

Diffusion in Amorphous Polymers

Many studies of diffusion rely upon Fick's laws¹ for the analysis of experimental data. When Fick stated that the flux of a diffusant across a surface of equal concentration was proportional to the concentration gradient at that surface, $J = -D \text{grad } c$ (with the proportionality constant, D , called the diffusion coefficient), he probably did not anticipate that this law would be applied to systems in which large interactions would prevail between diffusing molecules and the barrier to diffusion. Nevertheless, this relation has been used in treating the diffusion of vapors and liquids in polymeric materials which were swollen by (partially soluble in) the diffusant.

Typical of this type of adaptation to Fick's laws was the study of diffusion of organic vapors in polyvinyl acetate by Kokes and Long.² The concentration dependence of the diffusion coefficient was recognized, and integral diffusion coefficients $\bar{D}(c)$ were calculated:

$$\bar{D}(c) = 1/(c_e - c_i) \int_{c_i}^{c_e} D(c) dc \quad (1)$$

where c_i and c_e refer to the initial and final concentrations, respectively. Also the empirical relation:

$$D(c) = D_0 e^{\delta c} \quad (2)$$

was acknowledged wherein

$$\lim_{c \rightarrow 0} D(c) = D_0$$

and δ is constant characteristic of the system. Kokes and Long further proposed that the numerical value of δ was associated with the Flory-Huggins interaction parameter.³ Recently Lawson⁴ has suggested an empirical relationship of δ to the isothermal compressibility of some polymers.

The purpose of the present discussion is to demonstrate an alternative adaptation of Fick's first law to diffusion in amorphous polymers.

One might expect Fick's law to apply with a concentration-independent diffusion coefficient in an ideal system, one in which the diffusant does not appreciably strain bonding elements of the solid phase through which it passes, i.e., $J = -D_0 dc/dx$ for the one-dimensional case. For the non-ideal system, one may either accept D as a function of concentration, as done by most authors, or one may retain the concentration-independent coefficient D_0 and substitute an activity gradient for the concentration gradient:

$$\begin{aligned} J &= -D(c)dc/dx \\ &= -D_0 d\alpha/dx \\ &= -D_0 d[\gamma(c)c]/dx \end{aligned} \quad (3)$$

where α is the activity of the diffusant and $\gamma(c)$ a diffusive activity coefficient. The diffusive activity may not be identical to the thermodynamic activity. Since

$$d[\gamma(c)c]/dx = d[\gamma(c)c]/dc(dc/cx)$$

eq. (3) may be rewritten:

$$D(c) = D_0 d[\gamma(c)c]/dc \quad (4)$$

Now if $\gamma(c)$ is bounded as $c \rightarrow 0$, $\gamma(c)c$ also approaches zero, and so, using $c = 0$ as the lower limit of integration, we find:

$$\gamma(c)c = \int_0^c D(c)/D_0 dc \quad (5)$$

By comparing eqs. (1) and (5), one may express the diffusive activity coefficient in terms of the integral diffusion coefficient of Kokes and Long:

$$\gamma(c) = \bar{D}(c)/D_0 \quad (6)$$

where $c = 0$ is taken as the lower limit of integration in obtaining the integral diffusion coefficient.

Substitution of eq. (2) into eq. (5) establishes the relationship of the constant δ to the diffusive activity coefficient:

$$\gamma(c) = (1/\delta c)(e^{\delta c} - 1) \quad (7)$$

Hence, a diffusive activity coefficient can be determined and compared with the thermodynamic activity coefficient obtained from equilibrium sorption measurements. Discrepancy between the two coefficients would show that the presence of the diffusant is altering the resistance to flow. In other words, equilibrium effects that alone determine the thermodynamic coefficient would be separated from kinetic effects which, in addition to the equilibrium effects, contribute to the variation of the diffusion coefficient.

If the two activity coefficients should prove empirically to be equal, this would not only provide information about polymer structure but would also furnish a convenient predictive formula, since thermodynamic activity coefficients could be measured more easily than diffusive ones. Even if this should not hold true, the method might have value in supplying an interpolation formula.

References

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