Effect of Molecular Association on Diffusion in Binary Liquid Mixtures

A predictive equation for the mutual diffusion coefficient is developed for binary solutions which contain a self-associating component. The solution is modeled as a nonideal multicomponent mixture consisting of the solvent molecules and various association complexes. The model provides for a unique mobility for each of the species present and accounts for both physical and chemical contributions to the solution thermodynamics and their effects on the diffusive fluxes. The predictions of the theory were evaluated for *n*-alcohols in nonpolar solvents using data for six systems at temperatures ranging from 293 to 363 K. In each case, the predictions of this theory are found to be superior to other currently available methods.

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Introduction

The objective of this paper is to describe diffusion in a complex, but common, class of solutions—binary liquids in which one component self-associates. For such solutions, which are normally highly nonideal, it is impossible to accurately predict the behavior of the mutual diffusion coefficient using current methods. Although a variety of both theoretical and empirical approaches have been proposed in an attempt to predict diffusivities in concentrated nonideal solutions, none adequately describe the systems being considered here. In the most commonly used method, the mutual diffusion coefficient, D, is obtained by multiplying a reference value or "ideal" diffusion coefficient by a thermodynamic factor

$$D = D_o \, d \ln a_1 / d \ln x_1 \tag{1}$$

where a is the activity, x is the mole fraction and where the reference value, D_o, can be calculated by any of several methods, most typically by using a mole weighted average of the infinite dilution values of D,

$$D_o = x_1 D_2^o + x_2 D_1^o. \tag{2}$$

The thermodynamic factor of Eq. 1, first suggested by Darken (1948), can be derived using arguments from nonequilibrium thermodynamics (e.g., deGroot and Mazur, 1962; Fitts, 1962). The derivation requires the assumption that the molar flux varies linearly with the driving force, namely, the gradient in chemical potential. Although the appropriateness of assuming such a linear relationship has been questioned (Stanley, 1971), the resulting theory has met with considerable success. Equation 1 has been found to work well for dilute electrolyte solutions as well as for numerous moderately nonideal organic solutions (Oishi et al., 1974). However, when it is used to estimate the diffusion coefficient of a highly nonideal solution, this method almost always fails, predicting values of D which can be in error by as much as an order of magnitude.

Another reported weakness of the theory lies in its ability to treat liquids in the neighborhood of a solution critical point. The theory correctly predicts that the value of D should go to zero as the critical point is approached. However, it has been argued that Eq. 1 cannot explain the temperature dependence for D which one observes in the vicinity of a solution critical point (Cussler, 1980). Taken together, these apparent failings have brought this theory into question in recent years.

In an attempt to correct the deficiencies of Eq. 1, several authors have proposed modifications to the theory. Vignes (1966), and Kosanovich and Cullinan (1976) revised the method by which the value of D_o is calculated. Vignes' empirical modification, which employs a geometrical average of D_1^o and D_2^o, is widely used because it has been found to work for a number of systems for which Eq. 2 fails. However, for most highly nonideal solutions, it also fails. In addition to modifying the method by which D_o is calculated, Kosanovich and Cullinan observed that for some systems D appears to be proportional to the square root of the thermodynamic factor rather than to the first power as Eq. 1 indicates.

Taking a different approach, Cussler (1980) considered an analogy between nonideal concentrated solutions and solutions near consolute points to develop a theory in which diffusion is thought to occur through the movement of entire clusters of molecules. This theory of cluster diffusion predicts a more complicated form for the thermodynamic factor,

$$D = D_o\left[1 + \frac{C}{x_1x_2}\left(\frac{d\ln x_1}{d\ln a_1} - 1\right)\right]^{-1/2} \tag{3}$$

Although this theory contains an undetermined parameter, C, it does correct certain of the deficiencies in Eq. 1. Most notably it predicts the correct temperature dependence of D near a consolute point and it indicates a dependence of D on the thermodynamic factor which is close to the square-root dependence observed by Kosanovich and Cullinan. However, it will be shown that Eq. 3 has its own failings, perhaps more serious than those which it corrects.

In an attempt to overcome the indefiniteness of Eq. 3, Cullinan (1985) extended Cussler's treatment of cluster diffusion to arrive at an explicit predictive form of the theory,

$$D = \frac{kTN_A^{1/3}}{2\pi\eta V^{1/3}}\left[1 + \frac{1}{2\pi x_1x_2}\left(\frac{d\ln x_1}{d\ln a_1} - 1\right)\right]^{-1/2} \tag{4}$$

in which the reference diffusion coefficient of the earlier approach has been replaced by a Stokes-Einstein-like relationship. Equation 4 maintains the same dependence of D on the thermodynamic factor as Eq. 3 and, as a result, it is subject to similar shortcomings which diminish its usefulness as a replacement for Eq. 1.

It should be noted that of the systems for which Eq. 1 has been observed to fail, most are highly nonideal solutions and nearly all are complex solutions in which some type of molecular association occurs. These systems can possess a myriad of microstructures ranging from self-association of one or more of the components, to solvation reactions to other more elaborate supramolecular structuring. Perhaps, in such complicated systems, it is not Darken's theory which is incorrect but rather it is the naive manner in which it is often applied which is lacking.

Turner's (1975) arguments in support of Darken's approach include the observation that, even when Eq. 1 fails, division of D by the thermodynamic factor usually greatly simplifies the concentration dependence of the diffusion coefficient. The residual concentration dependence could be the result of a change in the average mobility of the molecules with concentration which would, of course, depend on the structure of the solution. Given the simplicity of its form and, more importantly, its success in describing diffusion in a variety of nonideal liquids, Eq. 1 should not be dismissed without first considering the other possible deficiencies in the description of the solutions which are being considered.

The situation we consider in this paper is that of a complicated solution to which direct application of Eq. 1 always results in failure. We will show that, through a more precise description of the solution's composition and careful application of Eq. 1, a useful predictive equation for diffusion in these solutions can be developed. Several previous investigators, recognizing the complexity of the systems under consideration, endeavored to incorporate more realistic descriptions of the solution microstructure into theories of diffusion for these systems (e.g., Carman, 1967, 1968; Oishi and Nanba, 1979). The approach in each case consisted of treating the solution as a multicomponent mixture consisting of the solvent and the differently sized association complexes and, in some way, taking into account the differing mobilities of the different sizes of association complexes. In the present work, we follow a similar approach but demonstrate the necessity of considering both the mobility and thermodynamic effects of molecular association to develop a realistic description of diffusion in these systems.

Our objective is to describe diffusion in concentrated binary solutions in which one component self-associates. Such solutions include those containing water, alcohols, carboxylic acids, amines, amides and a variety of heteroatom containing aromatic compounds. The mixture of any of these with a nonassociating solvent usually results in a highly nonideal solution in which diffusion cannot be accurately predicted by any of the current methods.

In such solutions, we would expect that the increase in the average degree of association with increasing concentration would by itself lead to a decrease in D with concentration, apart from any thermodynamic effects. By taking into account this diminished mobility of the associated component along with an appropriate description of the solution thermodynamics, we are able to predict the value of D for such solutions.

For binary liquid mixtures with one self-associating component, we find that the mutual diffusion coefficient can be predicted using

$$D = \left\{\left[(1 - x_A)(1 - K\phi_1)^2 \sum_{n=1}^{\infty} n^{3/2}(K\phi_1)^{n-1}\right](D\eta)_{A,o} + x_A(D\eta)_{B,o}\right\}\left(\frac{1}{\eta}\right)\frac{d\ln a_A}{d\ln x_A} \tag{5}$$

where the subscript A refers to the associating component and ϕ is the volume fraction, K is the equilibrium constant for isodesmic association, η is viscosity, and $(D\eta)_{A,o}$ is the limit of the diffusivity-viscosity product as $x_A \rightarrow 0$. The variable ϕ_1 represents the volume fraction of A present in monomer form and can be expressed as a function of ϕ_A and K.

Because values for K have been tabulated for many self-associating molecules (Nath and Bender, 1981), the concentration dependence of the mutual diffusion coefficient can be estimated for these systems given the pure component viscosities, the two infinite dilution values of D, and thermodynamic data. Although the data required to use this theory are the same as that required by most other methods currently in use, this theory has been found to be superior in predictive capability for the six binary systems investigated and should perform equally well for similar systems. These results point out the need to consider both physical and thermodynamic effects in modeling diffusion in associating systems.

The results presented here provide, without adjustable parameters, a complete description of the concentration and temperature dependence of the mutual diffusion coefficient in binary systems with one self-associating component. The theory can also be used as a framework by which to develop appropriate descriptions of diffusion in systems with more complicated association and solvation behavior.

Molecular Association

Association in liquid solutions can occur in a variety of forms. It may be limited in extent such as the dimerization of acetic acid or the formation of a solute-solvent adduct; it may involve only monomers and one favorably-sized cluster as in micellization; or there may be an equilibrium between several or many different size clusters. The latter case applies to many molecules which can form intermolecular hydrogen bonds or π-bonds. We will consider here the case of isodesmic association; that is when all of the intermolecular bonds are identical and the association of species A proceeds by the stepwise addition of a single molecule,

$$A_1 + A_1 \overset{K}{\rightleftharpoons} A_2$$

$$A_2 + A_1 \overset{K}{\rightleftharpoons} A_3$$

$$\cdots$$

$$A_{n-1} + A_1 \overset{K}{\rightleftharpoons} A_n \qquad (6)$$

where the subscript indicates the number of A monomers in the cluster. Each reaction is considered to be equally likely and thus to have the same equilibrium constant, K. Using Flory's theory for the thermodynamics of polymer solutions, Kretschmer and Weibe (1954) and later Renon and Prausnitz (1967) showed that K is correctly expressed in terms of volume fractions, ϕ_n as

$$K = \frac{\phi_n}{\phi_{n-1}\phi_1}\frac{(n-1)}{n} \qquad (7)$$

Through this equation, a relationship can be developed between the volume fractions of the various species present,

$$\phi_n = nK^{n-1}\phi_1^n \qquad (8)$$

and the volume fraction of monomer can be expressed in terms of the total volume fraction of component A,

$$\phi_A = \phi_1/(1 - K\phi_1)^2 \qquad (9)$$

$$\phi_1 = \frac{1 + 2K\phi_A - (1 + 4K\phi_A)^{1/2}}{2K^2\phi_A} \qquad (10)$$

Using the above equations, an expression for the excess Gibbs energy due to association, g^E, can easily be developed (Renon and Prausnitz, 1967). In Figure 1, a comparison is made between the values of g^E predicted by association theory and those observed experimentally for 1-propanol in carbon disulfide at 303 K. In this system, molecular association accounts for the majority, but definitely not all, of the excess Gibbs energy. In addition to association effects, there are physical interactions in the mixture which contribute to g^E. Also, it should be noted that isodesmic association theory predicts slightly higher values of g^E than are actually observed at low alcohol concentrations. This is to be expected as Flory's assumptions do not hold for low degrees of association and thus the model fails.

Overall, the behavior observed in this system is typical of the thermodynamics of mixtures of alcohols and nonpolar solvents. This suggests that if we wish to more accurately describe the diffusion process in such solutions, we should treat the solution as a nonideal mixture of solvent molecules and association complexes of varying size.

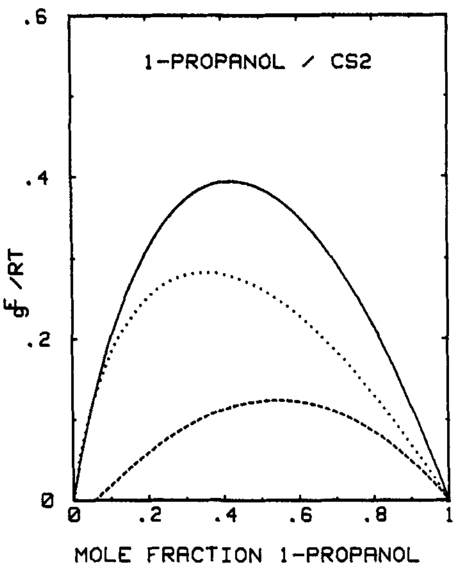


Figure 1. Excess Gibbs energy for 1-propanol in CS$_2$ at 303 K.

——, values obtained from experimental vapor-liquid equilibrium data
····, values predicted by isodesmic association theory
----, residual contribution to g^E due to physical interactions

Nonideal Multicomponent Diffusion Model

The model developed here is based on two primary assumptions about the nature of the solutions involved. First, we will assume that there exists a distribution of cluster sizes in solution and thus a distribution in the mobility of the associating component. This will be taken into account by treating the nonideal binary solution as a multicomponent solution as Carman (1967), and Oishi and Nanba (1979) did previously. Second, we will assume that this multicomponent solution is itself nonideal. This is a departure from most of the previous work along these lines which followed a chemical solution theory view which held that the nonideality stemmed solely from the association in solution and that the multicomponent solution would be thermodynamically ideal. In this work, we develop a model similar to Oishi and Nanba's but without the restrictive assumption of an ideal solution. In addition, the model incorporates our earlier findings (McKeigue and Gulari, 1984) on the relationship between the size and mobility of molecular clusters.

For an m-component mixture, nonequilibrium thermodynamics (e.g., de Groot and Mazur, 1962; Kirkwood et al., 1960; Fitts, 1962) provides a generalized form for the flux equation at constant temperature and pressure in any reference frame, R,

$$J_i^R = -\sum_{j=1}^{m} L_{ij}^R \nabla \mu_j \qquad (11)$$

where μ is the chemical potential, J_i^R is the molar flux of component i relative to R, and L_{ij}^R is the Onsager phenomenological coefficient which is a measure of the flux of component i due to a gradient in component j.

Darken (1948) first introduced the concept of an "intrinsic mobility," q_i, for each component which, together with the driving force, determines the diffusive flux of that component relative to a reference in which there is no diffusive driven bulk flow.

We will refer to this reference frame as the Darken frame, denoted by superscript D. The validity of Darken's approach has been demontrated for solid, liquid and gaseous solutions of up to four components (Oishi et al., 1974). Following Darken's approach, the phenomenological coefficients in reference frame D are given by

$$L_{ij}^{D} = -\,q_i c_i \delta_{ij} \tag{12}$$

and the fluxes are then given by

$$J_i^{D} = -\,q_i c_i \nabla \mu_i \tag{13}$$

where δ_{ij} is Kronecker's delta function and c_i is the molar concentration of component i. Thus, in Darken's theory, the flux of a component depends only on its own mobility and the gradient in its own chemical potential; it is independent of all other mobilities and gradients in the system. In the reference frame D then, the off-diagonal elements of the m by m $\underline{\underline{L}}^{D}$ matrix are identically zero. To relate the phenomenological coefficients to the more useful interdiffusion coefficients, D_{ij}, the flux equations must be rewritten using a more appropriate reference frame.

Diffusion coefficients are measured with respect to the laboratory-fixed frame of reference. Assuming that the partial molar volume of each species is independent of concentration, this is equivalent to the center of volume reference frame, v (Kirkwood et al., 1960). The flux of component i relative to this reference frame is

$$J_i^{v} = c_i(\boldsymbol{u}_i - \boldsymbol{u}_o^{v}) \tag{14}$$

where $\boldsymbol{u}_i$ is the mean diffusive velocity of component i and $\boldsymbol{u}_o^{v}$ is the volume-averaged diffusive velocity

$$\boldsymbol{u}_o^{v} = \sum_{j=1}^{m} \phi_j \boldsymbol{u}_j = \sum_{j=1}^{m} V_j J_j^{D} \tag{15}$$

where V_j is the partial molar volume of component j. Combining these equations gives an expression for the flux of component i as a function of the mobilities and gradients in the system

$$J_i^{v} = c_i \sum_{j=1}^{m} (-q_j \delta_{ij} + q_j V_j c_j) \nabla \mu_j \tag{16}$$

However, in an m-component constant volume system, there can be only $m - 1$ independent gradients and fluxes. The Gibbs-Duhem equation provides an additional constraint which can be used to eliminate one of the gradients. At constant temperature and pressure,

$$\sum_{i=1}^{m} c_i \nabla \mu_i = 0 \tag{17}$$

allowing the gradient in component 1 to be expressed in terms of the remaining $m - 1$ gradients.

$$c_1 \nabla \mu_1 = -\sum_{j=2}^{m} c_j \nabla \mu_j \tag{18}$$

Thus, in the center of volume reference frame, the flux equation becomes

$$-J_i^{v} = \sum_{j=2}^{m} L_{ij}^{v} \nabla \mu_j \quad i \neq 1 \tag{19}$$

where

$$L_{ij}^{v} = c_i q_i \delta_{ij} + c_i c_j (q_1 V_1 - q_j V_j) \tag{20}$$

Although the phenomenological coefficient matrix in the volume reference frame has nonzero off-diagonal elements, they are solely a consequence of the transformation between reference frames. It should be noted that there are still only m independent coefficients in the system.

Until this point in the derivation, we have considered a general m-component system. For the purposes of subsequent manipulations, it is convenient to distinguish between the species present in solution. The solvent or nonassociating component will be denoted by the subscript B. We will consider the case of isodesmic association equilibria denoting each species by a subscript indicating the number of monomer units it contains. The subscript A will refer to the associating component taken as a whole without regard to its association state. For isodesmic association the number of monomers per cluster ranges from 1 to ∞. Since no net volumetric flow occurs relative to the center of volume reference frame,

$$\sum_{j=1}^{m} V_j J_j^{v} = 0 \tag{21}$$

or

$$V_B J_B^{v} + \sum_{n=1}^{\infty} V_n J_n^{v} = 0 \tag{22}$$

Under the assumption that the volume occupied by a single molecule is independent of its association state, the partial molar volume of an n-mer will be nV_A. Using this result together with Eq. 16 allows Eq. 19 to be rewritten as

$$J_B^{v} = \frac{V_A}{V_B} \sum_{n=1}^{\infty} \left(n \sum_{k=1}^{\infty} L_{ik} \nabla \mu_k \right) \tag{23}$$

For isodesmic association, it can easily be shown that

$$\mu_n = n\mu_1 = n\mu_A. \tag{24}$$

Thus, the gradient in the chemical potential of an n-mer can be expressed in terms of the overall gradient in chemical potential of the alcohol,

$$\nabla \mu_k = k \nabla \mu_A. \tag{25}$$

This will of course only be valid if the system is locally at equilibrium. For alcohols, carboxylic acids and other small hydrogen-bonding molecules, the characteristic time for the association-dissociation reaction is many orders of magnitude faster than the characteristic time for diffusion, justifying the assumption of local equilibrium in these systems. Thus, the flux of B is proportional to the gradient in the chemical potential of A.

$$J_B^v = \left(\frac{V_A}{V_B}\sum_{n=1}^{\infty} n \sum_{k=1}^{\infty} L_{ik}^v k\right)\nabla\mu_A \tag{26}$$

To make the connection between the multicomponent solution of the model and the measured mutual diffusion coefficient, we consider the binary solution of A and B. For a binary mixture, the mutual diffusion coefficient is defined through Fick's law,

$$-J_A^v = D\nabla c_A \tag{27}$$

which, when combined with Eq. 23 and the constraint of

$$V_A J_A^v + V_B J_B^v = 0 \tag{28}$$

for a constant volume system gives

$$D = \sum_{n=1}^{\infty} n \sum_{k=1}^{\infty} k L_{ik}^v \frac{d\mu_A}{dc_A} \tag{29}$$

where $d\mu_A/dc_A$ can be expressed in terms of the conventional thermodynamic factor,

$$\frac{d\mu_A}{dc_A} = \frac{RTx_A}{c_A^2 V_B}\left(\frac{d\ln a_A}{d\ln x_A}\right). \tag{30}$$

When the last two equations are combined with the expressions for the L_{ij}^v coefficients, we can use several of the relationships from isodesmic association theory to derive an expression for the mutual diffusion coefficient in terms of the overall concentration of A, the mobility of each species present and the thermodynamic factor.

$$D = [x_B(1 - K\phi_1)^2 \sum_{n=1}^{\infty} n^2 (K\phi_1)^{n-1} q_n + x_A q_B] RT \frac{d\ln a_A}{d\ln x_A} \tag{31}$$

This equation is a general result which assumes no specific model for the mobility of an n-mer. Because ϕ_1 is a function of x_A, K, V_A, and V_B, the mutual diffusion coefficient is a function of only x_A, K, V_B, V_A, $d\ln a_A/d\ln x_A$ and the mobilities of each species present in solution.

Mobilities of Association Complexes

The mobility of a species is directly related to its tracer diffusion coefficient, D_i^T, by

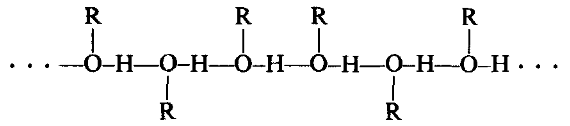
$$q_i = D_i^T/RT. \tag{32}$$

The tracer diffusion coefficient is commonly estimated using the Stokes-Einstein equation,

$$D_i^T = kT/\alpha\eta r_i \tag{33}$$

where r_i is the hydrodynamic radius of the diffusing species and α is a coefficient whose value depends on the hydrodynamic boundary conditions which are assumed. Although it may be argued that the application of a hydrodynamic theory to the case of molecular motion is unwarranted, there is ample evidence for, and explanations of, the validity of this approach (Hynes, 1977; Russel, 1981). Problems with this method usually arise because a molecular geometry must be assumed to calculate r_i and also because the appropriate value of α is often in doubt when the size of the solute is small (Chen et al., 1981). We avoid these particular ambiguities because, for our purposes, only the dependence of D_i^T on r and η is required. However, in this instance the value of the viscosity itself is unclear. In dilute solution, the solvent viscosity is clearly appropriate. In concentrated solutions the bulk viscosity includes contributions from solute-solvent interactions which are already accounted for in the thermodynamic factor. Such interactions should not affect the local viscosity which, according to molecular dynamics calculations (Hynes, 1977), depends on the reduced mass of the colliding molecules. For this reason, we will use a volume-weighted average of the pure component viscosities for η.

The effective radii of the monomer A molecules and the B molecules can be determined using the Stokes-Einstein equation and the infinite dilution values of the diffusion coefficient. Estimation of the effective radii of the n-mers requires that an assumption be made about their structure. In this paper, we test our results using data for alcohol solutions. Primary alcohols associate through intermolecular hydrogen bonding to form linear or possibly cyclic polymer-like structures in which the hydrocarbon chains project outward from a hydroxyl backbone:



$$\cdots-\overset{R}{\overset{|}{O}}-H-\underset{\overset{|}{R}}{O}-H-\overset{R}{\overset{|}{O}}-H-\overset{R}{\overset{|}{O}}-H-\underset{\overset{|}{R}}{O}-H-\overset{R}{\overset{|}{O}}-H\cdots$$

In such a structure, the "hydrodynamic surface" area of the n-mer is approximately n times that of a monomer; thus, $r_n = r_1\sqrt{n}$. Alternately, we could arrive at a comparable result by noting the similarity in appearance of the above structure to a polymer molecule. From scaling theory (deGennes, 1979), we note that for a Gaussian coil in a theta solvent, $r_n = r_1 n^{0.56}$. If the association results in globular type clusters we would expect r_n to be proportional to the cube root of n. In general, $r_n = r_1^{\beta}$. On the basis of our previous results (McKeigue and Gulari, 1984), we choose $\beta = 1/2$.

The value of r_1 can be determined from the infinite dilution value of the mutual diffusion coefficient. In the limit as $x_A \rightarrow 0$, only monomers of A are present in solution. Also, in this limit, the mutual diffusion coefficient approaches the tracer diffusion coefficient of A. It is convenient to work in terms of the product of the diffusion coefficient and viscosity ($D\eta$), which in this limit becomes

$$\lim_{x_A\rightarrow 0} (D\eta) = D_1^T\eta_B. \tag{34}$$

We will denote this limit of the diffusion-viscosity product as $(D\eta)_{A,o}$. An expression for D_n^T can then be obtained,

$$D_n^T = \frac{kT}{\alpha r_n \eta} = (D\eta)_{A,o} n^{-\beta}\eta^{-1} \tag{35}$$

Table 1. Input Parameter Values for Multicomponent Diffusion Model

System	T(K)	K	ΔH (J/kmol)	$(D\eta)_{A,o}$(pN)	$(D\eta)_{B,o}$ (pN)
Ethanol/CS_2	293	300.4	21.2	1.00	2.58
1-Propanol/CS_2	293	197.5	19.8	0.80	2.97
1-Butanol/CS_2	293	154.2	18.9	0.71	2.73
1-Pentanol/CS_2	293	138.6	18.7	0.62	2.67
Methanol/Benzene	293	38.5	31.0	2.48	1.51
	328	7.58	31.0	3.02	1.31
	363	3.59	31.0	3.96	1.50
Ethanol/Benzene	293	50.0	23.0	2.02	2.40
	313	32.8	23.0	2.24	2.47
	323	15.9	23.0	2.41	2.42

Using a similar argument, D_B^T is found to be

$$D_B^T = (D\eta)_{B,o}\eta^{-1} \tag{36}$$

The above results, combined with Eq. 31, yield a predictive equation for D,

$$D = \left\{\left[x_B(1 - K\phi_1)^2 \sum_{n=1}^{\infty} n^{3/2}(K\phi_1)^{n-1}\right](D\eta)_{A,o} + x_A(D\eta)_{B,o}\right\}\left(\frac{1}{\eta}\right)\frac{d\ln a_A}{d\ln x_A} \tag{37}$$

Comparison of Predictions

We recently reported extensive new diffusion data (McKeigue and Gulari, 1984; McKeigue, 1985) for the systems methanol/benzene, ethanol/benzene, methanol/CS_2, ethanol/CS_2, n-propanol/CS_2, n-butanol/CS_2, and n-pentanol/CS_2. These data, coupled with vapor-liquid equilibrium data for these systems (McKeigue and Gulari, 1986; Gmehling et al., 1977) allow a comparison to be made of the predictive capability of the multicomponent model with those of other theories currently in use.

Values of $d \ln a/d \ln x$ were obtained analytically from Wilson's (1964) equation which was found to well represent the thermodynamic data for each system. The intercepts $(D\eta)_{A,o}$ and $(D\eta)_{B,o}$ were determined by linear extrapolation of low concentration diffusion coefficients to zero concentration. Table 1 lists these values for each system.

Values for the association constant, K, for a large number of alcohols at 323 K were tabulated by Nath and Bender (1981). These values were corrected for temperature using the van t' Hoff equation

$$K(T) = K(T_o)\exp\left[\frac{\Delta H}{RT}\left(\frac{1}{T_o} - \frac{1}{T}\right)\right] \tag{38}$$

and the ΔH values also given by Nath and Bender. The values of K obtained in this manner are valid for any system in which the solvent does not interact chemically with the alcohol. This is the case for the systems in which carbon disulfide is the solvent. The values of K used for these systems are given in Table 1.

For the alcohol in benzene systems, there is a solvation reaction between the hydroxyl proton and the π-electrons which has been reported to have an energy of about 8 J/kmol (Van Ness et al., 1967). Thus, this reaction competes with self-association for the free alcohol monomers in solution. Under such circumstances, a different association model with two equilibrium constants would be more appropriate. Alternately, the isodesmic model could be retained if we employ a smaller "effective" equilibrium constant to account for the solvation reaction. While this might not be rigorously correct, it allows for a test of the multicomponent model to be made on these systems without the introduction of undue complexity. It does however necessitate treating K as an adjustable parameter for the systems in which benzene is the solvent. For these systems only, we used nonlinear least squares regresson to determine the optimal value of K. These values are also given in Table 1.

Some evidence to support the values of K obtained in this manner can be obtained through Eq. 38. Plots of ln K vs. inverse temperature are shown for the methanol-benzene and ethanol-benzene systems in Figure 2. The linearity of the resulting graphs indicates that the values of K obtained from the fits have somewhat more significance than just that of adjustable parameters. The values of ΔH obtained from the slopes of these graphs, 31 J/kmol for methanol-benzene and 23 J/kmol for ethanol-benzene, are comparable to values for alcohol self-association given in Table 1.

It should be noted that the values of K for the benzene systems are an order of magnitude smaller than those expected for a non-interacting solvent. The fact that the ethanol/benzene system has higher equilibrium constants than the methanol-benzene

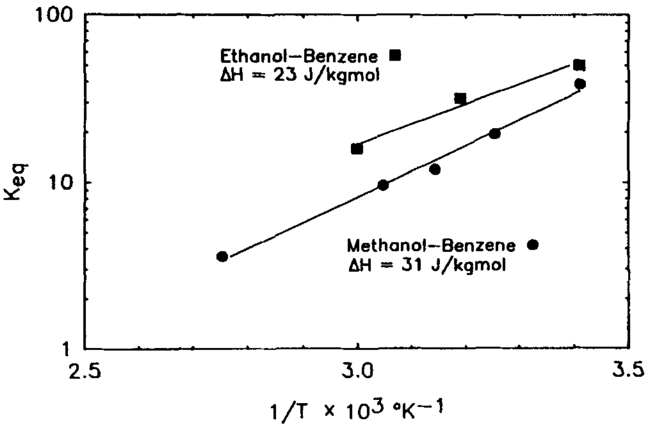


Figure 2. Self-association equilibrium constant vs. inverse temperature for methanol/benzene and ethanol/benzene.

Values for ΔH are obtained from the slope of the lines.

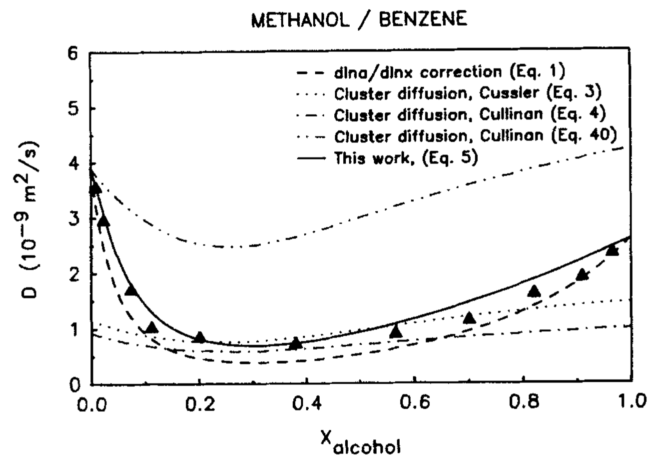


Figure 3. Mutual diffusion coefficient vs. concentration for methanol/benzene at 293 K.

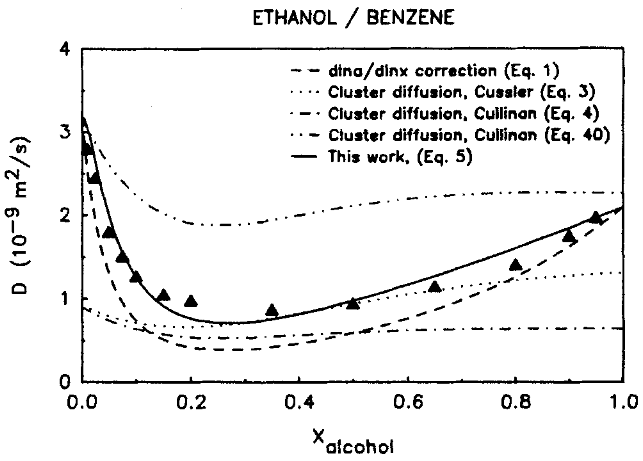


Figure 4. Mutual diffusion coefficient vs. concentration for ethanol/benzene at 293 K.

system appears at first to be counterintuitive. However, because the bond between the alcohol and the benzene is very weak, there should be a greater propensity for such bonding in the case of the smaller methanol molecules. With more hydroxyl groups tied up in solvation bonds, we would expect the effective self-association equilibrium constant for methanol to be lower than for ethanol.

In Figures 3 to 8, the predictions of the classical thermodynamic correction (Eq. 1), the cluster diffusion theories (Eqs. 3, 4 and 40), and the theory developed in the preceding section (Eq. 5) are compared with experimental data for the six systems at 293 K. For Eqs. 1, 3 and 5, the reference value of the diffusion coefficient was obtained using Darken's approach

$$D_o = x_B D_A^T + x_A D_B^T \tag{39}$$

Cullinan's result for cluster diffusion, Eq. 4, is explicit and requires no reference value. An alternative form utilizes one of the infinite dilution values of the diffusivity-viscosity product,

$$D\eta = \sqrt{f^o_{AB}}(D\eta)_{A,o}\frac{V_B^{1/3}}{V^{1/3}} \cdot \left[1 + \frac{1}{2\pi x_A x_B}\left(\frac{d\ln x_A}{d\ln a_A} + 1\right)\right]^{-1/2} \tag{40}$$

where

$$f^o_{AB} = 1 - \frac{1}{2\pi}\lim_{x_A \to 0}\frac{d}{dx_A}\left(\frac{d\ln a_A}{d\ln x_A}\right) \tag{41}$$

For the systems containing the lower molecular weight alcohols, the conventional approach (Eq. 1) consistently underestimates the value of the mutual diffusion coefficient throughout the entire concentration range, often by as much as a factor of 3 to 4. As the size of the alcohol molecule increases, the overall agreement between Eq. 1 and the data becomes better. However, for the lower alcohol concentrations, the conventional approach still greatly underestimates D. Cussler's result for cluster diffusion, Eq. 3, is very successful in the middle concentration range for each system but wholly unsuccessful in the

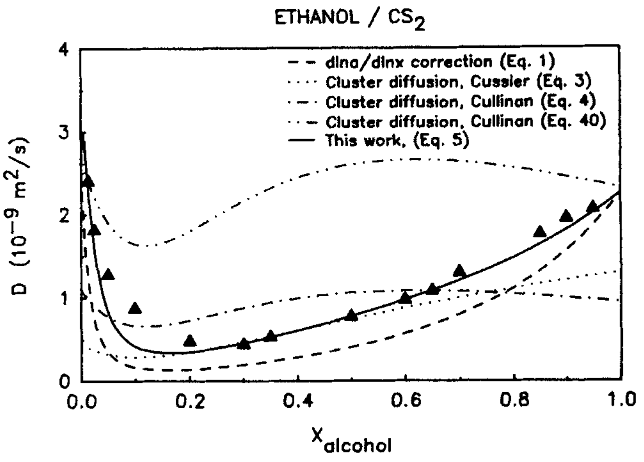


Figure 5. Mutual diffusion coefficient vs. concentration for ethanol/CS$_2$ at 293 K.

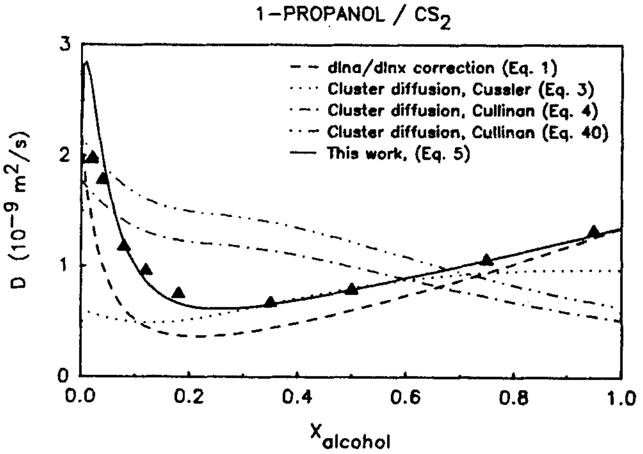


Figure 6. Mutual diffusion coefficient vs. concentration for 1-propanol/CS$_2$ at 293 K.

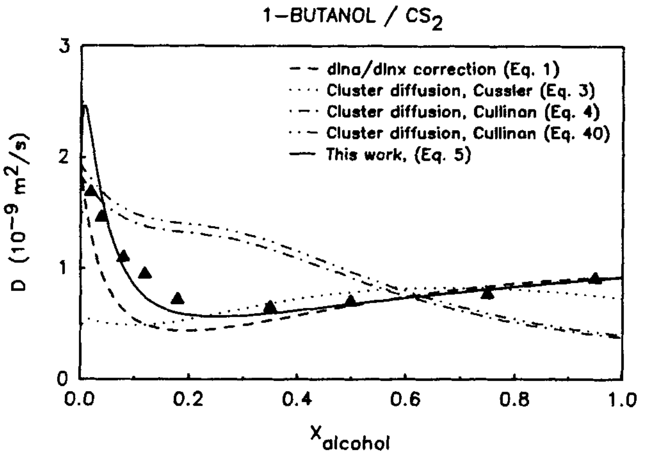


Figure 7. Mutual diffusion coefficient vs. concentration for 1-butanol/CS_2 at 293 K.

dilute concentration regions, predicting infinite dilution values which are too low by as much as a factor of 6.

Contrary to the findings of the original paper on cluster diffusion (Cussler, 1980) which showed D approaching D_o at infinite dilution for several nonideal systems, we observe that there is no possibility of this theory yielding the correct infinite dilution values for any nonideal solutions if a Darken reference value for D_o is employed. This can be demonstrated by taking the limit of the right hand side of Eq. 3 as x_1 goes to either 0 or 1. The only circumstances under which the equation will yield the correct value of D_o at these limits is if the value of $d\gamma/dx$ is zero. This can only be true when the activity coefficient is constant, that is, only for an ideal solution.

The failure of Eq. 3 at low concentrations stands in stark contrast to its remarkably accurate predictions of the diffusion coefficient in the midconcentration regions for each of the systems studied. Overall, these results suggest that, despite the obvious shortcomings, there appears to be potential for the cluster diffusion description. However, it is also clear that further work will be required to determine the range of applicability of the theory and to understand its failure in the dilute regions.

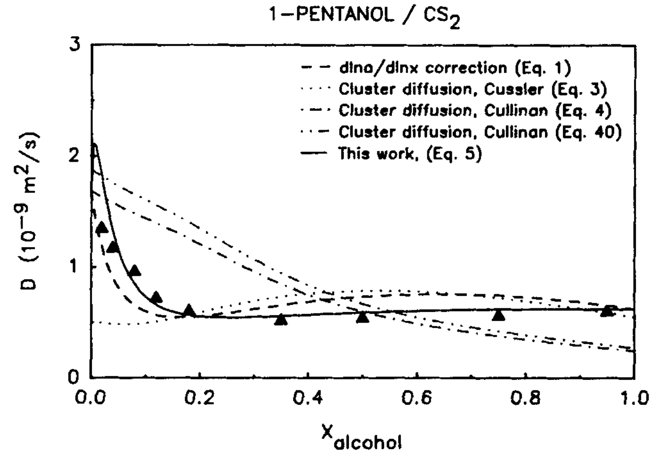


Figure 8. Mutual diffusion coefficient vs. concentration for 1-pentanol/CS_2 at 293 K.

The predictions of Cullinan's extensions of the cluster diffusion model are also shown in Figures 3 through 8. From these graphs, it is apparent that Eq. 4 is unreliable as a predictive tool. However, it must be noted that this equation does not make use of the infinite dilution limits of D, relying instead upon a Stokes-Einstein-like correlation for the self-diffusion coefficient of the pure components (Li and Chang, 1955). It might be this correlation rather than Cullinan's approach which is at fault here. To remove the dependence of this theory on such a correlation, Cullinan provides an alternative form, Eq. 40, which makes use of one of the limiting values of the diffusion coefficient. This modification results in a necessarily correct infinite dilution limit for D but an unacceptable concentration dependence in which D is undepredicted in some systems and overpredicted in others. It is interesting to note that for the higher alcohols, the predictions of Eq. 4 and Eq. 40 start to converge to the same values, suggesting that Li and Chang's equation might hold for these systems. This is an expected result; as the molecular weight increases, Stokes-Einstein type behavior is approached for molecular diffusion (McKeigue and Gulari, 1984).

It is apparent from Figures 3 through 8 that the nonideal multicomponent solution model is the most consistent in reliably predicting the behavior of the diffusion coefficient for the systems investigated here. The functional form of Eq. 5 insures the correct infinite dilution limits of D while the overall shape of the curve follows the data reasonably well with average errors of less than 15% overall. The predictions of the theory seem to be slightly better for the CS_2 systems, an expected result because the solvation reaction in the benzene systems is not fully accounted for in our analysis.

There is an obvious quirk in the predictions at low concentrations for the propanol, butanol and pentanol systems. For these systems the predicted value of D actually rises above the infinite dilution limit of D before decreasing as would be expected. This can be traced to a deficiency in the solution thermodynamics for isodesmic association. As we previously mentioned, the equilibrium constants for isodesmic association were derived from Flory's treatment of polymer solutions. These values are accurate for large association numbers. For the relatively low degrees of association that occur in dilute solutions, Flory's assumptions do not hold and thus the model fails, predicting values of g^E that are too high as shown in Figure 1. This problem could possibly be overcome by relaxing the assumption of large N in the development of the equilibrium constants and the solution thermodynamics. However, this would lead to unequal K's and a much more complex expression for D. Even with this problem, we see a maximum error of only 30% as compared with the order of magnitude error which can be expected when Eq. 1 is used directly.

The development of Eq. 5 is based on several assumptions, of which the presumed morphology of the alcohol clusters is the most unsubstantiated. For reasons previously stated, Gaussian coils ($\beta = \frac{1}{2}$) were assumed. However, because the exact structure of alcohol clusters is not known, an evaluation of the sensitivity of the predicted value of D to the structure parameter, β, is useful. This sensitivity analysis was performed for the ethanol/CS_2 system which had the largest predicted cluster sizes of the systems studied. The results of this analysis are given in Figure 9 where it can be observed that, had spherical clusters been assumed, the predictions for D would have been lowered by about 10 to 20%. Spherical clusters provide an absolute lower bound for this theory; a value of $\beta < \frac{1}{3}$ is physically unrealistic. As β increases above $\frac{1}{2}$, the predictions of D rise. However, only

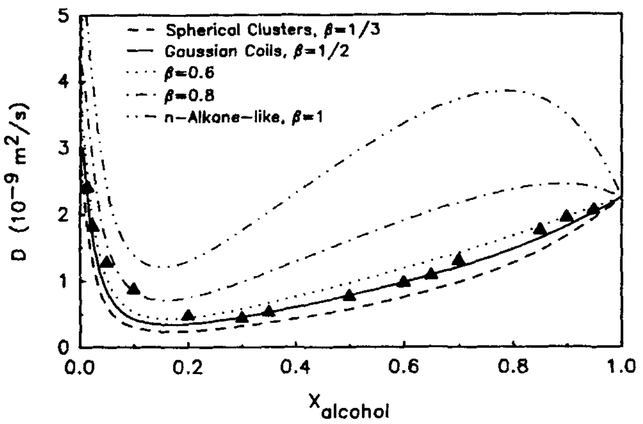


Figure 9. Sensitivity of the nonideal multicomponent diffusion model to the assumed shape of the alcohol clusters.

the region around $\beta = \frac{1}{2}$ represents physically reasonable morphologies. The predicted values of D are not terribly sensitive to β for $0.33 < \beta < 0.6$. As β increases to 1, the predictive ability of the theory is lost, providing further support for the selection of the value of $\beta = \frac{1}{2}$. It is interesting to note that a value of $\beta = 1$ corresponds to the diffusion behavior observed for short chain linear molecules (Dewan and Van Holde, 1963; McCall and Douglass, 1963). This suggests that alcohol clusters are probably closer to high polymers than to *n*-alkanes in their structure and mobility.

For the methanol/benzene and ethanol/benzene systems, the concentration dependence of D at several temperatures can be seen in Figures 10 and 11. The multicomponent model is found to work equally well at all temperatures studied. The dearth of diffusion and vapor-liquid equilibrium data away from room temperature precluded more exhaustive analysis of the temperature effects.

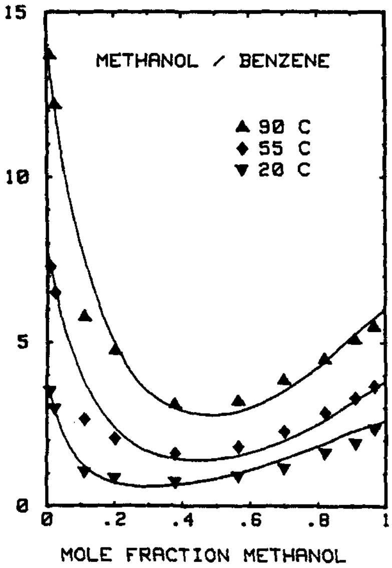


Figure 10. Mutual diffusion coefficient isotherms for methanol/benzene at 293, 328 and 363 K.

The lines indicate the predictions of the nonideal multicomponent solution model.

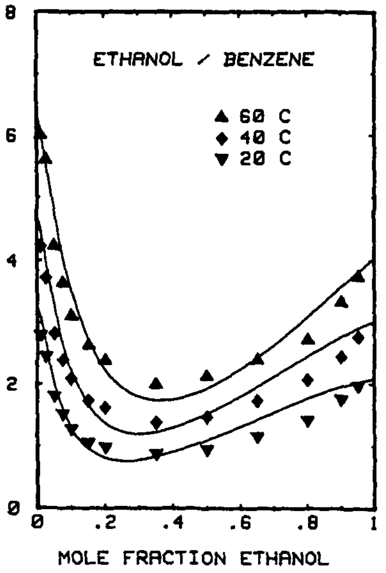


Figure 11. Mutual diffusion coefficient isotherms for ethanol/benzene at 293, 313 and 333 K.

The lines indicate the predictions of the non-ideal multicomponent solution model.

Considering the attention previous authors (Kosanovich and Cullinan, 1976; Cussler, 1980; Cullinan, 1985) have paid to the apparent square root dependence of D on $d \ln a/d \ln x$, it is interesting to investigate this dependence for the present systems. The crude model

$$D = D_o(d \ln a_1/d \ln x_1)^s \tag{42}$$

is simple but instructive. A plot of $\ln(D/D_o)$ vs. $\ln(d \ln a_1/d \ln x_1)$ will give a straight line of slope s if Eq. 42 is exact. If it is not exact, such a plot should at least indicate the power of $d \ln a_1/d \ln x_1$ upon which D depends. From the data plotted in Figure 12, we observe that although the points are scattered, the data do correlate well to a value of $s = \frac{1}{2}$. In fact, a least-squares regression of the data to Eq. 42 gives a value of $s = 0.58$ and a correlation coefficient of 0.85. This plot does not suggest that Eq. 42 is valid; on the contrary, the scatter of the data indicates that Eq.

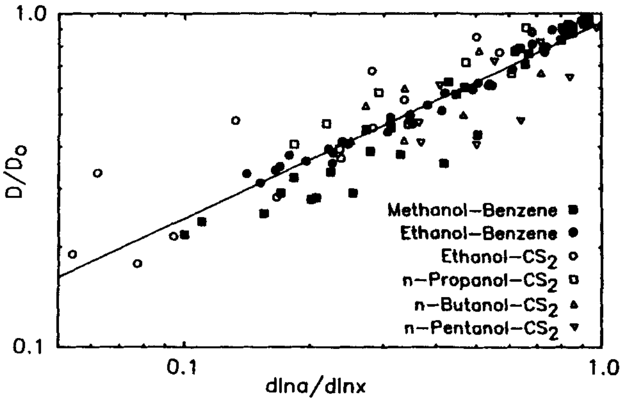


Figure 12. Correlation of D/D_o with the thermodynamic factor.

The slope indicates that the widely scattered data depend on $(d \ln a/d \ln x)^{0.58}$.

42 should not be used in a predictive manner. It does indicate that, like previous authors, we also observe a dependence of D on the square-root of the thermodynamic factor. However, we do not attribute this to an inherent dependence of the diffusion process on the square root of $d \ln a_1/d \ln x_1$. It is merely a cumulative effect of the many individual diffuse fluxes in this complex solution, each of which is linear in $d \ln a_1/d \ln x_1$, that combine to yield an overall dependence of D on $d \ln a_1/d \ln x_1$ which is approximately square root.

Conclusions

By considering all of the species present in a solution which contains a self-associating component we were able to generate an explicit predictive equation for D through the use of relatively simple models of the solution's physical and thermodynamic behavior. The theory predicts the concentration and temperature dependence of the mutual diffusion coefficient reasonably well, with average errors of about 15%, a substantial improvement over the existing methods. Although the final expression of the theory appears somewhat complex, it is easy to apply and requires no more information than the earlier methods.

As a predictive theory there are several shortcomings apparent in this method. It is not a general theory; it applies only to the particular class of solutions for which it was developed. However, for different association schemes, predictive equations could be developed by considering the appropriate association equilibria within the theoretical framework presented. Another drawback is suggested in the lack of quantitative agreement between the theory and the data to within experimental error. To improve performance, the assumptions of the theory regarding the association equilibrium constants and the mobility of the clusters might have to be reconsidered.

In addition to the predictive ability of the theory, the analysis sheds some light on the nature of diffusion in complex nonideal solutions. One of the basic precepts of the theory is that the diffusive flux is linearly proportional to the gradient in chemical potential, the assumption upon which Eq. 1 is based. Since its introduction, Eq. 1 has been plagued by controversy. Much of the debate was centered on the inability of this equation to deal effectively with highly nonideal solutions of the type considered here. While the results presented here obviously do not prove that Eq. 1 is correct, they do clearly show that Eq. 1 is applicable to complex highly nonideal solutions, so long as it applied in a physically realistic manner. This fact must be considered in the evaluation of Darken's theory.

Acknowledgment

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Notation

a_i = activity
c_i = molar concentration
C = constant in cluster diffusion model
D = mutual diffusion coefficient
D_o = reference diffusion coefficient
D_A^o = tracer diffusion coefficient of species A
D_{ij} = interdiffusion coefficient
$(D\eta)_{A,0}$ = limit of diffusion coefficient-viscosity product as $x_A \rightarrow 0$
g^E = excess Gibbs energy
H = enthalpy
J_i^R = molar flux of species i in reference frame R
k = Boltzmann's constant
K = equilibrium constant
L_{ij}^R = phenomenological coefficient
$\underline{L}$ = phenomenological coefficient matrix
$\overline{N_A}$ = Avogadro's number
q_i = mobility
r_i = hydrodynamic radius
R = gas constant
s = parameter in Eq. 41
T = absolute temperature
u_i = velocity
V_i = molar volume
x_i = mole fraction

Greek letters

α = friction coefficient in Stokes-Einstein equation
β = scaling exponent for hydrodynamic radius
γ = activity coefficient
δ_{ij} = Kronecker's delta function
η = viscosity
μ = chemical potential
ϕ = volume fraction

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