Activity Corrections to Diffusivities in Polymeric Materials

CHARLES GOLDSTEIN AND R. L. LAURENCE

The Johns Hopkins University, Baltimore, Maryland

In a recent correspondence by Morrison (*1*), it was shown without a theoretical basis that for some polymer-diluent systems a diffusion coefficient based on the activity is not as strongly dependent upon concentration as the diffusivity based on the mass fraction. A recent study (*2*) on liquid binary systems provided theoretical justification for the activity correction to the diffusion coefficient.

Since there exists a thermodynamics of polymer solutions, it is reasonable to assume that the theory can provide justification for the use of an activity correction, and establish whatever limitations it imposes on the systems and their nature.

The Flory-Huggins theory of polymer solutions (*3*), when applied to diffusion data such as that presented by Kokes and Long (*4, 5*), can provide a basis for the activity correction; however, it sets limitations upon the types of systems to which such corrections can be applied. As a supplement to Morrison's paper, we will provide a basis for and the limitations on activity corrections to diffusion coefficients.

The Flory-Huggins relation for the chemical potential of a diluent in a solution of long chain polymers is

$$\frac{\mu_1 - \mu_1^\circ}{RT} = \ln a_1 = \ln v_1 + v_2 + \chi_1 v_2^2 \qquad (1)$$

Equation (1) was derived by assuming a constant interaction parameter χ_1. When we use a relation between the volume fraction v_1 and the mass fraction ω_1 in systems where volume changes upon mixing are negligible

$$v_1 = \frac{\omega_1}{\omega_1 + \dfrac{\rho_1}{\rho_2}\omega_2} \qquad (2)$$

the activity correction is given by

$$\frac{\partial a_1}{\partial \omega_1} = \frac{\rho_1}{\rho_2}\left(\frac{v_1}{\omega_1}\right)^2 \{v_2(1 - 2\chi_1 v_1)\}\exp\{v_2(1 + \chi_1 v_2)\} \qquad (3)$$

The interaction parameter χ_1 imposes limitations on the *systems to which an activity correction can be applied.* When $\chi_1 < 0.5$, polymer and diluent are miscible. For a value of $\chi_1 > 0.5$ the components are not miscible. The activity correction would result, for the latter system, in a negative diffusion coefficient if it is not taken into account that the miscibility limit might have been reached.

In the data reported by Kokes, DiPietro, and Long (*5*), some diluents in polyvinyl acetate have $\chi_1 > 0.5$ at low concentration. For these materials, propyl chloride, propylamine, and isopropylamine, χ_1 decreases with increasing concentration to a value less than 0.5 and the systems are miscible in the whole range of volume fraction. An activity correction for such systems is still justified since the inequality [imposed by Equation (3)]

$$v_1 < \frac{1}{2\chi_1} \qquad (4)$$

is not violated.

The activity correction $\partial a_1/\partial \omega_1$, given by Equation (3), assumes the value (ρ_2/ρ_1) exp $(1 + X_1)$ as $v_1 \to 0$. However, as v_1 increases, the correction eventually becomes less than 1. This is obvious in the limiting case of $\chi_1 = 0$ since in the limit of $v_1 \to 1$, $\partial a_1/\partial \omega_1 = 0$. For such a case, the concentration dependence of the activity-based coefficient is greater than the dependence on the mass fraction-based coefficient. The correction, if it is to be used to modify the concentration dependence of diffusivity, should be used with discretion at higher concentration in miscible systems or not at all in partially miscible systems such as propanol-polyvinylacetate.

NOTATION

a_1 = activity $\cong P_1/P_1^\circ$
P_1 = partial pressure of diluent, dynes/sq cm.
P_1° = vapor pressure of pure diluent, dynes/sq. cm.
R = gas constant, cal./g.-mole °C.
T = temperature, °C.
v_1 = volume fraction of diluent
v_2 = volume fraction of polymer

Greek Letters

μ_1 = chemical potential of diluent
μ_1° = standard chemical potential of diluent
ρ_1 = density of diluent, g./cc.
ρ_2 = density of polymer, g./cc.
χ_1 = Flory-Huggins interaction parameter
ω_1 = mass fraction of diluent
ω_2 = mass fraction of polymer

LITERATURE CITED

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