1.24	1.44
n-propyl alcohol	288	0.87	0.93
n-butyl alcohol	288	0.77	0.79
Benzyl alcohol	293	0.82	0.93
Acetic acid	293	1.19	1.24
Ethyl acetate	293	1.00	0.88
Acetone	293	1.16	1.08
	298	1.28	1.24
Aniline	293	0.92	0.91
Acetonitrile	293	1.26	1.08
Allyl alcohol	288	1.04	0.97

are outside the range of validity for the original assumptions in the derivation. As such, the F-factor should be considered as a correction which allows extension of Equation (27) to systems with alcohol and water as solvents.

The correlating parameter used was the critical volume. It was used merely for convenience as the critical volumes are tabulated for many organic compounds in Reid and Sherwood (1966). However, for systems in which the critical volumes are not available the liquid volume at the melting point may be employed with little loss in accuracy.

NOTATION

b = molecular covolume
D_{ij} = binary diffusion coefficient, sq.cm./sec.
$\mathcal{D}_{ij}^0$ = dilute gas diffusivity, sq.cm./sec.
D_{ij}^{∞} = infinite binary diffusion coefficient, sq.cm./sec.
E = interaction parameter
F = constant
g = radial distribution function
k = Boltzmann's constant
M = molecular weight
N = Avogadro's number
n = number density
P = interaction parameter
R = length parameter ratio
T = temperature, °K
V = molar volume, cu.cm./g.-mole
x = mole fraction
Y_n = $\Sigma x_i R^n$

Greek Letters

$\alpha, \beta, \gamma, \epsilon$ = empirical parameters
δ = Kronekker delta
ζ = reduced density
η = viscosity, centipoise
ρ = density, g./cu.cm.
σ = length parameter
ϕ = association parameter

Subscripts

c = critical
i, j, k = components
m = melting

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