TABLE 1. EQUILIBRIUM DATA FOR THE SYSTEM
AMYL ALCOHOL-AMYL ACETATE

| Mole fraction alcohol in | | Temper- |
Liquid	Vapor	ature, °C.
0.456	0.521	140.55
0.489	0.547	140.00
0.530	0.577	139.50
0.577	0.626	138.85
0.639	0.664	138.20
0.674	0.710	137.75
0.738	0.756	137.35
0.804	0.828	136.85
0.870	0.878	136.45
1.000	1.000	136.00

Pressure: 755.8 mm. Hg.

Fig. 3. Vapor-liquid equilibrium of methanol-
ethyl acetate at 760 mm. Hg.

(7) for this binary are presented in Figure 3, along with the equilibrium predicted by Barker's theoretical model using the same values for interaction energies as in the other systems. The fit of the theoretical curve is even better than for the most closely related systems within the series, that is, methanol-methyl acetate and ethanol-ethyl acetate. The Sweeney and Rose method thus has further verification within the homologous series, and for binary systems of alcohols and esters outside the series but with the esters of the same type.
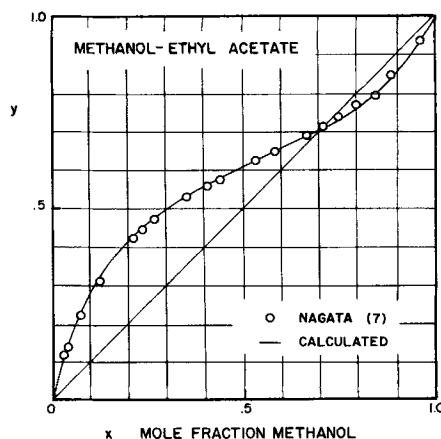
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Diffusion Coefficients for Organic Vapors in Polyvinyl Acetate

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For the diffusion of vapors into polymers, the Fick diffusion coefficient (1) varies with concentration. This has been attributed to swelling of the polymer and dilution effects of the condensed vapors. In particular the diffusion of organic vapors in polyvinyl acetate has been studied by Kokes and Long (2). Kokes and Long found experimentally that

$$\overline{D}_{ij}(C_i) = \overline{D}_o e^{\beta C_i} \qquad (1)$$

where

$$D_{ij}(C_i) = \frac{d[C_i \overline{D}_{ij}(C_i)]}{dC_i} \qquad (2)$$

Because the diffusion coefficient $D_{ij}(C_i)$ changes rapidly with concentration in these systems, recent comments (3) have been made that a diffusion coefficient based on an activity gradient might not vary with concentration. This paper discusses the evaluation of diffusion coefficients based on an activity gradient for benzene, acetone, and propylamine in polyvinyl acetate.

The flux of organic vapor (i) through a polymer with mass fraction as a driving force for diffusion can be written as

$$n_i = \rho_i v - \rho D_{ij}(\omega_i) \nabla \omega_i \qquad (3)$$

If activity is considered the driving force for diffusion

$$n_i = \rho_i v - \rho D_{ij}(a_i) \nabla a_i \qquad (4)$$

Consideration of Equations (3) and (4) yields

$$D_{ij}(a_i) \nabla a_i = D_{ij}(\omega_i) \nabla \omega_i \qquad (5)$$

If we consider the fact that activity is a function of state, then

$$a_i = f(T, P, \omega_1, \omega_2, \ldots, \omega_{n-1}) \qquad (6)$$

Therefore

$$\nabla a_i = \left(\frac{\partial a_i}{\partial T}\right)_{P,\omega_i} \nabla T + \left(\frac{\partial a_i}{\partial P}\right)_{T,\omega_i} \nabla P$$
$$+ \sum_{k=1}^{k=n-1} \left(\frac{\partial a_i}{\partial \omega_k}\right)_{T,P,\omega_j} \nabla \omega_k \qquad (7)$$

For a binary system at constant temperature and pressure, Equation (7) reduces to

$$\nabla a_i = \left(\frac{\partial a_i}{\partial \omega_i}\right) \nabla \omega_i \qquad (8)$$
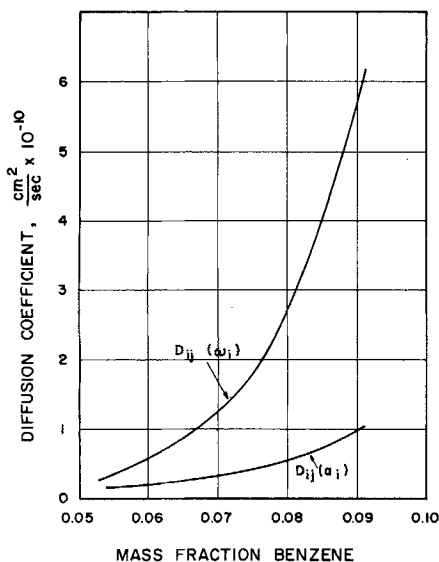
Fig. 1. Comparison of $D_{ij}(\omega_i)$ and $D_{ij}(a_i)$ for benzene in polyvinyl acetate as a function of the benzene concentration.
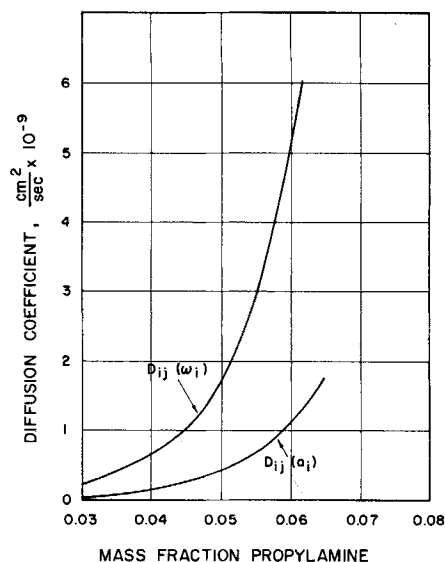

Fig. 3. Comparison of $D_{ij}(\omega_i)$ and $D_{ij}(a_i)$ for propylamine in polyvinyl acetate as a function of the propylamine concentration.

Comparison of Equations (5) and (8) yields

$$D_{ij}(a_i) = D_{ij}(\omega_i) \bigg/ \left(\frac{\partial a_i}{\partial \omega_i}\right)_{T,P,\omega_j} \qquad (9)$$

Values of the Fick diffusion coefficient for three organic compounds diffusing into polyvinyl acetate are shown in Figures 1, 2, and 3. The diffusion coefficients are those reported by Kokes and Long (1) at 40°C. The diffusion coefficients are seen to be functions of the concentration of the system.

Using equilibrium absorption techniques, Kokes et al. (4) have reported the activity of the organic vapor in the polyvinyl acetate. These values for the activity were used in conjunction with Equation (9) to evaluate the diffusion coefficient based on an activity gradient. The results are shown in Figures 1, 2, and 3 for the benzene–polyvinyl acetate, acetone–polyvinyl acetate, and propylamine–polyvinyl acetate systems at 40°C. The diffusion coefficient based on an activity gradient does not vary as significantly with concentration as the Fick diffusion coefficient for the benzene–polyvinyl acetate system. For the diffusion of acetone or propylamine in polyvinyl ace-
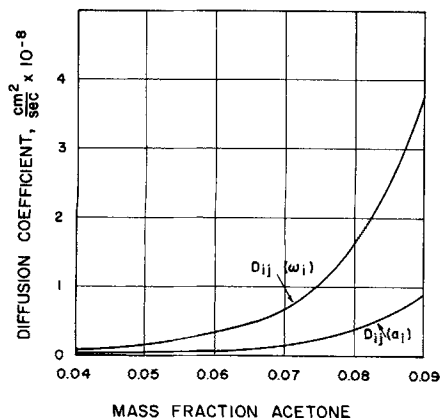
tate, both $D_{ij}(a_i)$ and $D_{ij}(\omega_i)$ appear to be quite concentration dependent.

Based on the results reported above, it would appear that diffusion coefficients for certain vapors in polymers might best be correlated when based on an activity gradient rather than on a mass fraction gradient. Since existing techniques (2) for measurement of the diffusion coefficients require measurement of the activity-mass fraction profile, essentially no additional experimental work would be required to report $D_{ij}(a_i)$ as opposed to $D_{ij}(\omega_i)$.

NOTATION

a_i = activity = P_i/P^o_i
C_i = mass concentration of i, g. of i/g. of j
$D_{ij}(\omega_i)$ = Fick diffusion coefficient as defined by Equation (3), sq.cm./sec.
$D_{ij}(a_i)$ = diffusion coefficient as defined by Equation (4), sq.cm./sec.
n = mass flux, g./(sq.cm.)(sec.)
P = pressure, dyne/sq.cm.
P_i = partial pressure of component i, dynes/sq.cm.
P^o_i = saturation vapor pressure of component i, dynes/ sq.cm.
v = mass average velocity, cm./sec.

Greek Letters

ω_i = mass fraction i, ρ_i/ρ
β = constant
ρ_i = mass concentration of i, g. of i/cc.
ρ = density, g./cc.
∇ = gradient operator

Subscripts

i = organic vapor
j = polymer

Fig. 2. Comparison of $D_{ij}(\omega_i)$ and $D_{ij}(a_i)$ for acetone in polyvinyl acetate as a function of the acetone concentration.

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