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GRADUATE COLLEGE

INFINITE DILUTION DIFFUSION COEFFICIENTS IN LIQUIDS

A DISSERTATION

SUBMITTED TO THE GRADUATE FACULTY

in partial fulfillment of the requirements for the

degree of

DOCTOR OF PHILOSOPHY

BY

CHARLES STEPHEN JEROME VADOVIC

Norman, Oklahoma

1972

INFINITE DILUTION DIFFUSION COEFFICIENTS IN LIQUIDS

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ABSTRACT

Based on the Enskog theory of transport in a dense rigid sphere fluid expressions are developed for the prediction of infinite dilution diffusivities in liquid systems. Two expressions are presented. The first development utilizes approximations for the size, mass, and radial distribution function factors in the Enskog development. The resulting relationship is shown to be a function of the critical volumes of the constituent species. During the course of this analysis it was demonstrated that the quantity $D_{ij}\eta_j M_j/\rho_j T$ is constant with temperature. Good agreement with data is obtained; a slight modification allows the use of the expression with water or alcoholic solvents. The second procedure involves the development of accurate expressions for the size and mass of constituent species. This method utilizes the concept of equilibrium between associated species to develop average parameters for the diffusing species. Excellent agreement with data is achieved. Experimental data at 25°C is presented for binary systems at infinite dilution conditions. Cyclohexane is either solute or solvent in all cases.

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INFINITE DILUTION DIFFUSION COEFFICIENTS IN LIQUIDS

CHAPTER I

INTRODUCTION

Molecular diffusion is defined as the motion of molecules, in the absence of external forces, which tends to dissipate the concentration gradients within the fluid. At infinite dilution conditions this motion may be considered to be the movement of a solute molecule in a medium composed entirely of solvent molecules. If the solute molecule is simply a radioactive species of the solvent molecule the self-diffusion coefficient may be measured. Thus infinite dilution diffusion in a binary system differs from self-diffusion only in the size and mass of the solute molecule and in the applicable solute-solvent interaction. The purpose of this work is to obtain accurate binary infinite dilution data for molecules for which there is accurate self-diffusion data available and to develop expressions for the prediction of these diffusion coefficients by accounting for the molecular properties such as size, mass and interactions.

The interest in diffusion processes has existed for over a century. The first significant result was obtained by Fick (25) who reasoned that mass transfer by molecular diffusion was analogous to heat conduction in solids. Fick proposed that diffusional flow was the result of a concentration gradient and that the flow was proportional to the driving force. This may be written as

$$J_i = -D_i \text{ grad } C_i \qquad (1)$$

This relation is also valid for the second component in a binary mixture.

$$J_j = -D_j \text{ grad } C_j \qquad (2)$$

For a process in which a plane is defined such that no net volume

transfer occurs it may be shown (10) that

$$D_i = D_j = D_{ij} \tag{3}$$

where D_{ij} is the mutual diffusion coefficient.

In a binary system the concentration gradient may be maintained in a thermodynamic equilibrium condition by the application of a force (75), which is

$$F = \partial\mu/\partial x \tag{4}$$

where μ is the chemical potential. The rate of transfer by diffusion due to this force is then

$$J_i = F_i C_i/\sigma_i\eta = (C_i/\sigma_i\eta)\ \partial\mu_i/\partial x \tag{5}$$

From the definitions of the chemical potential and the activity it can be shown that Equation (5) may be written as

$$D_i = (RT/\sigma_i\eta)\ \partial \ln a_i/\partial \ln C_i \tag{6}$$

In these expressions $\sigma_i\eta$ is a resistance coefficient. At infinite dilution conditions the activity term reduces to unity and the diffusivity is simply a function of the molecular parameters of the constituent species.

CHAPTER II

LITERATURE SURVEY

There have been many approaches presented in the literature for the calculation of infinite dilution diffusion coefficients in binary systems. In this chapter the major theoretical and empirical results will be discussed.

Theoretical

In 1858 Wiedeman (82) observed that the diffusivity of dilute solutions was inversely proportional to the viscosity of the solvent. Walden (80) combined these findings with the Exner Rule (23), the liquid equivalent of Graham's Law, to obtain

$$(D\eta M)^{\frac{1}{2}} = \text{constant} \tag{7}$$

This relationship was supported to some extent by the experimental results of Thovert (74).

In this same period, Einstein (21) and Sutherland (70), in completely independent studies, suggested that diffusional flow is a balance between a driving force and a resistance to flow. They proposed that the driving force was osmotic pressure. Sutherland and Einstein considered only ideal solutions and consequently the diffusion coefficient was represented by

$$D_{ij} = kT/\zeta \tag{8}$$

Stokes (69), from hydrodynamic considerations showed that for a spherical particle of radius r_i moving in a solvent with viscosity η_j the viscous resistance to flow may be given as

$$\zeta = 6\pi\eta_j r_i \ (1 + 2\eta_j/\beta r_i)/(1 + 3\eta_j/\beta r_i) \tag{9}$$

where β is the coefficient of sliding friction between the solute molecule i and the surrounding medium j. For the case of a large spherical molecule diffusing through a solvent of small molecular size and mass, Sutherland reasoned that little slip would occur and consequently

$$\beta \to \infty \quad \text{and} \quad \zeta = 6\pi\eta_j r_i \tag{10}$$

Combination of Equation (8) with Equation (10) yields the familiar Stokes-Einstein equation

$$D_{ij} = RT/(6\pi\eta_j r_i) \tag{11}$$

Sutherland also considered the case of similar sized solute and solvent molecules as in the case of self-diffusion. In this situation it was assumed that there were free spaces in the solvent medium through which the solute molecule could move at will. Therefore

$$\beta = 0; \quad \zeta = 4\pi\eta_j r_i \quad \text{and} \quad D_{ij} = RT/(4\pi\eta_j r_i) \tag{12}$$

In this case the solute molecule is no longer in motion in a continuous medium.

In 1922, in an attempt to describe dense gas and liquid behaviour, Enskog (22) developed expressions for dense fluid transport properties. Enskog considered a dense medium composed of rigid spherical molecules of diameter σ. For this model two body collisions are considered. Through this assumption and by taking into account the finite size of the molecules, Enskog was able to superimpose a dense fluid theory onto the previously developed dilute gas theory. In this theory the coefficient of self-diffusion is given as

$$\rho D = (\rho\mathcal{D})^{o}/\chi \tag{13}$$

where the superscript o denotes dilute gas conditions and χ is a correction factor for the probability of collisions. The dilute gas value (63) has the form

$$(\rho\mathcal{D})^{o} = (3/8)(\pi kT/m)^{\frac{1}{2}}(1/N\pi\sigma^{2}) \tag{14}$$

For rigid spheres the correction factor χ is directly related to the rigid sphere compressibility, z, by

$$\chi = (z - 1)/b\rho \tag{15}$$

where b is the molecular covolume equal to $(2/3)N\pi\sigma^{3}$. Thus, the self-diffusion coefficient is given as

$$D = (\sigma/4)(\pi kT/m)^{\frac{1}{2}}/(z - 1) \tag{16}$$

The Enskog theory in effect corrects for the finite volume of the

molecules and the increased frequency of molecular collisions. A similar expression has been developed by Longuet-Higgins and Pople (41) from a consideration of the exponential decay of the autocorrelation function. This theory has been extended to the binary case by Thorne (16) and to the multicomponent case by Tham and Gubbins (72).

Eyring and coworkers (24,27) have applied the theory of rate processes in conjunction with the cell model concept of a liquid to develop a general theory of fluids. In this theory the diffusivity is given by

$$D_{ij} = K\lambda^2/\xi \tag{17}$$

where λ is the distance between equilibrium positions of i, ξ is a geometrical configuration parameter, and K is the rate constant for a unimolecular rate process. From absolute rate theory

$$K = (kT/h)(F'_{ij}/F_{ij}) \exp(-E_{D,ij}/RT) \tag{18}$$

F'_{ij} and F_{ij} are the partition functions in activated and equilibrium states respectively and $E_{D,ij}$ is the diffusional activation energy. The viscosity of a fluid is given by

$$\eta_j = (h\lambda_{1j}/\lambda_{2j}\lambda_{3j}\lambda_j^2)(F_{jj}/F'_{jj}) \exp(E_{\eta,j}/RT) \tag{19}$$

where the λ's denote distances between molecules and $E_{\eta,j}$ is the activation energy for viscosity. Combining these results gives

$$D_{ij} = (kT/\xi\eta_j)(\lambda_{1j}/\lambda_{2j}\lambda_{3j})(F_{jj}F'_{ij}/F'_{jj}F_{ij}) \cdot \exp((E_{\eta,j} - E_{D,ij})/RT) \tag{20}$$

Assuming that $\lambda_{1j} = \lambda_{2j} = \lambda_{3j} = (V_j/N)^{1/3}$ and that $F_{jj}F'_{ij}/F'_{jj}F_{ij} = 1$ Equation (20) reduces to

$$D_{ij} = (kT/\xi\eta_j)(N/V_j)^{1/3} \exp((E_{\eta,j} - E_{D,ij})/RT) \tag{21}$$

Eyring, et al. (24) have assumed that the diffusional and viscous activation energies are equivalent. This is true for the case of self-diffusion, but not for a binary system. Several estimates for the quantity $(E_{\eta,j} - E_{D,ij})$ have been proposed by Olander (51) and by Gainer and Metzner (26).

Olander suggested that an estimate for $(E_{\eta,j} - E_{D,ij})$ may be

given by

$$E_{\eta,j} - E_{D,ij} = E_{\eta,j}/2 - f(E_{\eta,i}E_{\eta,j})^{\frac{1}{2}} \qquad (22)$$

f is the fraction of the activation energy associated with the motion of the molecule from one equilibrium position to another similar position. In a similar development, Gainer and Metzner (26) have proposed the following relationship

$$E_{\eta,j} - E_{D,ij} = E_{\eta,j}/2 - (\xi_i/\xi_j) \cdot \{[(r_{ii}/r_{ij})(E_{\eta,jH}/2)(r_{jj}/r_{ij})(E_{\eta,iH}/2)] + [(r_{ii}/r_{ij})^{12}(E_{\eta,jD}/2)(r_{jj}/r_{ij})^{12}(E_{\eta,iD}/2)]^{\frac{1}{2}}\} \qquad (23)$$

where the r's represent intermolecular spacings and the subscripts H and D designate contributions due to hydrogen bonding and dispersive forces respectively.

In order to predict the temperature dependence of self-diffusivities Eyring used the following expression which was based on the activation energy (ΔH) and the activation entropy (ΔS)

$$D = e\lambda^2(kT/h)\exp(\Delta S^*/R)\exp(-\Delta H^*/RT) \qquad (24)$$

Walls and Upthegrove (81) presented a similar expression which contains three parameters; a configuration constant γ; a geometrical parameter which relates interparticle spacing to particle size, b; and the enthalpy and entropy of activation which are assumed to be equal for viscous and diffusional flow.

$$D = kT\gamma^{1/3}\exp(\Delta S^*/R)\exp(-\Delta H^*/RT)/(2\pi bh(2b + 1))(V_m^{2/3}/N) \qquad (25)$$

or in terms of viscosity

$$D = kT\gamma^{1/3}N^{\frac{1}{2}}/(2\pi\eta V_m b(2b + 1)) \qquad (26)$$

It should be noted that this model does not consider interatomic potentials and as such is not strictly applicable to binary diffusion.

Cohen and Turnbull (17), considering a fluid composed of rigid spheres, postulated that the diffusion process occurs by the motion of molecules into holes in the surrounding medium. The hole size is somewhat greater than a critical value. Swalin (71) developed

expressions for self-diffusion by considering the motion of a group of five atoms. These motions result in a time dependent density fluctuation with respect to a given group of atoms. The jump distance is no longer discrete, but is a continuous distribution of distances. These two methods have been applied with some success to liquid metals.

Thomaes and Van Itterbeek (73) have attempted to establish a theorem of corresponding states for the diffusivities of pure liquids based upon the Prigogine theory of liquid solutions. The assumptions in this development are: simple, spherical molecules; the potential energy is represented by $e(r) = \epsilon^* \varphi(r/r^*)$ where φ is a universal function and; the parameters ϵ^*, r^*, and m completely characterize the molecular species. The resulting expression

$$D_i(T_i) = D_j(T_i \epsilon^*_j/\epsilon^*_i)(m_j/m_i)^{\frac{1}{2}}(\epsilon^*_i/\epsilon^*_j)^{\frac{1}{2}}(r^*_i/r^*_j) \tag{27}$$

has been shown to be in fair agreement with experimental data.

In recent years the various statistical mechanical approaches to the prediction of diffusion coefficients have been discussed in great detail. McLaughlin and coworkers (1,40,46,47) have presented several papers which represent a detailed application of the results of statistical mechanical theory. McLaughlin (47) in 1969 utilized the extension of the rigid sphere theory as presented by Thorne (16) to develop an expression for the binary mutual diffusion coefficient as a function of composition. The expression

$$nD_{ij} = n^o \mathfrak{D}^o_{ij}/g_{ij} \tag{28}$$

was used as the basis for further work. For a mixed sphere fluid Lebowitz (38) obtained

$$g_{ij} = (\sigma_{jj} g_{ii} + \sigma_{ii} g_{jj})/2\sigma_{ij} \tag{29}$$

where

$$g_{ii} = \{(1 + \tfrac{1}{2}\xi) + (\pi/4) n_j \sigma^2_{jj} (\sigma_{ii} - \sigma_{jj})\}(1 - \xi)^{-2} \tag{30}$$

and

$$\xi = \pi(n_i \sigma^3_{ii} + n_j \sigma^3_{jj})/6 \tag{31}$$

At infinite dilution conditions the result may be expressed as

$$n_j D_{ij} = n^o \mathcal{D}^o_{ij} / \{\sigma_{jj}[(1 + \xi/2) + (\pi/4) n_j \sigma_{jj}(\sigma_{ii} - \sigma_{jj}) + \sigma_{ii}(1 + \xi/2)](1 - \xi)^{-2}\} \quad (32)$$

It can be seen that the principle parameters are the number density and the rigid sphere diameters.

Loflin and McLaughlin (40), using the Rice-Allnatt extension of the Rice-Kirkwood theory, also presented expressions for the concentration dependence of the diffusivity. In applying these results to infinite dilution the following relationship was obtained

$$2a^2/a + 1 = (\epsilon_{jj}/\epsilon_{ii})^{\frac{1}{2}}[(\sigma_{ii} + \sigma_{jj})/\sigma_{ii}][m_j/(m_i + m_j)] \quad (33)$$

where $a = D^{\infty}_{ii}/D^{\infty}_{ji}$. This result has been shown to be in fair agreement with data. McConalogue and McLaughlin (46), as well as Al-Chalabi and McLaughlin (1), further point out the various applications of these theories.

Tham and Gubbins (72) extended the Enskog theory of a dense rigid sphere fluid to the multicomponent case. These equations reduce to Equation (28) for the binary case. A further improvement is that the binary radial distribution function as developed by Mansoori et al. (44) is utilized. Raveche and Meyer (58) have presented a method for obtaining the diffusion coefficient for a liquid system of monatomic molecules near equilibrium. However the resulting equation is in integral form and cannot be used for direct calculations.

At the present time statistical mechanical approaches must use the rigid sphere model to simplify the resultant integral forms or to solve the integral equations directly through the use of numerical methods. In applying the former to diffusion in real fluids the assumptions made may lead to calculational errors; the latter requires large computers to solve the equations.

Nir and Stein (50) proposed that two modes of diffusion are present in liquids. The first mode results from the movement of solvent molecules and is the only one available to macromolecules in solution. Smaller molecules may use this mode but also move by activated diffusion within the lattice of the solvent matrix. The

resulting relationship has the form

$$D = D_{fl_o} \exp(- E_{fl}/RT) + D_{lat_o} \exp(- E_A/RT) \qquad (34)$$

The parameters in this equation must be obtained semiempirically, thereby reducing the effectiveness of the result.

In summary, it may be said that since there is not yet an accurate description of the liquid state in general, the prediction of binary infinite dilution diffusion coefficients by theoretical means is not practical. The theoretical approaches presented here will yield only fair agreement with experiment; many of the approaches are further limited by being applicable only to particular cases.

Empirical

The lack of a truly accurate liquid state model has left the accurate prediction of infinite dilution diffusion coefficients to the realm of empiricism. There have been many approaches presented in the literature; the most successful of which will be discussed in detail here. Other correlations will be discussed briefly.

In 1936 Herzog (33) proposed that

$$D = 2RT/6\pi N^{0.67}\eta(V - b)^{0.33} \qquad (35)$$

where b is the van der Waals' volume. This relationship was shown to restricted to use in the Stokes-Einstein region.

Arnold (6) proposed an equation for liquid diffusion that resulted from an extension of a modified gaseous kinetic theory. The resultant relationship is

$$D^{\infty}_{ij} = 0.01\{(M_i + M_j)/M_iM_j\}^{\frac{1}{2}}/A_iA_j\eta^{\frac{1}{2}}_j(V_i^{1/3} + V_j^{1/3})^2 \qquad (36)$$

where A_i and A_j are abnormality factors which account for association and intermolecular attractions. These factors are essentially empirical and the relationship is further limited to a temperature of 20°C, to very dilute solutions, and to relatively low boiling solvents.

At dilute concentrations Olson and Walton (52) related the diffusivity for aqueous solutions of organic liquids to the slope of the surface

tension lowering-concentration plot. The final correlation presented was a plot of $(D^{\infty}_{ij}\,\eta/T)$ vs. $(\Delta\sigma/C_i)$. Due to a lack of adequate data this result has not been extensively tested. These authors also showed that the ratio of an unknown diffusion coefficient of a given compound in a solvent to a known coefficient for another molecule in the same solvent is approximately equal to the ratio of the diffusivities of the same solutes in water, or

$$D^{\infty}_{ij}/D^{\infty}_{kj} = D^{\infty}_{i\text{-}H_2O}/D^{\infty}_{k\text{-}H_2O} \tag{37}$$

This is commonly referred to as the common solvent effect.

Based on the Stokes-Einstein equation and the Eyring theory of absolute reaction rates Wilke (83) proposed a general equation for infinite dilution diffusivities. It was asserted that the group, $T/D\eta$, was essentially constant with temperature for a particular solute-solvent system. It was also found that $T/D\eta$, for a given solvent, is a function of the solute molar volumes. The results of this work were curves of $T/D\eta$ vs. the molal volume of the solvent. In general it was assumed that $T/D\eta$ was identical to the Stokes-Einstein result at large solute molal volumes.

Wilke and Chang (84), in 1955, on the basis of new data, extended this work by developing an explicit empirical function to describe the effect of solvent properties as well as association effects. The result may be written as

$$D^{\infty}_{ij} = 7.4 \times 10^{-8}(\chi M)^{\frac{1}{2}}T/\eta_j V_i^{0.6} \tag{38}$$

where χ is an association parameter. For non-associated solvents $\chi = 1$. χ differs from according to the solvent under study.

Othmer and Thakar (54), by considering the Eyring expression in conjunction with the Clausius-Clapeyron equation showed that

$$\ln D = (E_A/L)\ln P^{o} + C \tag{39}$$

where L is the latent heat of vaporization. Thus if ln D is plotted versus ln P^{o} for a reference fluid a straight line results with a

slope of E_A/L. It was further shown that

$$\ln D = - (E_D/E_\eta) \ln \eta + C' \tag{40}$$

and that

$$E_D/E_\eta = 1.1\ L_s/L_{H_2O} \tag{41}$$

Combining these results and comparing with data led to the following result

$$D_{ij}^{\infty} = 14.0 \times 10^{-5}/\eta_w (1.1\ L_s/L_w) V_m^{0.6} \eta_s^o \tag{42}$$

where the subscript w indicates water and η_s^o is the viscosity of any solvent at 20°C.

Scheibel (65) was the first of several authors to develop explicit formulations for the curves of $T/D\eta$ presented by Wilke. He presented the empirical relation

$$F = T/D\eta = 1.22 \times 10^7\ V_i^{1/3}/(1 + (3V_j/V_i)^{2/3}) \tag{43}$$

From this the diffusivity is given by

$$D_{ij}^{\infty} = 8.2 \times 10^{-8}\ T(1 + (3V_j/V_i)^{2/3})/\eta_j V_i^{1/3} \tag{44}$$

This equation was found to represent diffusivity data for solvent volumes up to one-half the solute volume.

Sitaraman, Ibrahim and Kuloor (68) interpreted the association parameter in the Wilke-Chang equation in terms of determinable properties. In this development the original expression of Wilke and Chang was empirically modified in order to obtain a best fit of the data. The association parameter, χ, was replaced by the latent heat to obtain the final result, which is

$$D_{ij}^{\infty} = 5.4 \times 10^{-8}\ (M_j^{\frac{1}{2}} L_j^{1/3} T/\eta_j V_m^{\frac{1}{2}} L_j^{0.3})^{0.93} \tag{45}$$

This equation was shown to be as accurate as the original Wilke-Chang expression.

Based on the empirical fact that $D\eta/T$ is nearly constant for self-diffusion King, Hsueh and Mao (37) presented a correlation for

the prediction of diffusivities. They observed that in comparision to self-diffusion in a particular solvent mutual diffusion differs only by the solute species under study. It was stated that the diffusivity should be a function of the solute to solvent size ratio and to the ratio of solute-solvent tc solvent-solvent interactions. Their final result is

$$D_{ij}^{\infty} = 7.37 \times 10^{-9}\ T(V_j/V_i)^{1/6}(L_j/L_i)^{\frac{1}{2}} \tag{46}$$

This equation was shown to be significantly better than previous correlations for selected cases.

Reddy and Doraiswamy (59) presented the following modifications for the Wilke-Chang equation

for $V_j/V_i \leq 1.5$

$$D_{ij}^{\infty} = 10 \times 10^{-8}\ M^{\frac{1}{2}}T/\eta_j V_i^{1/3} V_j^{1/3} \tag{47}$$

for $V_j/V_i > 1.5$

$$D_{ij}^{\infty} = 8.5 \times 10^{-8}\ M^{\frac{1}{2}}T/\eta_j V_i^{1/3} V_j^{1/3} \tag{48}$$

The association parameter has again been replaced without any significant improvement in results.

On the basis of absolute reaction rates as well as hydrodynamic theory Lusis and Ratcliff (42) showed that

$$D_{ij}^{\infty}/D_{jj}^{\infty} = F(V_i/V_j) \tag{49}$$

The following empirical relation was found to describe this functionality

$$F(V_i/V_j) = C_1(C_2(V_j/V_i)^{1/3} + C_3(V_j/V_i)) \tag{50}$$

It was further shown that

$$D_{jj}^{\infty} = C_4 T/\eta_j V_j^{1/3} \tag{51}$$

Combining these expressions and least squares fitting for the constants yields

$$D_{ij}^{\infty}\eta_j/T = 8.52 \times 10^{-10}\ (V_j)^{-1/3}\{1.40(V_j/V_i)^{1/3} + (V_j/V_i)\} \tag{52}$$

This equation described the tested data as well as previously published correlations.

These same authors (43) presented an expression for diffusivities in complex forming mixtures. It was assumed that complexes were formed according to the following equilibrium relations

$$A_i + B_g \overset{K_i}{=} A_i B_g \tag{53}$$

$$B_1 + B_g \overset{K_j}{=} B_{g+1} \tag{54}$$

A diffusivity was then calculated for each $A_i B_g$-B_{g+1} combination. The binary diffusivity was then then to be a concentration average of the individual diffusivities. Errors of less than 10 per cent resulted for test cases involving alcohols.

Hayduk and Cheng (32) stated that, in general, diffusivity and solvent viscosity are not inversely related but that the infinite dilution diffusivity was related to the solvent viscosity raised to some power, i.e.

$$D_{ij}^{\infty} = A\eta^{B} \tag{55}$$

The constants in this formula must be calculated for each individual diffusing molecule thus limiting the use of this equation.

Based on a simplification of the relationship between viscosity and tracer diffusion in mixtures Dullien presented the following relationship for self-diffusivities (20)

$$D_{jj}^{\infty}\eta_j V_j/RT = 0.124 \times 10^{-16} (V_{cj})^{2/3} \tag{56}$$

This result, which directly relates the diffusivity to a molecular length parameter squared, accurately reproduces self-diffusion data for many substances.

Summary of Prior Correlations

In a comparision of correlations for the prediction of infinite dilution diffusion coefficients Reid and Sherwood (60) have presented percentage deviations for two cases: for aqueous solutions - Wilke and Chang, Scheibel, and Othmer and Thakar, 11 per cent, Sitaraman et

al., 12 per cent, and Kamal and Canjar (35), 20 per cent; for organic solutions - Wilke and Chang, 27 per cent, Othmer-Thakar, 28 percent, Sitaraman et al., 26 per cent, and Scheibel, 25 per cent. In a similar type compararision Lusis and Ratcliff (42) presented the following deviations: Wilke-Chang, 20 per cent; Othmer-Thakar, 33 per cent; Sitaraman et al., 32 per cent; Scheibel, 23 per cent; and Lusis-Ratcliff, 16 per cent. From these figures it can be seen that no one correlation can accurately predict infinite dilution diffusivities. Accurate relations are needed for use in multicomponent predictive techniques which are usually based on self and infinite dilution diffusion coefficients, as well as for industrial design techniques.

CHAPTER III

EXPERIMENTAL

Experimental Basis

The experimental apparatus used in this study is based on the so-called free diffusion model. The mathematical basis for the diffusion process is Fick's second law

$$\partial C_i/\partial t = \text{div } (D_{ij} \text{ grad } C_i) \tag{57}$$

For unidirectional flow and in conjunction with the following boundary conditions

$$t = 0 \qquad \partial C_i/\partial x = 0 \qquad \text{for all } x \neq 0 \tag{58}$$

$$t > 0 \qquad C_i = C_{i1} \qquad x \rightarrow \infty \tag{59}$$

$$t > 0 \qquad C_i = C_{i0} \qquad x \rightarrow -\infty \tag{60}$$

the solution to Equation (57) is

$$(C_i(x,t) - C_{i0})/(C_{i1} - C_{i0}) = \tfrac{1}{2}[1 + \text{erf}(x/\sqrt{4D_{ij}t})] \tag{61}$$

Thus the concentration at any point and at any time may be calculated.

In order to approximate these conditions the following must be valid. There must exist at zero time and at $x = 0$ a step function in concentration; this step function must be sufficiently small to allow the validity of Fick's law. At $x = \pm \infty$, for the duration of the experiment, the concentrations must remain at C_{i1} and C_{i0} respectively. Since an infinite diffusion field is not possible the apparatus used must have sufficient length to ensure these conditions.

Experimental Apparatus

The apparatus used in this work was developed by Merliss (48) and modified by Haluska (29) and Alimadadian (2). Since this apparatus has been described in great detail elsewhere only a brief description will be given here.

The flowing junction test cell, used to simulate the mathematical model, was designed by Alimadadian (2). A schematic diagram of the cell is given in Figure 1. The cell was made of two 316 stainless steel plates and held together with two bolts. The cell cavity was 3½ inches high, ½ inch wide and 3 inches in depth. The slits, at the junction, were 0.006 inch wide. These slits, through which fluid was withdrawn, were connected by a series of five perpendicular holes to a manifold which collected the withdrawal fluid. The manifolds were then connected to the drain line. Two cell windows, fabricated of high quality optical glass, were held in place by adjustable plates. These windows allowed the passage of a light beam, without distortion, through the test cell.

In order to follow the diffusion process a double Savart plate birefringent interferometer was utilized and is illustrated in Figure 2. Its' operation is explained as follows: a spatially and temporally coherent light beam from a helium-neon gas laser is expanded and collimated by meshing the focal points of the lenses L_1 and L_2. It then passes through the test cell. After passing through the test cell the beam is reconverged, demagnified and recollimated by meshing the focal points of lenses L_3 and L_4. The beam then passes through the first Savart plate, S_1, and is converged before passing through the second Savart plate, S_2. The fringe patterns are then formed on film after passing through a polarizer.

In order to maintain a constant temperature in the test cell an air bath was utilized. It consisted of a double wall box, with perlit insulation between walls. Windows constructed of two glass plates with internal air spaces were mounted in the walls to align with the optical path. Additional equipment consisted of heater elements, baffles, a fan and temperature sensing elements. The bath temperatures were controlled to within $0.01^{\circ}C$. by a Thermotrol. The temperature in the bath was measured with a calibrated platinum resistance thermometer used with a Mueller Temperature Bridge and a D.C. null voltmeter.

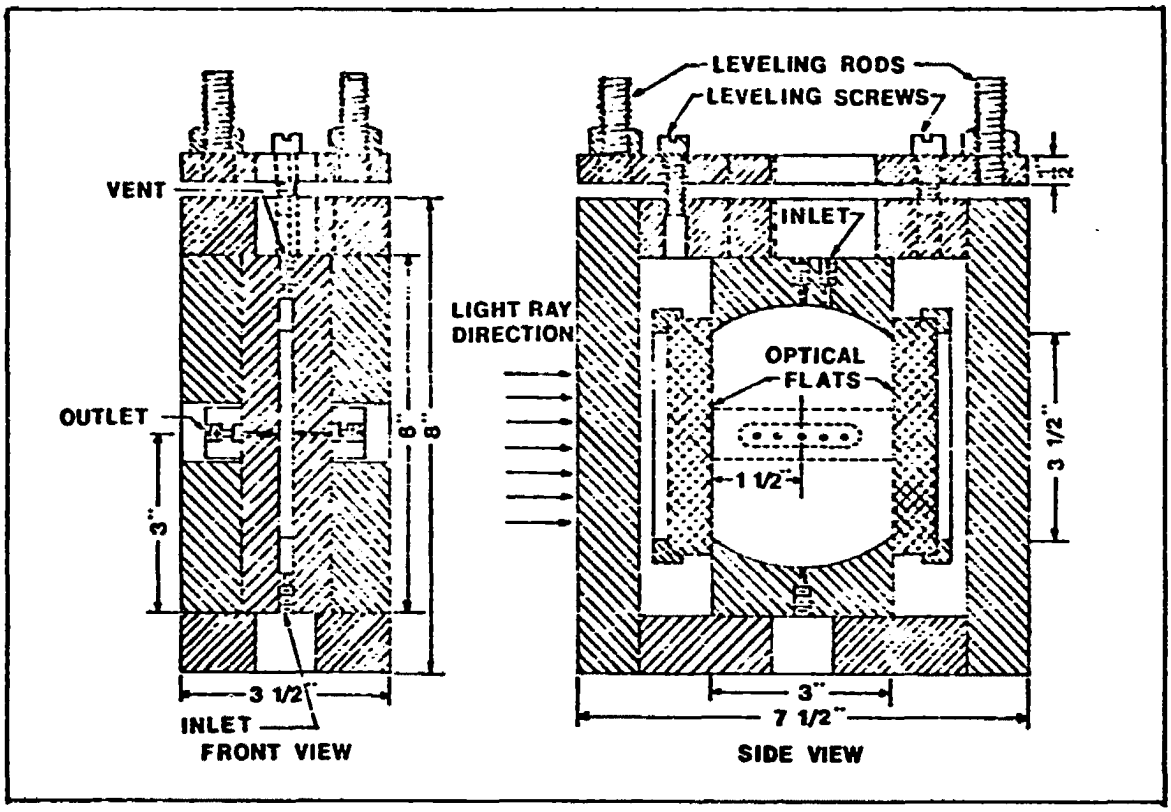


Figure 1. Flowing Junction Test Cell

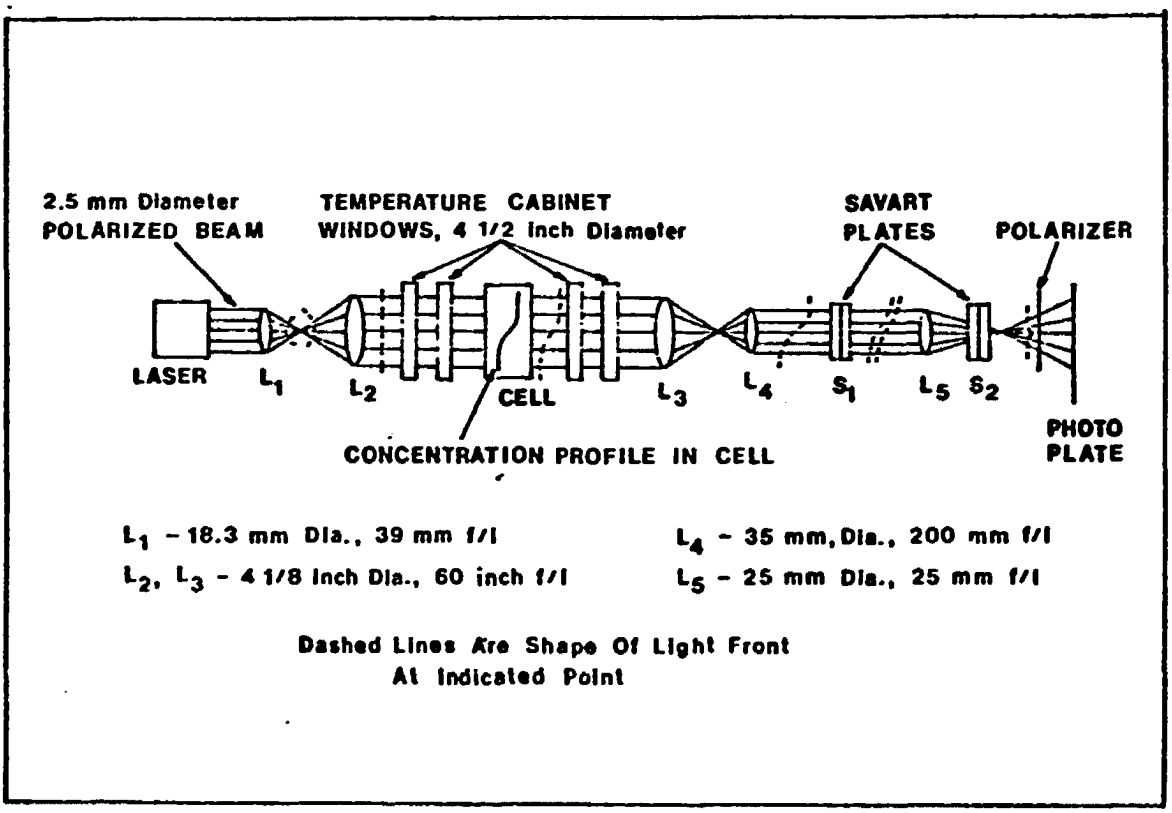


Figure 2. Birefringent Interferometer

The camera used in this study was a Nikkormat FT 35 mm camera without a lens. Kodak Plus-X Panchromatic film (ASA 125) was utilized.

Experimental Technique

In this section the experimental procedure used throughout this work will be discussed. Prior to obtaining any experimental data the diffusion cell as well as the lens system were thoroughly cleaned. The lens system was then carefully aligned with the test cell in place. Immediately before the start of each diffusion run fresh test solutions were prepared. Since this investigation is primarily concerned with infinite dilution diffusion coefficients one solution consisted entirely of pure solvent. The second solution was prepared by adding sufficient solute to ensure a refractive index difference of 5×10^{-5} between the two solutions. This difference was established as the practical operating limit of the interferometer. Smaller differences resulted in poor interface formation as well as short run times. The heavier solution was then placed in the reservoir inletting to the bottom of the cell; the lighter solution was placed in the upper reservoir. The temperature bath cover was then put in place and both the auxilliary and control heaters were turned on. The input to the auxilliary heater was decreased until the control heater controlled the temperature exclusively. At this point the test cell and the reservoir contents were allowed to come to temperature equilibrium; this procedure took about three hours. At the end of this period the entire cell was filled with fluid from the bottom reservoir. The side withdrawal valve was then opened and fluid was allowed to drain from the withdrawal slits. This procedure removed all the air pockets in the slits and in the manifold. After this was completed the cell was refilled with heavy solution. The air vent was then closed. At this point the test cell was completely sealed off. The valve to the light reservoir was then opened and the withdrawal valve was opened slightly. This allowed light solution to replace heavy solution in the top half of the cell. The withdrawal of fluid continued until light fluid reached the slits.

The heavy solution was then allowed to flow again and the process of interface sharpening began. When a sharp interface was achieved all valves were closed and the timer was started. Photographs of the spreading diffusion pattern were taken at various times during the run until sufficient photographs were obtained. At this time the run was stopped and the test cell and the reservoirs were drained. The cell and reservoirs were then cleaned with acetone and dried with air. Before the next run the alignment of the system was again checked. The resulting photograghs were developed in Microdol-X and measured.

Chemical Specifications and Properties

In Table 1 the manufacturers' specifications for the chemicals used are presented. All chemicals were used without further purification. Table 2 represents a tabulation of the physical properties of the materials studied as found in the literature.

Data Analysis and Reduction

The optical path length, z, is defined as the product of the refractive index, n, and the length, a, through the test cell. If small concentration ranges are considered then

$$z(x,t) = an = a[n_o + n_1(C_i(x,t) - C_{i0})] \tag{62}$$

Substituting this result into Equation (61) yields

$$(z(x,t) - z_0)/(z_1 - z_0) = \tfrac{1}{2}[1 + \operatorname{erf}(x/\sqrt{4D_{ij}t})] \tag{63}$$

where z_1 and z_0 are the optical path lengths which correspond to C_{i1} and C_{i0} respectively. To obtain the optical path gradient Equation (63) is differentiated, or

$$\partial z(x,t)/\partial x = \{(z_1 - z_0)/2\sqrt{\pi D_{ij}t}\} \exp[-(2x)^2/16D_{ij}t] \tag{64}$$

This equation then represents the interference patterns photographed during a run. Now any perpendicular to the interface and in the same direction as the light beam represents a constant value of the optical path gradient. Therefore Equation (64) produces equal values of $\partial z/\partial x$ provided the width of the fringe is measured at the same plane

Table 1. Chemical Specifications

Chemical(Grade)	Impurities	Source
Acetone(Spectrophotometric)	< 0.03 %	J.T. Baker
Aniline(A.R.)	< 0.02 %	J.T. Baker
Bromobenzene(A.R.)	< 0.002 %	J.T. Baker
Chlorobenzene(A.R.)	< 0.003 %	J.T. Baker
Chloroform(A.R.)	< 0.76 %	J.T. Baker
Methanol(Spectrophotometric)	< 0.004 %	J.T. Baker
Ethanol(A.R.)	-	U.S.I. Chem.
n-Propanol(A.R.)	< 0.002 %	J.T. Baker
n-Butanol(A.R.)	< 0.04 %	J.T. Baker
n-Amyl Alcohol(A.R.)	< 0.01 %	J.T. Baker
Cyclohexane(Pure)	< 0.05 %	Phillips

Table 2. Chemical Properties

Molecule	$D \times 10^5$ cm^2/sec	ρ gm/cm^3	M gm/mole	η cp	V_c cc/mole
Acetone	4.77	0.78508	58.08	0.316	211
Aniline	0.486	1.01750	93.13	3.71	274
Bromobenzene	1.14	1.48824	157.01	1.055	324
Chlorobenzene	1.758	1.10037	112.56	0.6883	308
Chloroform	2.58	1.47985	119.38	0.3635	240
Methanol	2.27	0.7871	32.04	0.547	118
Ethanol	1.01	0.78404	46.07	1.101	167
n-Propanol	0.646	0.7998	60.09	1.938	218.2
n-Butanol	0.504	0.800	74.12	2.624	274.6
n-Amyl Alcohol	0.478	0.810	88.15	3.55	333
Cyclohexane	1.42	0.7743	84.16	0.93	308

for all times. Mathematically, this is

$$(1/\sqrt{t_i})\exp[-(2x)^2/16D_{ij}t_i] = (1/\sqrt{t_m})\exp[-(2x)^2/16D_{ij}t_m] \quad (65)$$

The time of maximum fringe width, $2x_m$, is denoted by t_m. At t_m $\partial^2 z/\partial x^2 = 0$ and

$$(2x_m)^2 = 8D_{ij}t_m \quad (66)$$

Substituting Equation (66) into Equation (65) and rearranging yields

$$(2x_i)^2 = 8D_{ij}t_i[1 + \ln(t_m/t_i)] \quad (67)$$

Since an infinitely sharp interface is not possible experimentally a time correction factor must be employed. Haluska (29) showed that Equation (67) may be rewritten as

$$(2x_i)^2 = 8D_{ij}(t_i + t_o)[1 + \ln\{(t_m + t_o)/(t_i + t_o)\}] \quad (68)$$

This equation was then used as the model for the calculational procedure used to determine the diffusivity. As can be seen from these equations the data obtained from the photographs consists of $2x_i$ as a function of time.

The method used in this work to extract the diffusivity was a pattern search procedure. The method is composed of two parts. The first consists of making small steps in the vicinity of a basepoint, calculated from initial guesses, to determine the trend of the function at that point. Each parameter is incremented by a set amount and the value of the function is calculated at the new value. Only those increments which improve the function are allowed. After these local explorations are completed a pattern move is made. This consists of changing all the parametric values simultaneously; the changes are based on the local explorations. The procedure is repeated with the length and direction of each pattern move dependent on the previous local exploration. If no improvement is made the step size is reduced. The search is ended when the step size reaches a desired minimum. In this work the parameters are D_{ij}, t_m and t_o. The calculated function is $(2x_i)^2_{calc} - (2x_i)^2_{exp}$. The program used in this work was developed by Rimmer (62) and is shown in Table 3.

```
C-FOCAL, 1969

01.05 A N,A,B;F I=1,N;A T(I),C,D;D 2.0

02.05 S P(I)=(FABS(C-D)*.635/FABS(A-B))↑2

05.01 A "D"X(2),"T0"X(3),"TM"X(1)
05.03 S D(1)=10;S D(2)=.1E-05;S D(3)=5.;S G=0
05.05 S A=1;D 10.0;S B=D;F I=1,3;S Z(I)=0
05.10 S C=0;F I=1,3;D 6.0
05.15 I (A+C-1)5.20,5.45,5.25
05.20 S A=1;F I=1,3;S X(I)=X(I)-Z(I)*D(I);S Z(I)=0
05.22 G 5.10
05.25 F I=1,3;S X(I)=X(I)+Z(I)*D(I)
05.30 D 10.0;I (B-D)5.35,5.40,5.40
05.35 S A=2;S B=D;G 5.10
05.40 S A=0;G 5.10
05.45 S A=1;S G=G+1;F I=1,3;S D(I)=D(I)/2
05.47 T ""
05.50 I (G-12)5.10;T %,!,"DAB"X(2),"   T0"X(3),"   TM"X(1),!!
05.55 S A=0;F J=1,N;D 11.05;S D=100*FABS(E-P(J))/P(J);D 5.65
05.60 S A=A/N;T "AV "A,"%";0
05.65 T %4.1,T(J),%,P(J),E,%4.2,D,!;S A=A+D

06.01 S X(I)=X(I)+D(I);D 10.0;I (B-D)6.05,6.10,6.10
06.05 S B=D;S C=4;S Z(I)=Z(I)+1;R
06.10 S X(I)=X(I)-2*D(I);D 10.0;I (B-D)6.15,6.20,6.20
06.15 S B=D;S C=4;S Z(I)=Z(I)-1;R
06.20 S X(I)=X(I)+D(I)

10.05 S D=0;F J=1,N;D 11.0

11.05 S E=8*X(2)*(T(J)+X(3))*(1+FLOG(X(1)/(T(J)+X(3))))
11.10 S D=D-(P(J)-E)↑2
```

Table 3. Pattern Search Program

Experimental Results

The systems studied in this work were chosen for several reasons. One of these is that each binary pair must be composed of on associated molecule and one unassociated molecule. The premise leading to this choice is this: if a normally associated molecule is infinitely dilute in an unassociated solvent, the measured diffusion coefficient represents the motion of an associated molecule in an unassociated state. The unassociated molecule chosen for study was cyclohexane. The second reason is that self-diffusion coefficients for these molecules are readily available in the literature. A summary of the experimental data obtained is given in Table 4.

Table 4. Experimental Diffusion Coefficients With Cyclohexane As Component j.

Molecule (i)	Initial Mass Fraction i	$D_{ij}^{\infty} \times 10^5$ cm^2/sec	Initial Mass Fraction j	$D_{ji}^{\infty} \times 10^5$ cm^2/sec
Acetone	0.000723	2.745	0.000712	3.564
Aniline	0.000316	1.758	0.000183	0.478
Bromobenzene	0.000461	1.458	0.000125	1.286
Chlorobenzene	0.000568	1.620	0.000281	1.772
Chloroform	0.003049	1.936	0.000836	2.184
Methanol	0.000620	4.876	0.000551	2.425
Ethanol	0.000826	2.950	0.000789	1.706
n-Propanol	0.001238	2.504	0.001160	1.193
n-Butanol	0.001815	2.242	0.001701	0.907
n-Amyl Alcohol	0.002885	1.765	0.002669	0.878

CHAPTER IV

THE PREDICTION OF INFINITE DILUTION DIFFUSION COEFFICIENTS

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 (see Chapman and Cowling (16)). Loflin and Mclaughlin (40), by an application of the Rice-Allnatt theory (61), have descibed 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 exhibiting this type of interaction was provided by Enskog. Thorne (see Chapman and Cowling (16)) extended this work to binary systems; Tham and Gubbins (72) 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.

Equation Development

The general expression for diffusion in a mixture of rigid spheres has been presented by Tham and Gubbins (72) as

$$D_{ij} = (P_2 E_{11} - P_1 E_{12})/(n_i P_1 + n_j P_2)\cdot(n^o \delta^o_{ij}/g_{ij}) \qquad (69)$$

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

$$E_{h\ell} = \delta_{h\ell} + 2\rho b_{\ell h} g_{h\ell} + \sum_i n_h \rho b_{hi} (\partial g_{hi}/\partial n_\ell) \tag{70}$$

and

$$P_m = \sum_i \{\delta_{im} + 2\rho b_{mi} g_{im} + \sum_k n_i \rho b_{ik} (\partial g_{ik}/\partial n_i)\} = \sum_i E_{im} \tag{71}$$

where δ is the Kronekker delta and

$$\rho b_{\ell h} = \zeta x_h (R_\ell + R_h)^3/2Y_3 \tag{72}$$

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 (15) and is

$$\begin{aligned} g_{ij}(\sigma_{ij}) = {} & 1/(1 - \zeta) \\ & + [3/(1 - \zeta)^2]\{[R_i R_j/(R_i + R_j)](\zeta Y_2/Y_3)\} \\ & + [2/(1 - \zeta)^3]\{[R_i R_j/(R_i + R_j)](\zeta Y_2/Y_3)\}^2 \end{aligned} \tag{73}$$

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

$$D^\infty_{ij} = \lim_{n_i \to 0} \{D_{ij}\} = n^o\mathcal{D}^o_{ij}/(n_j g^\infty_{ij}) \tag{74}$$

The radial distribution function reduces to

$$\begin{aligned} g^\infty_{ij} = {} & 1/(1 - \zeta) + [3/(1 - \zeta)^2][\zeta\sigma_{ii}/(\sigma_{ii} + \sigma_{jj})] \\ & + [2/(1 - \zeta)^3][\zeta\sigma_{ii}/(\sigma_{ii} + \sigma_{jj})]^2 \end{aligned} \tag{75}$$

The dilute gas value for a binary mixture is given by

$$n^o\mathcal{D}^o_{ij} = (3/2)(NkT/2\pi)^{\frac{1}{2}}[(M_i + M_j)/M_i M_j]^{\frac{1}{2}}/(\sigma_{ii} + \sigma_{jj})^2 \tag{76}$$

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 (74), (75), and (76) reduce to

$$D^{\infty}_{ij}\ (i = j) = D^{\infty}_{jj} \tag{77}$$

$$g^{\infty}_{jj} = 1/(1 - \zeta) + [3/(1 - \zeta)^2][\zeta/2] + [2/(1 - \zeta)^3][\zeta/2]^2 \tag{78}$$

$$n^{o}\mathfrak{D}_{jj} = (3/8)(NkT/\pi M_j)^{\frac{1}{2}}(1/\sigma_{jj})^2 \tag{79}$$

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

$$D^{\infty}_{ij}/D^{\infty}_{jj} = [2\sigma_{jj}/(\sigma_{ii} + \sigma_{jj})]^2[(M_i + M_j)/2M_i]^{\frac{1}{2}}[g^{\infty}_{jj}/g^{\infty}_{ij}] \tag{80}$$

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 3 the radial distribution function ratio is plotted versus the length parameter ratio σ_{ii}/σ_{jj} for the solvent cyclohexane. This represents a typical plot for liquids. 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 ratio may be represented by

$$g^{\infty}_{ij}/g^{\infty}_{jj} = \alpha(\sigma_{ii}/\sigma_{jj}) + \beta \tag{81}$$

However, it may be shown that

$$g^{\infty}_{ij}/g^{\infty}_{jj} = \sigma_{ii}/\sigma_{jj} \tag{82}$$

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

In Figure 4 the quantity $[2\sigma_{ii}/(\sigma_{ii} + \sigma_{jj})]^2$ is plotted versus the

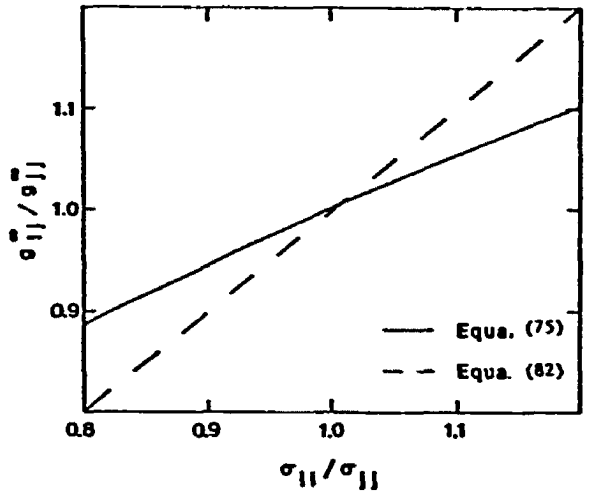


Figure 3. Radial Distribution Function Ratio.

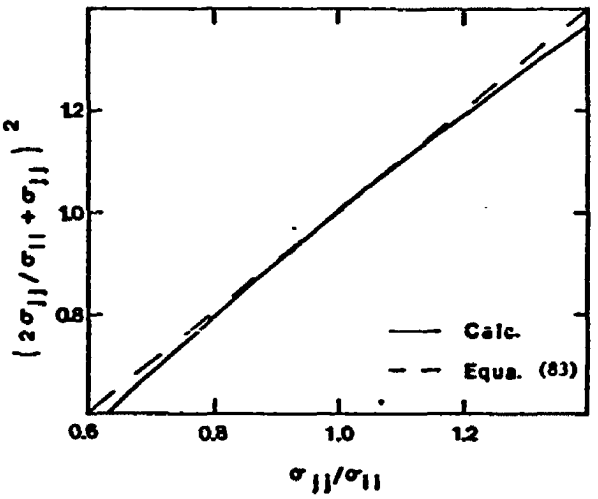


Figure 4. Size Factor Plot.

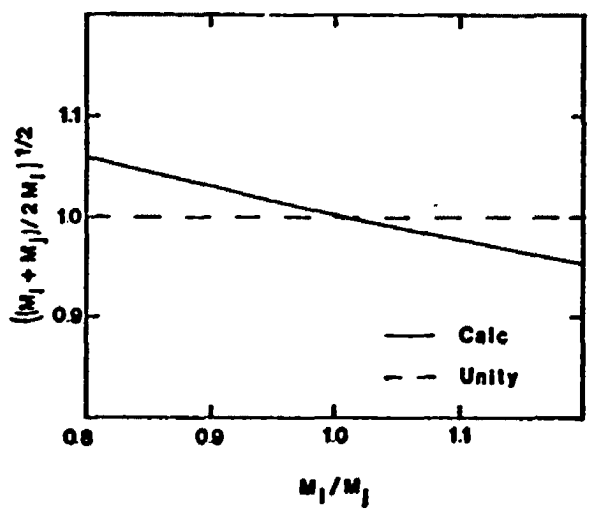


Figure 5. Mass Factor Plot.

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

$$[2\sigma_{ii}/(\sigma_{ii} + \sigma_{jj})]^2 = \sigma_{jj}/\sigma_{ii} \tag{83}$$

introduces almost no error in the region in which most liquid mixtures occur. Thus, Equation (80) may be rewritten as

$$D^{\infty}_{ij}/D^{\infty}_{jj} = (\sigma_{jj}/\sigma_{ii})^2[(M_i + M_j)/2M_i]^{\frac{1}{2}} \tag{84}$$

Here it is seen that the ratio of the coefficients of infinite dilution diffusion 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 (7) and Vadovic and Colver (76) have related the molecular length parameter to the volume at the melting point, or

$$\sigma_{ii} = \alpha V_{mi}^{1/3} \tag{85}$$

Where α is a constant for a given class of compounds. Dullien (20) has suggested that the critical volume be used to obtain the length parameter, that is

$$\sigma_{ii} = \beta V_{ci}^{1/3} \tag{86}$$

It has further been shown by Vadovic and Colver (77) that for most organic compounds, the following relationship holds

$$V_{mi} = 0.310\ V_{ci} \tag{87}$$

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 (20) presented an expression which may be written as

$$D^{\infty}_{jj}\eta_j M_j/\rho_j T = 0.103 \times 10^{-8} V_{cj}^{2/3} \tag{88}$$

Alternately, Vadovic and Colver (78), from a consideration of the rigid

sphere theory of Longuet-Higgins and Pople (41), have presented the following equation

$$D^{\infty}_{jj}\eta_j M_j/\rho_j T = 0.219 \times 10^{-8} V_{mj}^{2/3} \qquad (89)$$

Both these equations have been shown to accurately predict self-diffusion in liquids.

Substituting these results into Equation (84) yields

$$D^{\infty}_{ij}\eta_j M_j/\rho_j T = 0.103 \times 10^{-8}(V_{cj}/V_{ci})^{2/3}[(M_i + M_j)/2M_i]^{\frac{1}{2}}(V_{cj})^{2/3} \qquad (90)$$

or

$$D^{\infty}_{ij}\eta_j M_j/\rho_j T = 0.219 \times 10^{-8}(V_{mj}/V_{mi})^{2/3}[(M_i + M_j)/2M_i]^{\frac{1}{2}}(V_{mj})^{2/3} \qquad (91)$$

It is immediately apparent that the quantity $D^{\infty}_{ij}\eta_j M_j/\rho_j T$ should be a constant with temperature for a particular binary mixture. This is indeed the case as shown in Table 5 for the data of Haluska and Colver (29) and that of Sanni, Fell and Hutchison (64).

In order to test the developed relationship, Equation (90) was tested with the data for binary mixtures of n-alkanes at 25°C. The molecules in this series are normally considered to be non-associated and undergo uniform interaction with other members of the series. This interactions are somewhat ideal and, as such, a rigid sphere approach would be expected to yield at least qualitative results. In Table 6 the calculated results are compared to the literature values. The proposed equation reproduces both the infinite dilution diffusion coefficient and the ratio of diffusivities, $D^{\infty}_{ij}/D^{\infty}_{jj}$, with good accuracy. Also presented in the table are the results as calculated by the Wilke-Chang (84) equation

$$D^{\infty}_{ij} = 7.4 \times 10^{-8} (\phi M_j)^{\frac{1}{2}} T/\eta_j V_i^{0.6} \qquad (92)$$

The average errors produced by Equations (90) and (92) are 5.86 and 10.02 per cent respectively. Also it should be noticed that Equation (90) reproduces the data for the solvents dodecane and hexadecane with good agreement whereas the Wilke-Chang equation does not. The Wilke-Chang result predictes 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 (42)

Table 5. Diffusion Coefficient Group For Associated Systems

i	j	T	D_{ij}^{∞}	$D_{ij}^{\infty}\eta_j M_j/\rho_j T$	D_{ji}^{∞}	$D_{ji}^{\infty}\eta_j M_j/\rho_j T$	Reference
$C_6H_5CH_3$	$C_6H_{11}CH_3$	298	1.65	4.63	2.21	4.40	29
		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	29
		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	64
		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	64
		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	64
		313	1.915	4.79	1.611	3.76	
		328	2.415	4.72	1.979	3.76	
$n\text{-}C_7H_{14}$	C_6H_6	298	1.785	3.26	3.915	7.60	64
		313	2.279	3.33	4.744	7.78	
		328	2.795	3.29	5.616	7.90	

Table 6. Diffusivities in Paraffinic Systems

Solute	Solvent	$(D_{ij})_e$	Ref.	$(D_{ij}^{\infty})_c$		$D_{ij}^{\infty}/D_{ij}^{\infty}$		
				Equa.(90)	Wilke-Chang	Exp.	Equa.(84)	Wilke-Chang
C_5	C_5	5.45	11	5.62	5.07	1	1	1
C_6	C_6	4.21	19	4.08	3.73	1	1	1
C_{12}		2.73	9	2.27	2.67	0.608	0.556	0.718
C_{16}		2.19	8	1.80	2.30	0.498	0.442	0.618
C_7	C_7	3.12	11,19	3.06	2.86	1	1	1
C_{16}		1.78	9	1.52	1.89	0.543	0.497	0.662
C_8	C_8	2.368	79	2.28	2.17	1	1	1
C_{12}		1.719	79	1.61	1.77	0.732	0.705	0.816
C_9	C_9	1.70	19	1.72	1.66	1	1	1
C_{10}	C_{10}	1.31	19	1.32	1.29	1	1	1
C_6	C_{12}	1.45	9	1.51	1.14	2.05	1.91	1.39
C_8		1.143	79	1.15	1.00	1.53	1.45	1.23
C_{12}		0.809	79	0.795	0.817	1	1	1
C_{16}		0.67	36	0.618	0.70	0.796	0.777	0.857
C_6	C_{16}	0.869	8	0.847	0.59	2.71	2.53	1.64
C_7		0.760	9	0.729	0.55	2.47	2.18	1.53
C_{12}		0.49	36	0.435	0.42	1.53	1.30	1.17
C_{16}		0.32	79	0.334	0.36	1	1	1

results in an average error of 13.96 per cent for these binary pairs.

To further test the proposed equation the results were compared with the data given in Table 5. In these systems either one or both of the mixture constituents have associative properties. As such these molecules are non-ideal 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 5 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 (90) may be rewritten as

$$D_{ij}^{\infty}\eta_j M_j/\rho_j T = 0.103 \times 10^{-8}(V_{cj}/V_{ci})^{2/3}[(M_i + M_j)/2M_i]^{N/2}(V_{cj})^{2/3} \quad (93)$$

where N = 1 for non-associated systems and N = 0 for a system where one or both of the species exhibits associative tendencies. Hence, for associative systems Equation (93) is rewritten as

$$D_{ij}^{\infty}\eta_j M_j/\rho_j T = 0.103 \times 10^{-8}(V_{cj}/V_{ci})^{2/3}(V_{cj})^{2/3} \quad (94)$$

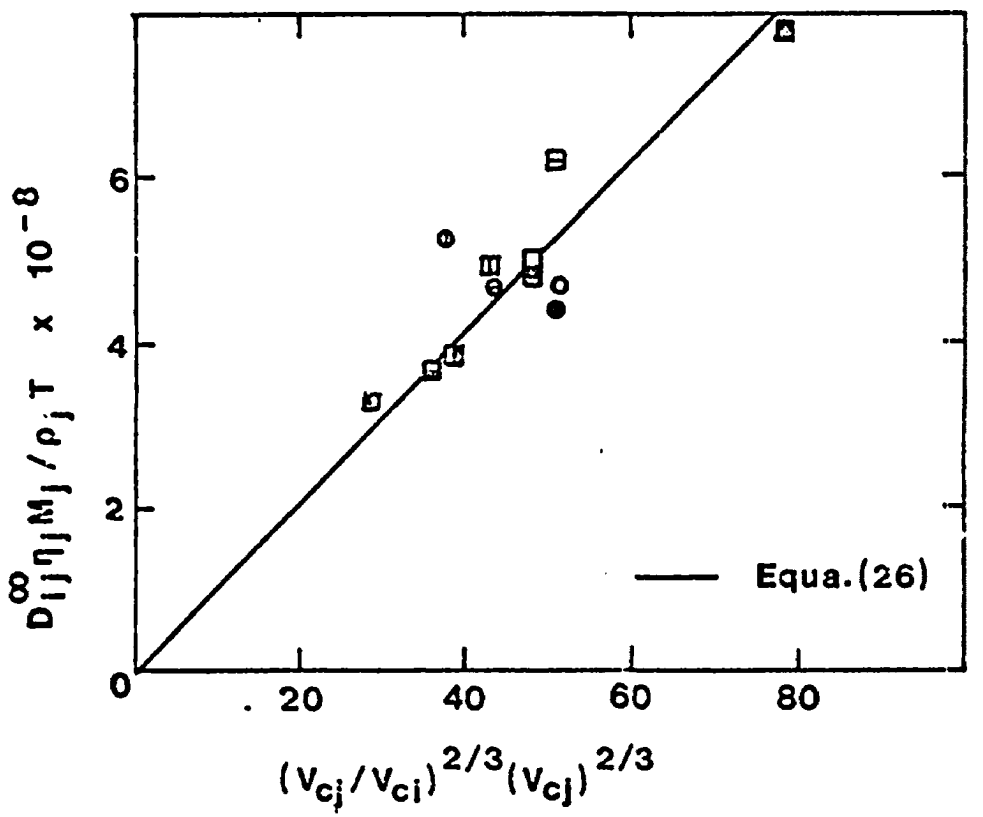
The results of this equation when compared with the data given in Table 5 are plotted in Figure 6. As can be seen good agreement with experiment is achieved over a wide range of variables. The average error resulting from the use of Equation (94) is less than 9 per cent. Use of the Wilke-Chang and Lusis-Ratcliff expressions results in errors of 13 and 15 per cent respectively. Thus the proposed equation is significantly better than the previously published correlations for the data tested.

To further test the developed result the expression

$$D_{ij}^{\infty} = (V_{cj}/V_{ci})^{2/3}D_{jj}^{\infty} \quad (95)$$

was used to calculate mixture diffusivities when the solvent self-diffusion coefficient is known. The results of this test are shown in Table 7. Again good results are achieved.

In this work the correlating parameter used was the critical



	SOLUTE	SOLVENT
o	$C_6H_5CH_3$	$C_6H_{11}CH_3$
●	$C_6H_{11}CH_3$	$C_6H_5CH_3$
o	$C_6H_5CH_3$	$C_6H_5NH_2$
●	$C_6H_5NH_2$	$C_6H_5CH_3$
□	C_6H_{12}	$C_6H_5CH_3$
▣	$C_6H_5CH_3$	C_6H_{12}
⊟	C_6H_6	C_6H_{12}
⊟	C_6H_{12}	C_6H_6
⊟	CCl_4	C_6H_{12}
▣	C_6H_{12}	CCl_4
▣	nC_7H_{16}	C_6H_6
▣	C_6H_6	nC_7H_{16}

Circles: Haluska and Colver (29)

Squares: Sanni, Fell and Hutchison (64)

Figure 6. Diffusivity Group For Associated Molecules

Table 7. Calculated Mixture Diffusivity With Known Solvent Self-Diffusion Coefficient at 25°C.

Solute	Solvent	$(D_{ij}^{\infty})_e$	Ref.	$(D_{ij}^{\infty})_c^*$	% error
Benzene	Acetone	4.15	45	4.16	0.24
Bromoform		3 23	57	3.76	16.40
CCl_4		3.54	4	3.99	12.71
Chloroform		3.63	45	4.38	12.71
Cyclohexane		3.564		3.49	2.07
Benzene	Aniline	0.54	56	0.50	6.85
CCl_4		0.52	56	0.48	7.11
Cyclohexane		0.478		0.45	5.85
Toluene		0.478	29	0.44	9.25
Acetone	Benzene	2.75	45	2.46	10.54
Aniline		1.96	56	2.08	6.12
CCl_4		1.912	85	2.08	8.78
Chlorobenzene		2.11	31	1.93	8.53
Cyclohexane		2.09	45	1.93	7.65
Toluene		1.847	64	1.90	2.86
Chlorobenzene	Bromobenzene	1.342	13	1.17	12.81
Cyclohexane		1.286		1.19	7.46
Toluene(30°C)		1.41	13	1.27	9.92
Acetone	CCl_4	1.69	4	1.58	6.50
Aniline		1.58	56	1.33	15.82
Benzene		1.419	85	1.37	3.59
Chloroform		1.505	85	1.49	0.99
Cyclohexane		1.275	64	1.23	3.52
Methyl Ethyl Ketone		1.552	3	1.35	13.01

* Equation (95)

Table 7 Continued.

Solute	Solvent	$(D_{ij}^{\infty})_e$	Ref.	$(D_{ij}^{\infty})_c^*$	% error
Benzene	Chlorobenzene	1.869	31	0.97	5.40
Bromobenzene		1.342	13	1.17	12.81
Cyclohexane		1.772		1.76	0.68
Toluene		1.70	13	1.73	1.76
Acetone	Chloroform	2.35	45	2.81	19.57
n-Butyl Acetate		1.85	57	1.71	8.18
CCl_4		1.945	85	2.35	20.80
Cyclohexane		2.184		2.37	8.51
Diethyl Ether		2.13	64	2.36	10.79
Ethyl Acetate		2.29	57	2.02	13.36
Methyl i-Butyl Ketone		1.89	57	1.92	2.11
Methyl Ethyl Ketone		2.13	57	2.40	12.67
Acetone	Cyclohexane	2.745		1.85	32.60
Aniline		1.758		1.57	10.69
Benzene		1.88	45	1.59	15.42
Bromobenzene		1.458		1.38	5.34
CCl_4		1.486	64	1.53	2.93
Chlorobenzene		1.620		1.42	12.34
Chloroform		1.936		1.66	14.26
Toluene		1.57	64	1.39	11.46
Aniline	Toluene	2.10	29	2.46	14.76
Benzene		2.545	64	2.49	2.16
Bromobenzene($30^{\circ}C$)		2.27	13	2.24	0.99
Chlorobenzene($30^{\circ}C$)		2.23	13	2.23	0.00
Cyclohexane		2.42	64	2.23	7.85
Methylcyclohexane		2.21	29	2.07	6.29
		Average Absolute Error			8.87 %

* Equation (95)

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

Conclusion

It has been 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 $D^{\infty}_{ij}\eta_j M_j/\rho_j T$ 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. For associated molecules the mass effect is overshadowed by molecular interactions. Finally, the result

$$D_{ij}\eta_j M_j/\rho_j T = 0.103 \times 10^{-8}(V_{cj}/V_{ci})^{2/3}[(M_i + M_j)/2M_i]^{N/2}(V_{cj})^{2/3} \qquad (96)$$

has been shown to represent both binary and self-diffusion data with good precision.

CHAPTER V

THE PREDICTION OF DIFFUSIVITIES WITH ALCOHOL AND WATER AS SOLVENTS

In the preceding chapter a basis for the prediction of diffusivities has been developed. The binary Enskog dense fluid transport model was modified and simplified by applying approximations for the liquid state. For associative systems it was shown that

$$D_{ij}^{\infty}/D_{jj}^{\infty} = (V_{cj}/V_{ci})^{2/3} \tag{97}$$

This equation was tested with the data for numerous organic molecules and was found to yield good agreement with data. However, in some cases, most notably for the alcohol solvents and water as solvent, the predicted values of the diffusivities 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

$$D_{ij}/D_{jj} = F(V_{cj}/V_{ci})^{2/3} \tag{98}$$

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

In the consideration of the primary alcohols as solvents it was found that Equation (97) when applied to the prediction of the diffusivity of organic non-alcoholic solutes was approximately 50 per cent lower than the experimentally observed values. It was found that the use of a value of F = 2.08 gave much closer agreement with the experimental data. A tabulation of experimental and calculated values is found in Table 8. For the data tested a deviation of 10.17 per cent was calculated. It should be noted that the experimental self-diffusivities, as listed by Dullien, were utilized in the calculations.

A similar situation was found for water as a solvent. The predicted values, however, were only 20 per cent lower than those

Table 8. Diffusivities of Organic Solutes In Alcohols

Solute	Solvent	T	$(D_{ij}^{\infty})_e$	Ref.	$(D_{ij}^{\infty})_c^*$
Benzene	Methanol	300	2.76	14	2.79
Bromobenzene		288	1.75	34	2.03
CCl_4		298	2.30	30	2.68
Cyclohexane		298	2.425		2.49
Ethyl Bromide		288	2.40	34	2.66
Toluene		298	2.56	66	2.45
Benzene	Ethanol	298	1.81	4	1.56
CCl_4		298	1.50	30	1.50
Cyclohexane		298	1.706		1.40
Toluene		288	1.60	39	1.04
Benzene	n-Propyl Alcohol	298	1.28	43	1.20
Cyclohexane		298	1.193		1.08
Toluene		298	1.35	67	1.05
Benzene	n-Butyl Alcohol	298	0.988	43	1.09
Cyclohexane		298	0.907		0.97
Benzene	n-Amyl Alcohol	298	0.985	43	1.17
Cyclohexane		298	0.878		1.05

* Equation (98), F = 2.06

measured experimentally. From a consideration of the data the following relationship was found to be valid

$$D^{\infty}_{ij}/D^{\infty}_{jj} = 1.165\ (V_{cj}/V_{ci})^{2/3} \tag{99}$$

To facilitate the calculation of the binary diffusivity it was found that the self-diffusivity of water could be calculated to within 2 percent through the use of the following equation

$$D^{\infty}_{jj}\eta_j M_j/\rho_j T = 0.0926 \times 10^{-8}\ (V_{cj})^{2/3} \tag{100}$$

Equation (100) is valid from the normal melting point of water to the normal boiling point. Equation (99) with Equation (100) was tested with the data of Bonoli and Witherspoon (12) and for data cited in Reid and Sherwood (60). The data of Bonoli and Witherspoon was for cyclic hydrocarbons in water in the temperature range of 2 to 60 ^{o}C. The proposed equation reproduced this data to within 5.5 per cent and all of the data tested to within 6.5 per cent. This deviation is significantly lower than those produced by previously published correlations; the Wilke-Chang equation, for example, yields an average error of 11 per cent. A comparision of the results as calculated in this work with the experimental values is found in Table 9.

In the consideration of these systems it must be remembered that they exhibit conditions which are outside the range of validity of the original assumptions used in the derivation of Equation (97). As such the F-factor may be considered to be a correction factor which allows the use of Equation (97) in a much wider sense. It may be said, however, that Equation (98) does provide a good description of experimental behaviour for the two cases tested here.

Table 9. Diffusivities With Water As Solvent

Solute	T	$(D_{ij}^{\infty})_e$	$(D_{ij}^{\infty})_c$ *
Data of Bonoli and Witherspoon (12)			
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

* Equation (98), F = 1.165

Table 9 Continued.

Solute	T	$(D_{ij}^{\infty})_e$	$(D_{ij}^{\infty})_c$ *
Data of Bonoli and Witherspoon (12)			
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 (60)			
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

* Equation (98), F = 1.165

CHAPTER VI

THE PREDICTION OF BINARY INFINITE DILUTION DIFFUSION COEFFICIENTS IN ORGANIC NON-ALCOHOLIC SYSTEMS

In the measurement of a diffusivity in a binary system the diffusivity is normally taken to be that which results from the diffusion of a pure solute in a pure solvent. For non-associated systems this is indeed the case. A single solute molecule is diffusing in a medium composed entirely of solvent monomers. For an associated system this condition is not necessarily valid. The measured diffusivity is the result of the diffusion of an average solute molecule in a medium composed of average solvent molecules. The characteristics of these average molecules are determined by the properties of the individual solute and solvent species as well as the interactions between them. In this study a procedure will be developed for the determination of average parameters as well as for the effect that association has on infinite dilution diffusion coefficients.

Equation Development

The basis for this approach is the Enskog theory of the transport of dense rigid spheres as applied to diffusion. For self-diffusion the Enskog result is

$$D^{\infty}_{jj} = n^{o}\mathcal{D}^{o}_{jj}/n_j g^{\infty}_{jj} \tag{101}$$

where the dilute gas value is

$$n^{o}\mathcal{D}^{o}_{jj} = (3/8)(NkT/\pi M_j)^{\frac{1}{2}}(1/\sigma_{jj}^{2}) \tag{102}$$

and the radial distribution function is

$$g^{\infty}_{jj} = 1/(1 - \zeta) + [3/(1 - \zeta)^2](\zeta/2) + [2/(1 - \zeta)^3](\zeta/2)^2 \tag{103}$$

Thorne (See Chapman and Cowling (16)) has extended this result to the binary case to yield

$$D_{ij}^{\infty} = n^{o}\mathcal{D}_{ij}^{o}/n_j g_{ij}^{\infty} \tag{104}$$

where

$$n^{o}\mathcal{D}_{ij}^{o} = (3/2)(NkT/2\pi)^{\frac{1}{2}}[1/(\sigma_{ii} + \sigma_{jj})]^2[(M_i + M_j)/M_i M_j]^{\frac{1}{2}} \tag{105}$$

and the radial distribution function for a binary system of rigid spheres is given by

$$g_{ij}^{\infty} = 1/(1 - \zeta) + [3/(1 - \zeta)^2]\{[\sigma_{ii}/(\sigma_{ii} + \sigma_{jj})]\zeta\} + [2/(1 - \zeta)^3]\{[\sigma_{ii}/(\sigma_{ii} + \sigma_{jj})]\zeta\}^2 \tag{106}$$

where $\zeta = (\pi/6)n_j\sigma_{jj}^3$. It can be seen that the principle dependent parameters are the mass and diameter of the solute and solvent species. These then are the descriptive equations for diffusion in either a pure fluid or for a binary mixture at infinite dilution.

There are four general cases of diffusion in binary systems. The first of these is the diffusion of an unassociated solute in an unassociated solvent. In this case there are neither solvent-solvent interactions or solute-solvent interactions. This corresponds to diffusion in mixtures of n-alkanes. The second case involves the diffusion of a normally associated molecule in a non-associated system. Infinite dilution conditions imply that the solute molecule is isolated from interaction with similar molecules. Consequently, the solute behaves as if it were noninteracting. Again there are no solvent-solvent interactions. An example of this type of diffusion is aniline in cyclohexane. Diffusion of an unassociated molecule in an associated solvent represents the next case. In this instance there are solvent-solvent interactions and the diffusion process is characterized by the diffusion of unassociated molecule in a medium composed solvent complexes. These complexes behave as larger, heavier species. Cyclohexane in aniline is this type of system. The last case represents the most complex. Solute-solvent as well as solvent-solvent association occurs. The result is the diffusion of an average solute molecule, composed of solute-solvent complexes, into a medium composed of solvent-solvent complexes. Examples of this

type of diffusion are aniline-toluene and chloroform-carbon tetrachloride. Each case will be discussed individually in the following paragraphs.

The most simple type of diffusion is represented by the motion of an unassociated solute in an unassociated solvent. The diffusion of the paraffin hydrocarbons is a good example of this case. For these species the diameter of the molecule under study may be calculated from the self-diffusion value as represented by Equation (101). The calculated values for several hydrocarbons are presented in Table 10. These values may then be used to calculate the infinite dilution diffusivity for any binary pair. It is found, however, that the calculated values are slightly lower than the experimental values. Therefore the use of a correction factor is suggested. This factor is to be multiplied by the diffusivity as calculated by Equation (104) and is

$$C_f = \{1 + (|\sigma_{ii} - \sigma_{jj}|/\sigma_{jj})\}^{\frac{1}{4}} \tag{107}$$

A comparision of calculated and experimental values is also given in Table 10. For the n-alkane pairs considered the average deviation is less than 4 per cent. Thus the result

$$D_{ij}^{\infty} = C_f \pi^o \mathfrak{D}_{ij}^o / n_j g_{ij}^{\infty} \tag{108}$$

represents an excellent means for calculating the diffusivities in non-associating systems.

For an associated molecule diffusing in an unassociated medium the defining equation is identical to Equation (108). In this case the normally associated solute species can not associate with itself or with solvent monomers. It therefore behaves as an unassociated molecule, enabling the calculation of the size of an associated monomer. In Table 11 the calculated diameters of several species are presented. In each case the unassociated solvent is cyclohexane and the temperature is 25°C. Also presented are the diameters as calculated from the dilute gas viscosity where available.

Now that the diameter of an associated monomer is known the self-diffusion coefficient of an associated species may be considered.

Table 10. Length Parameters and Diffusivities For n-Alkanes

Solute (i)	Solvent (j)	σ_{jj}	$(D_{ij}^{\infty})_e$	Ref.	$(D_{ij}^{\infty})_c$ *
C_5	C_5	5.47	5.45	11	5.44
C_6	C_6	5.86	4.21	19	4.18
C_{12}			2.73	9	2.53
C_{16}			2.19	8	2.08
C_7	C_7	6.25	3.12	11,19	3.11
C_{16}			1.78	9	1.69
C_8	C_8	6.60	2.368	79	2.28
C_{12}			1.719	79	1.74
C_9	C_9	6.69	1.70	19	1.69
C_{10}	C_{10}	7.30	1.31	19	1.30
C_6	C_{12}	7.90	1.45	9	1.63
C_8			1.143	79	1.22
C_{12}			0.809	79	0.795
C_{16}			0.670	36	0.632
C_6	C_{16}	8.90	0.869	8	0.914
C_7			0.760	9	0.776
C_{12}			0.49	36	0.433
C_{16}			0.32	79	0.320

* Equation (108)

Table 11. Length And Association Parameters For Organic Molecules

Molecule	$(D^{\infty}_{jj})_e$	Ref.	$(\sigma_{jj})_D$	$(\sigma_{jj})_{\eta_o}$	$k_j n_{jl}$
Acetone	4.77	45	4.28	4.600	0.260
Aniline	0.486	5	5.22		0.316
Benzene	2.16	18	5.14	5.628	0.146
Bromobenzene	1.14	49	5.47		0.191
CCl_4	1.32	18	5.36	5.881	0.147
Chlorobenzene	1.758	31	5.34		0.175
Chloroform	2.58	45	4.76	5.430	0.156
Toluene	2.20	53	5.27	5.932	0.221

The coefficient of self-diffusion is simply representative of the motion of a solute in an identical medium. If the solvent is associative the solute will also complex. From a consideration of the continuous asssociation model of Prigogine and Defay (55) the following solute-solvent relations hold

$$J_1 + J_g \overset{k_j}{=} J_{g+1} \qquad g = 1,2,\ldots,\infty \qquad (109)$$

and

$$I_1 + J_g \overset{k_{ij}}{=} I_1 J_g \qquad g = 1,2,\ldots,\infty \qquad (110)$$

The assumptions made are that all degrees of association are possible for the solvent species, J, and that the solute, I, may interact with any of the solvent complexes. Also only two subspecies may interact at at any time. k_i and k_{ij} are assumed to be the same for each particular interaction. For the case of self-diffusion I is experimentally a radioactive species of J, with the same size and mass of J. Consequently, Equations (109) and (110) are identical. As previously stated the size and mass are the principle dependent parameters in the present approach. In an associative system the size and mass are some value which is different from the monomer value. In order to calculate these parameters, at least in an average sense, let the total number density be the sum of the monomer, dimer, trimer, etc. number densities, or

$$n_j^T = n_{j1} + n_{j2} + n_{j3} + \ldots + n_{j\infty} \qquad (111)$$

Noting that

$$n_{j\ell} = k_j^{\ell - 1} n_{j1}^{\ell} \qquad (112)$$

Equation (111) may be reduced to

$$n_j^T = n_{j1}/(1 - k_j n_{j1}) \qquad (113)$$

Now the average solute and solvent parameters may be calculated by

$$\bar{P} = \sum_i x_{ji} P_i \qquad (114)$$

where $x_{ji} = n_{ji}/n_j^T$. For the size of the average molecule the volumes of the associating molecules are assumed to be additive or

$$(\sigma_{jj}^{3})_i = i\sigma_{jj}^{3} \tag{115}$$

Therefore the average molecular size is

$$\overline{\sigma_{jj}^{3}} = \sum_i i\, k_j^{i-1} n_{j1}^{i-1} (1 - k_j n_{j1}) \sigma_{jj}^{3} \tag{116}$$

or

$$\overline{\sigma_{jj}} = (\overline{\sigma_{jj}^{3}})^{1/3} = \sigma_{jj}/(1 - k_j n_{j1})^{1/3} \tag{117}$$

Thus $\overline{\sigma_{jj}}$ represents the average solvent diameter. In the case of self-diffusion it also represents the average solute diameter. A similar expression may be developed for the mass of the complex

$$\overline{M_j} = M_j/(1 - k_j n_{j1}) \tag{118}$$

Thus the average solute and solvent parameters have been established for the self-diffusion coefficient of an associated species. Using these expressions in Equations (101), (102), and (103) the solvent interaction parameter, $k_j n_{j1}$, may be calculated. In Table 11 the interaction parameters are presented. The number density in Equation (101) is taken to be the number of monomers available for complexing.

Once the interaction parameters for a solvent have been established the calculation of a diffusivity for an unassociated solute in an associated solvent is relatively simple. Equations (104), (105), and (106) are utilized; the mass and diameter of the solute are used and Equations (117) and (118) are used to represent the solvent parameters.

For the case of an associated solute diffusing in an associated solvent an additional parameter is necessary to characterize the diffusion process. The solvent parameters may still be calculated through the use of Equations (117) and (118). However, the properties of an average solute molecule must be defined. Recalling that

$$I_1 + J_g \overset{k_{ij}}{=} I_1 J_g \qquad g = 1,2,\ldots,\infty \tag{119}$$

the following relation may be developed

$$n_i^T = n_{i1} + n_{i2} + n_{i3} + \ldots + n_{i\infty} \tag{120}$$

Now

$$n_{im} = k_{ij} n_{i1} k_j^{m-2} n_{j1}^{m-1} \qquad m = 2,3,\ldots,\infty \tag{121}$$

Thus the total number density of I is

$$n_i^T = n_{iI}[1 + k_{ij}n_{jI}/(1 - k_j n_{jI})] \tag{122}$$

The number fraction of each solute subspecies is then

$$x_{im} = k_{ij}k_j^{m-2}n_{jI}^{m-1}/\{1 + [k_{ij}n_{jI}/(1 - k_j n_{jI})]\}$$
$$m = 2,3,\ldots,\infty \tag{123}$$

with $x_{iI} = 1/[1 + k_{ij}n_{jI}/(1 - k_j n_{jI})]$. From these results the average solute diameter and mass may be calculated

$$\overline{\sigma_{ii}^3} = \sigma_{ii}^3 + \sigma_{jj}^3(k_{ij}n_{jI}/k_j n_{jI})[k_j n_{jI}/(1 - k_j n_{jI})]/$$
$$\{1 + (k_{ij}n_{jI}/k_j n_{jI})[k_j n_{jI}/(1 - k_j n_{jI})]\} \tag{124}$$

A similar expression may be developed for the mass of the solute. In the present study the solute-solvent interaction parameter was taken to be

$$k_{ij}n_{jI} = \sqrt{k_i n_{iI} k_j n_{jI}} \tag{125}$$

Thus the diffusion of an associated solute in an associated solvent is completely characterized. A comparision of calculated results is made with experiment in Table 12. Both $k_{ij}n_{jI} = 0$ and $k_{ij}n_{jI} = \sqrt{k_i n_{iI} k_j n_{jI}}$ are considered. Good agreement with the data is obtained.

Discussion of Results

The method presented here provides an extremely useful method for the evaluation of diffusion data and also for the examination of solute-solvent interactions. From the particular molecules studied several statements may be made. Carbon tetrachloride as well as bromobenzene act as if unassociated in the solute state. However both these molecules tend to act as if associated in the solvent state. Aniline, as expected, exhibited the highest degree of association of the molecules tested and was associating as both solute and solvent. Toluene interacted with all benzene derivative solvents. Most solutes tended not to associate with the solvents acetone and chloroform. The solute results are presented in simplified form in Table 13. In

Table 12. Calculated Diffusivities For Associated Systems

Solute	Solvent	$(D_{ij}^{\infty})_e$	$(D_{ij}^{\infty})_c$ $k_{ij} = 0$	$(D_{ij}^{\infty})_c$ $k_{ij}n_{jl}=\sqrt{k_i n_{il} k_j n_{jl}}$
Benzene	Acetone	4.15	4.01	3.78
CCl_4		3.54	3.31	3.14
Chloroform		3.63	3.98	3.70
Cyclohexane		3.49	3.28	-
Benzene	Aniline	0.54	0.669	0.554
Cyclohexane		0.478	0.496	-
Toluene		0.478	0.604	0.493
CCl_4		0.520	0.514	0.433
Acetone	Benzene	2.75	3.44	2.90
Aniline		1.96	2.18	1.97
Bromobenzene		-	1.81	1.71
CCl_4		1.912	1.88	1.76
Chlorobenzene		2.11	2.02	1.89
Cyclohexane		2.09	1.87	-
Toluene		1.847	2.15	1.99
Benzene	Bromobenzene	-	1.79	1.57
Chlorobenzene		1.342	1.48	1.31
Cyclohexane		1.286	1.35	-
Toluene		1.36	1.64	1.42
Acetone	CCl_4	1.69	2.85	2.37
Aniline		1.58	1.76	1.54
Benzene		1.419	1.92	1.73
Chloroform		1.505	1.89	1.59
Cyclohexane		1.275	1.47	-
Benzene	Chlorobenzene	2.11	2.33	2.09
Bromobenzene		1.708	1.73	1.58
Cyclohexane		1.76	1.80	-
Toluene		1.70	2.11	1.87
Acetone	Chloroform	2.35	4.21	3.65
CCl_4		1.945	2.25	2.15
Cyclohexane		2.184	2.33	-
Aniline	Toluene	2.10	2.58	2.21
Benzene		2.545	2.79	2.46
Bromobenzene		2.08	2.10	1.89
Chlorobenzene		2.23	2.37	2.10
Cyclohexane		2.42	2.15	-

Table 13. General Summary Of Solute Interactions

Solute	Normal State	Comments
Acetone	Associated	Acetone-$CHCl_3$ is non-associating.
Aniline	Associated	All cases
Benzene	Associated	All cases except Benzene-Acetone
Bromobenzene	Unassociated	No non-Benzene derivative data
CCl_4	Unassociated	All cases except CCl_4-$CHCl_3$
Chlorobenzene	Associated	All cases
Chloroform	Associated	No Benzene derivative data
Toluene	Associated	No non-Benzene derivative data

general similar type molecules tend to interact with each other.

The method also provides an excellent means for calculating diffusivities. For the systems studied an average deviation of 5.28 per cent was calculated. Excluded from this analysis were the acetone as solute points which produced large deviations. For pairs composed of benzene derivatives the average deviation was less than 4.3 per cent. It is interesting to note that for aniline as solute and solvent an average error of 2.74 per cent was achieved. All previous correlations have been noticeable in their failure to predict the diffusivity of aniline in solution.

CHAPTER VII

CONCLUSIONS AND RECOMMENDATIONS

From the results of this research it is concluded that the rigid sphere model for a dense fluid is extremely useful in the development of predictive equations for diffusion at infinite dilution conditions. The Enskog approach and subsequent extensions have been utilized as the basis for these developments. Two courses of action were followed and both were found to yield good results. The first of these was the development of a predictive equation in which the rigid sphere diameter was replaced by the cube root of the critical volume. This approach resulted in an expression which is explicit in readily available parameters. During the course of this analysis it was found that the quantity $D^{\infty}_{ij}\eta_j M_j/p_j T$ is invariant with temperature over the temperature ranges studied. The second method involved the calculation of average parameters for associated systems. It was found that these parameters were not identical to size and mass of the monomer species. It was further shown that the diffusity of an associated system could be characterized by the size and mass of the monomer constituents as well as two association parameters. This approach provides an excellent insight into the diffusion process as well as to the effects of association on diffusion.

For future work it is recommended that additional binary diffusivity data be taken with one component being non-associated and one component associated. There is a noticeable lack of this type of data in the literature. It is also suggested that a facility for the measurement of self-diffusion coefficients be established. The understanding of self-diffusion is intrinsic to the development of expressions for the diffusivities of mixtures. It is further recommended that the k-value approach be extended to the concentration dependence of the diffusivity. It is possible, through this means, to develop expressions which do not rely on the thermodynamic factor to predict the concentration dependence.

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