An Explicit Formulation of the Theory of Cluster Diffusion

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In this note, the cluster diffusion concept of Cussler (1980) is modified and extended to produce a comprehensive description of binary mutual diffusion in liquid solutions. The result is a complete prediction of the composition and temperature variations of the product of the mutual diffusion coefficient and solution viscosity. With no adjustable parameters, the theory provides a direct relationship, which is not phenomenological in origin, between transport behavior and solution thermodynamics.

The concept of cluster diffusion has its basis in the representation of the binary mutual diffusion coefficient in terms of the velocity and concentration correlation functions:

$$D_{12} = \frac{\langle G(r)F(r)\rangle}{\langle G(r)\rangle} \tag{1}$$

A useful result can be developed by taking the velocity correlation function to be (Ferrell, 1970):

$$F(r) = \frac{kT}{2\pi\eta r} \tag{2}$$

and the concentration correlation function to be (Stanley, 1971):

$$G(r) = \frac{a}{r}e^{-r/\xi} \tag{3}$$

Combining Eqs. 1–3 gives

$$D_{12} = \frac{kT}{2\pi\eta\xi} \tag{4}$$

in which the key quantity is ξ, the size of the diffusing clusters.

To consider the general case of a concentrated, highly nonideal liquid mixture, it is useful to compare its transport behavior to that of a corresponding ideal solution in which the two species are equivalent. In this hypothetical case

$$(D_{12}\eta)_0 = \frac{kT}{2\pi\xi_o} \tag{5}$$

In the actual nonideal solution, the connection between the solution thermodynamics and the transport coefficients is embedded in the Kirkwood-Buff (1951) relationship:

$$\frac{\partial\mu_1}{\partial X_1} = \frac{kT}{X_1}\alpha_{12} = \frac{kT}{X_1}[1 + nX_1X_2(g_{11} + g_{22} - 2g_{12})]^{-1} \tag{6}$$

where

$$\alpha_{12} = 1 + \frac{d\ \ln\gamma_1}{d\ \ln X_1} \tag{7}$$

and

$$g_{ij} = 4\pi a_{ij}\xi_{ij}^2 \tag{8}$$

To extract an explicit transport-thermodynamics relationship for Eq. 6, we begin by noting that for an ideal solution

$$\Delta g = g_{11} + g_{22} - 2g_{12} = 0 \tag{9}$$

and in this case Eq. 5 applies. In other words, Δg vanishes when $\xi = \xi_o$. Using this as a basis and noting the form of Eq. 8, we take for the general case

$$\Delta g = 4\pi a(\xi^2 - \xi_o^2) \tag{10}$$

which is equivalent to Cussler's (1980) development.

When Eqs. 4, 5, 6, and 10 are combined, we get

$$D_{12}\eta = (D_{12}\eta)_0\left[\frac{\beta X_1X_2\alpha_{12}}{1 + \alpha_{12}(\beta X_1X_2 - 1)}\right]^{1/2} \tag{11}$$

where

$$\beta = 4\pi an\xi_o^2 = 2\pi n\xi_o^3 \tag{12}$$

in which, following Cussler, we take $a = 1/2\xi_o$.

We now observe that Eq. 5 represents the hypothetical case in which the two species are identical. This situation must coincide with the case of self-diffusion for which (Li and Chang, 1955)

$$(D_{12}\eta)_0 = \frac{kT}{2\pi n^{-1/3}} \tag{13}$$

so that, comparing Eqs. 5 and 13

$$n = \xi_o^{-3} \tag{14}$$

and Eq. 12 becomes simply

$$\beta = 2\pi \tag{15}$$

Use of Eqs. 13 and 15 converts Eq. 11 to the explicit predictive form:

$$D_{12}\eta = \frac{kT}{2\pi V^{1/3}}\left[\frac{2\pi X_1X_2\alpha_{12}}{1 + \alpha_{12}(2\pi X_1X_2 - 1)}\right]^{1/2} \tag{16}$$

which, without adjustable parameters, describes the complete concentration and temperature dependence of the transport coefficient product in terms of the classical thermodynamic factor, α_{12}. With Cussler, we find a square root dependence on α_{12}, rather than first power as suggested by phenomenological arguments.

For an ideal solution ($\alpha_{12} = 1$), Eq. 16 reduces to the self-diffusion case, and $D_{12}\eta$ is independent of composition. For nonideal solutions, the limit of Eq. 16 corresponding to infinite dilution is interesting.

$$\lim_{X_1 \to 0}(D_{12}\eta) = D_{12}^0\eta_2 = \frac{kT}{2\pi V_2^{1/3}}\cdot\frac{1}{\sqrt{f_{12}^0}} \tag{17}$$

where

$$f_{12}^0 = 1 - \frac{1}{2\pi} \lim_{X_1 \to 0} \frac{d\alpha_{12}}{dX_1} \tag{18}$$

For an ideal solution $f_{12}^0 = 1$ and Eq. 17 reduces to the self-diffusion case. Otherwise f_{12}^0 contains the necessary thermodynamic correction for dilute diffusion.

Also, an alternate form of Eq. 16 can be written by utilizing Eq. 17:

$$D_{12}\eta = \sqrt{f_{12}^0}\, D_{12}^0 \eta_2 \left(\frac{V_2}{V}\right)^{1/3} \left[\frac{2\pi X_1 X_2 \alpha_{12}}{1 + \alpha_{12}(2\pi X_1 X_2 - 1)}\right]^{1/2} \tag{19}$$

Although Eqs. 16 and 19 contain no adjustable parameters, their utilization is probably best facilitated by the use of appropriate thermodynamic models for the activity coefficient.

For regular solutions (Prausnitz, 1969)

$$\alpha_{12} = 1 - \frac{2(\delta_1 - \delta_2)^2}{kT} \cdot \frac{X_1 X_2 V_1^2 V_2^2}{(X_1 V_1 + X_2 V_2)^3} \tag{20}$$

$$f_{12}^0 = 1 + \frac{V_1^2}{V_2} \cdot \frac{(\delta_1 - \delta_2)^2}{\pi k T} \tag{21}$$

For solutions described by the Wilson equation (Wilson, 1964)

$$\alpha_{12} = 1 - \frac{X_1(1 - \Lambda_{12})}{X_1 + \Lambda_{12} X_2} - X_1 \left(\frac{\Lambda_{12}}{X_1 + \Lambda_{12} X_2} - \frac{\Lambda_{21}}{\Lambda_{21} X_1 + X_2}\right) + X_1 X_2 \left[\frac{\Lambda_{21}}{(\Lambda_{21} X_1 + X_2)^2}(\Lambda_{21} - 1) - \frac{\Lambda_{12}}{(X_1 + \Lambda_{12} X_2)^2}(1 - \Lambda_{12})\right] \tag{22}$$

$$f_{12}^0 = 1 + \frac{1 - \Lambda_{21}^2}{2\pi} \tag{23}$$

The results for other thermodynamic models are easily developed. We include the regular solution form here because of its rich theoretical basis and well-understood limitations. The Wilson equation results are presented because of its proven ability to represent accurately the thermodynamic behavior of a wide variety of binary liquid systems. In the context of such models, once the model parameters are known, Eqs. 16 and 17 provide a complete description of the behavior of $D_{12}\eta$.

For systems that display liquid-liquid critical points, the nonrandom two-liquid model of Renon and Prausnitz (1968) is recommended.

These results remove the deficiencies pointed out by Cussler (1980) in his original development. That is, Eqs. 16 and 19 do not contain an adjustable constant or an arbitrary reference transport coefficient. As such, these equations are directly useful for predictive purposes.

Also, Eq. 17 is a satisfying alternative to the myriad semiempirical expressions previously suggested for dilute diffusion coefficients. For example, when Eq. 23 is substituted into Eq. 17, one obtains

$$D_{12}^0 = \sqrt{\frac{2\pi}{2\pi + 1 - \Lambda_{21}^2}}\, D_{22} \tag{24}$$

which relates the diffusion coefficient of dilute solute (*1*) in solvent (*2*) to the self-diffusion coefficient of the solvent in terms of a single thermodynamic parameter.

Cussler (1980) showed that the basis for the present results is consistent with experiments, particularly for highly nonideal solutions. The explicit relationships derived in this note deserve further investigation and testing.

Notation

a, a_{ij} = characteristic lengths
D_{12} = binary mutual diffusion coefficient
D_{22} = self-diffusion coefficient
f_{12}^0 = thermodynamic correction, Eq. 18
$F(r)$ = time integrated velocity correlation function
g_{ij} = defined by Eq. 8
$G(r)$ = concentration correlation function
k = Boltzmann's constant
n = molecular density
r = radial distance
T = absolute temperature
V = molecular volume
X_i = mole fraction

Greek Letters

α_{12} = thermodynamic factor, Eq. 7
β = constants, Eqs. 12 and 15
γ_1 = activity coefficient
δ_i = solubility parameter
η = viscosity
Λ_{ij} = Wilson parameter
μ_1 = chemical potential
ξ, ξ_{ij} = correlation lengths

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