# The Effect of Competitive Adsorption on the Rate of Diffusion

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## Synopsis

Evidence is presented that the apparent diffusion coefficient of one penetrant can be increased by competition from another penetrant for the same adsorption sites in polyester. The competition is governed by the relative diffusivities of the penetrants and their affinities for the adsorption sites.

## INTRODUCTION

Ott and Rys[1] have recently examined the effect of competitive adsorption of a pair of cationic dyestuffs by alumino-silicate beads on their respective rates of sorption. Their treatment of the problem was based on ideas of Weisz,[2] who dealt with the influence of adsorption on diffusion, and Weisz and Zollinger,[3] who predicted the effect of competitive adsorption on the rates of diffusion of the competitors. The choice of alumino-silicate beads by Ott and Rys may seem unusual for an investigation of dye sorption, but these authors quite rightly selected a substrate which was strictly definable structurally and incapable of undergoing any structural changes in the course of the sorption process.

Hemming and Datyner,[4] in an investigation of the mechanism of the action of "carriers" in dyeing polyester with disperse dyestuffs, examined the effect of additions of benzoic, salicylic, and $p$-hydroxybenzoic acids on the diffusion of some models for disperse dyestuffs into a roll of polyester film. The diffusion profiles of the dyes[4] showed in all cases the usual decrease in concentration along the direction of penetration. The diffusion profile of salicylic acid, which had the greatest effect, also showed such a decrease in concentration. $p$-Hydroxybenzoic acid, which is adsorbed hardly at all by polyester, had no effect on the diffusion profile of the dye. When apparent diffusion coefficients ($D_{app}$) were calculated from the diffusion profiles, using the Boltzmann-Matano method, the curves shown in Figure 1 were obtained. The shape of these curves could not be reconciled with the idea that the acceleration in dyeing is solely or even mainly a function of swelling of the substrate caused by either or both penetrants. If it were, one would expect the largest value of $D_{app}$ in the outermost layer of the film roll and then a decrease in inner layers related to the concentration of the penetrant responsi-
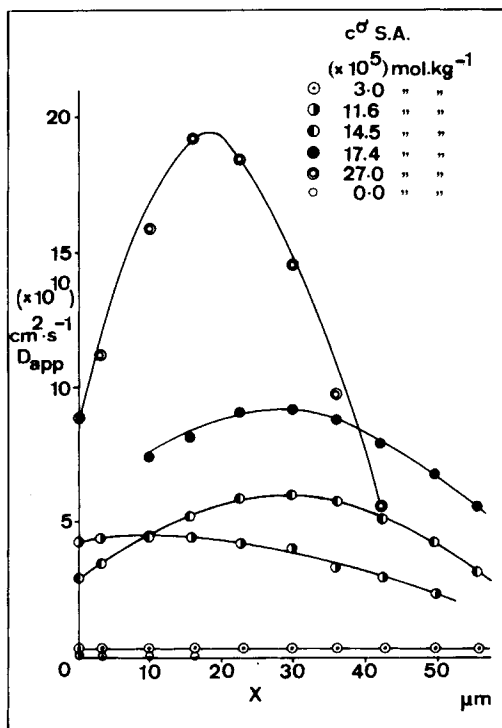
Fig. 1. Effect of salicylic acid on the apparent diffusion coefficient of 1-aminoanthraquinone.

ble for swelling. A curve rising to a maximum and then falling is indicative of the existence of more than one effect.

While the existence of swelling is not discounted, the magnitude and type of change in $D_{app}$ cannot be explained as being due to swelling, and Hemming and Datyner suggested that the observed variations in $D_{app}$ of the dyes were due to competition of salicylic and benzoic acids for dye adsorption "sites" in the polymer.[4] A more thorough scrutiny of the suggestion has been under-taken using the ideas referred to before[1-3] and the results obtained from the theoretical model compared with experimental ones. The complication due to the effects of polymer chain motion in the course of the experiment has not been taken into account because at 90°C, at which the experiments were carried out, which is above the glass transition point of polyester, polymer chain motion will be random.

## EXPERIMENTAL

### Materials

**Substrate.** Polyester film (Mylar, supplied by du Pont de Nemours Inc., Wilmington, Delaware, U.S.A.), 5 cm wide, of average thickness 6.6 $\mu m$ (determined with a Minicom E-MD-M304 High Speed Electric Micrometer, Tokyo Siemitsu Co. Ltd., Tokyo, Japan).

**Penetrants.** 1-Aminoanthraquinone; salicylic acid, analytical reagent

grade and $C^{14}$-labeled at —COOH (supplied by the Radiochemical Centre, Amersham, U.K.).

## Method

1-Aminoanthraquinone and salicylic acid were applied from an infinite bath at 90°C to Mylar polyester film using Sekido's film roll technique[5] and their diffusion profiles determined. Diffusion profiles of salicylic acid alone were determined by measuring the concentration in the film at 307.5 nm spectrophotometrically (Hitachi Perkin-Elmer Model 139). In the presence of dye, the concentration had to be determined by microdensitometry of an autoradiograph. For this, radio-labeled acid was added to a solution of salicylic acid to give a radioactivity of 175 $\mu$Ci/kg. After dyeing, the film was removed from the bath, unrolled, wiped, and dried. X-Ray film [Kodirex, Kodak (Australasia) Ltd.] was then sandwiched between two layers of radioactive polyester film, kept in contact for 14 days, and the developed film scanned on a double-beam microdensitometer (Joyce, Loebl and Co. Ltd., Gateshead-on-Tyne, U.K.). The concentrations of 1-aminoanthraquinone were determined spectrophotometrically at 484 nm and its diffusivity, at 90°C in a Northrup and Anson cell.[6]

## RESULTS AND DISCUSSION

In unidirectional nonsteady-state diffusion accompanied by immobilization of some of the diffusing molecules by adsorption, eq. (1) applies:

$$D' \frac{\partial^2 c^{\phi}_m}{\partial x^2} = \frac{\partial c^{\phi}}{\partial t} \tag{1}$$

where $D'$ is the effective diffusion coefficient, which is a constant related to the diffusivity, the porosity of the substrate $P$, and the "tortuosity" factor $b$ as follows:

$$D' = D \frac{P}{b}. \tag{2}$$

This factor expresses numerically the extent to which the voids through which diffusion proceeds are not straight and parallel to the direction of measurement of the diffusion path.

The left side of eq. (1) represents the difference between flux into and out of a volume element of the substrate and depends on the concentration of mobile molecules $c^{\phi}_m$ alone, whereas the right side is the rate of change in the concentration $c^{\phi}$ of all penetrant molecules in that element; some of these molecules may be immobilized. Thus, $c^{\phi}_m + c^{\phi}_{im} = c^{\phi}$ where $c^{\phi}_{im}$ is the concentration of immobilized molecules. Equation (1) can be rewritten as

$$D_{\text{app}} \frac{\partial^2 c^{\phi}_m}{\partial x^2} = \frac{\partial c^{\phi}_m}{\partial t} \tag{3}$$

where $D_{\text{app}}$ is the apparent diffusion coefficient.[1]

By use of the Boltzmann variable, $\eta = x/2t^{1/2}$, where $x$ is the distance of
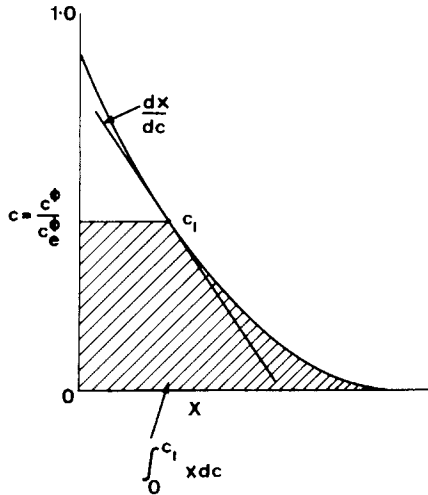
Fig. 2. Use of the diffusion profile in the calculation of the apparent diffusion coefficient.

penetration through the substrate and $t$ is the time taken for it, eqs. (1) and (3) become

$$D'\frac{d^2c^\phi_m}{d\eta^2} = -2\eta\frac{dc^\phi}{d\eta} \tag{1a}$$

and

$$D_{app}\frac{d^2c^\phi_m}{d\eta^2} = -2\eta\frac{dc^\phi_m}{d\eta} \tag{3a}$$

respectively, and therefore

$$D_{app} = D'\frac{dc^\phi_m}{dc^\phi}. \tag{4}$$

It follows from eq. (4) that $D_{app}$ varies with $dc^\phi_m/dc^\phi$, since $D'$, the effective diffusion coefficient, is constant.

Integration of eq. (1a) and substitution of $x/2t^{1/2}$ for $\eta$ gives

$$D' = -\frac{1}{2t}\frac{dx}{dc^\phi_m}\int_0^{c^\phi} x\,dc^\phi. \tag{5a}$$

$D_{app}$ can be obtained graphically from the diffusion profile ($c^\phi$ versus $x$) at time $t$ by measuring the reciprocal of the tangent at $c^\phi = c^\phi_1$ and the shaded area (Fig. 2), because it follows from eqs. (4) and (5a) that

$$D_{app} = -\frac{1}{2t}\frac{dx}{dc^\phi}\int_0^{c^\phi} x\,dc^\phi. \tag{5b}$$

The curves shown in Figure 1 were obtained using the experimental results to calculate $D_{app}$ from eq. (5b). To explain their shapes, it is necessary to examine how $D_{app}$ varies with $dc^\phi_m/dc^\phi$, see eq. (4). This can be done by considering that the substrate immobilizes some of the penetrant by adsorption and making the following assumptions: (a) that the maximum concentration

$S^\phi$ of penetrant capable of being adsorbed is constant and one and the same for different species of penetrant, and (b) that at the time of determination of $c^\phi$ equilibrium had been reached between $c^\phi_m$ and $c^\phi_{im}$, at each point in the substrate, because the rate of change in the concentration of penetrant at any point in the substrate is very small after diffusion has proceeded for several hours. It can therefore be expected that the rates of adsorption and desorption have become equal.

Two cases will be considered: the first will deal with the diffusion of one species of penetrant and the second, with two species diffusing simultaneously and competing for the same adsorption sites in the substrate.

## One Penetrant

At equilibrium, the rate of adsorption (immobilization)

$$\frac{dc^\phi_{im}}{dt} = k_{im} \cdot c^\phi_m \cdot (S^\phi - c^\phi_{im}) \tag{6}$$

must equal the rate of desorption (mobilization)

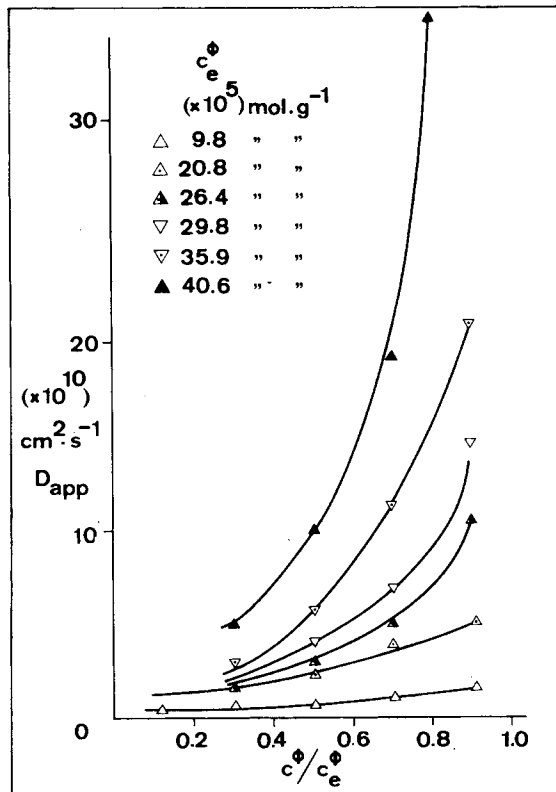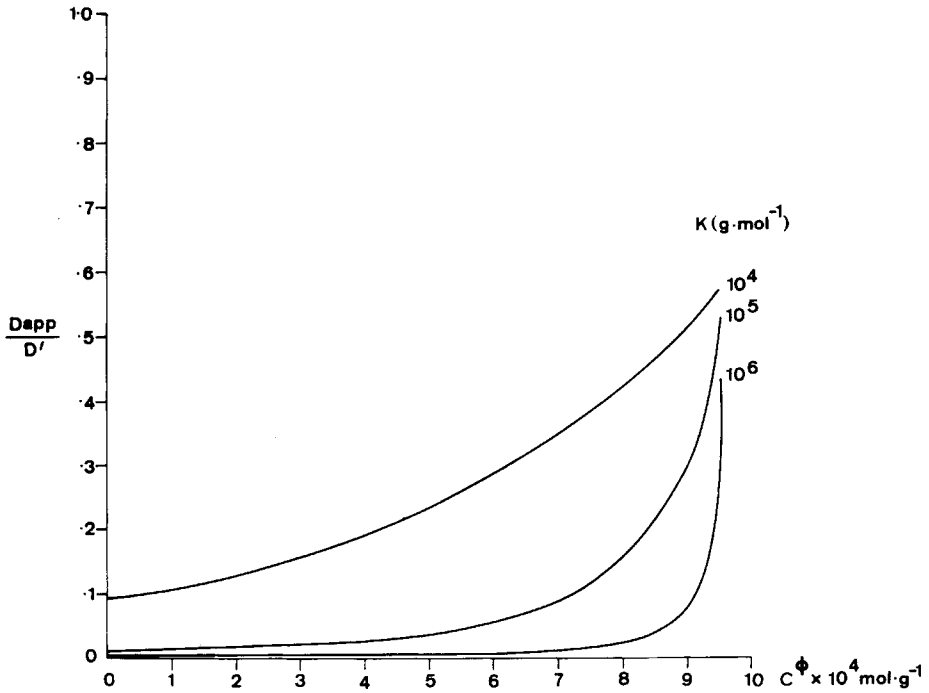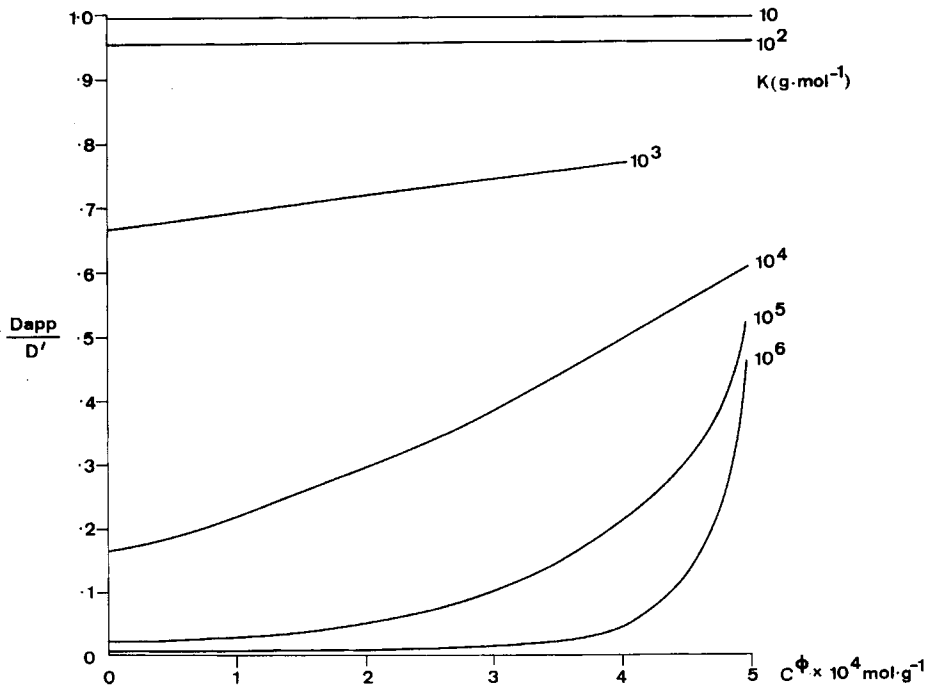$$-\frac{dc^\phi_{im}}{dt} = k_m \cdot c^\phi_{im}. \tag{7}$$



Fig. 3. Experimental apparent diffusion coefficients of salicylic acid as a function of concentration.
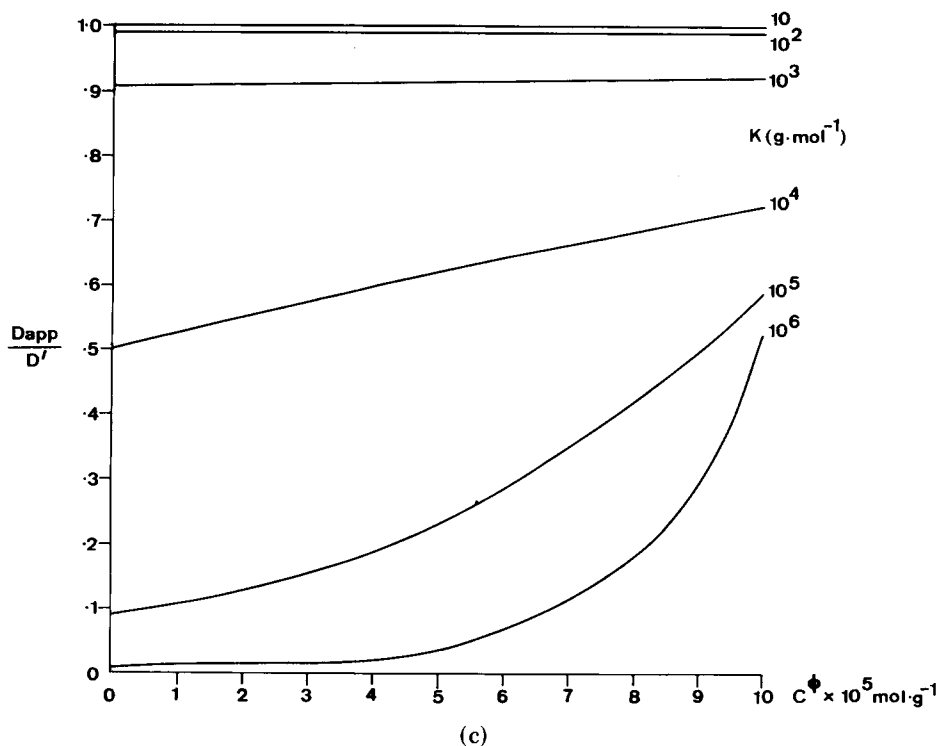
(a)



(b)

Fig. 4 (*continued*)

Fig. 4. Calculated $dc\,\phi_m/dc^\phi$ (= $D_{app}/D'$) as a function of concentration at $K = 10^n$ g/mole: (a) $S^\phi = 10^{-3}$ mole/g for $n = 4, 5, 6$; (b) $S^\phi = 5 \times 10^{-4}$ mole/g for $n = 1, 2, 3, 4, 5, 6$; (c) $S^\phi = 10^{-4}$ mole/g for $n = 1, 2, 3, 4, 5, 6$.

Thus,

$$k_{im} \cdot c^\phi_m \cdot (S^\phi - c^\phi_{im}) = k_m c^\phi_{im}. \tag{8}$$

Let $k_{im}/k_m = K$; then, since $c^\phi_{im} = c^\phi - c^\phi_m$,

$$K(c^\phi_m)^2 + [1 + K(S\phi - c^\phi)]c^\phi_m - c^\phi = 0. \tag{9}$$

Thus,

$$c^\phi_m = \frac{1}{2K}[-1 - K(S^\phi - c^\phi) + \{[1 + K(S^\phi - c^\phi)]^2 + 4Kc^\phi\}^{1/2}] \tag{10}$$

and

$$\frac{dc^\phi_m}{dc^\phi} = 0.5\left[1 + \frac{1 - K(S^\phi - c^\phi)}{\{[1 + K(S^\phi - c^\phi)]^2 + 4Kc^\phi\}^{1/2}}\right]. \tag{11}$$

The question now arises how to account theoretically for the existence of either a constant apparent diffusion coefficient (1-aminoanthraquinone at $c^\phi = 5 \times 10^{-5}$ mole/g in Fig. 1) or a variable one as shown by the curves given by salicylic acid in Figure 3. The first follows from the Langmuir adsorption isotherm

$$c^\phi_{im} = S^\phi \frac{Kc^\phi_m}{1 + Kc^\phi_m} \tag{12}$$

which can be rewritten

$$c^\phi_{im} = S^\phi \frac{c^\phi_m}{\dfrac{1}{K} + c^\phi_m}. \tag{12a}$$

Thus, for low values of $K$ and/or small values of $1/K \gg c^\phi_m$,

$$c^\phi_{im} = S^\phi K c^\phi_m \tag{12b}$$

from which it follows that $D_{app}$ is a constant equal to $D'$ $(KS^\phi + 1)^{-1}$, [eq. (4)]. To obtain curves of the shape shown in Figure 3, $dc^\phi_m/dc^\phi$ was calculated assuming different values for $S^\phi$, $K$, and $c^\phi$. The results of the calculations are represented graphically in Figures 4a, 4b, and 4c, from which one can see that at $K \approx 10^5$ g/mole, $S^\phi \approx 5 \times 10^{-4}$ mole/g and $c^\phi \approx 2.0$–$4.0 \times 10^{-4}$ mole/g, $dc^\phi_m/dc^\phi$ changes similarly to the curves shown in Figure 3, whereas at $K < 10^3$ g/mole and $c^\phi \ll 5 \times 10^{-5}$ mole/g (which is low compared with $S^\phi \approx 5 \times 10^{-4}$ mole/g) $dc^\phi_m/dc^\phi$ is constant.

### Two Penetrants, C and D

At equilibrium, by analogy with eq. (8),

$$c^\phi_{imD} = K_D(S^\phi - c^\phi_{imD} - c^\phi_{imC})c^\phi_{mD} \tag{13a}$$

and

$$c^\phi_{imC} = K_C(S^\phi - c^\phi_{mD} - c^\phi_{imC})c^\phi_{mC}. \tag{13b}$$

Since $c^\phi_{im} = c^\phi - c^\phi_m$, eqs. (13a) and (13b) convert to

$$c^\phi_D - c^\phi_{mD} = K_D(S^\phi - c^\phi_D + c^\phi_{mD} - c^\phi_C + c^\phi_{mC})c^\phi_{mD} \tag{13c}$$

and

$$c^\phi - c^\phi_{mC} = K_C(S^\phi - c^\phi_D + c^\phi_{mD} - c^\phi_C + c^\phi_{mC})c^\phi_{mC}. \tag{13d}$$

From eq. (13c) one can obtain $c^\phi_{mC}$ as a function of $c^\phi_D$ and $c^\phi_{mD}$ and substitution in (13d) gives

$$a_1(c^\phi_{mD})^3 + a_2(c^\phi_{mD})^2 + a_3 c^\phi_{mD} + a_4 = 0 \tag{14}$$

where

$$a_1 = K^2_D - K_C K_D$$

$$a_2 = K_D + S^\phi K^2_D + 2K_C K_D c^\phi_D - K_C - S^\phi K_D K_C + K_C K_D c^\phi_C - K^2_D c^\phi_D$$

$$a_3 = -K_D c^\phi_D + 2K_C c^\phi_D + S^\phi K_C K_D c^\phi_D - K_C K_D(c^\phi_D)^2 - K_C K_D c^\phi_C c^\phi_D$$

$$a_4 = -K_D(c^\phi_D)^2.$$

Let us analyze two cases:
**Case 1.** $K_C = K_D = K$.
Equation (14) then becomes

$$K^2(c^\phi_C + c^\phi_D)(c^\phi_{mD})^2 + c^\phi_D[K^2(S^\phi - c^\phi_C - c^\phi_D) + K]c^\phi_{mD} - K(c^\phi_D)^2 = 0 \tag{14a}$$
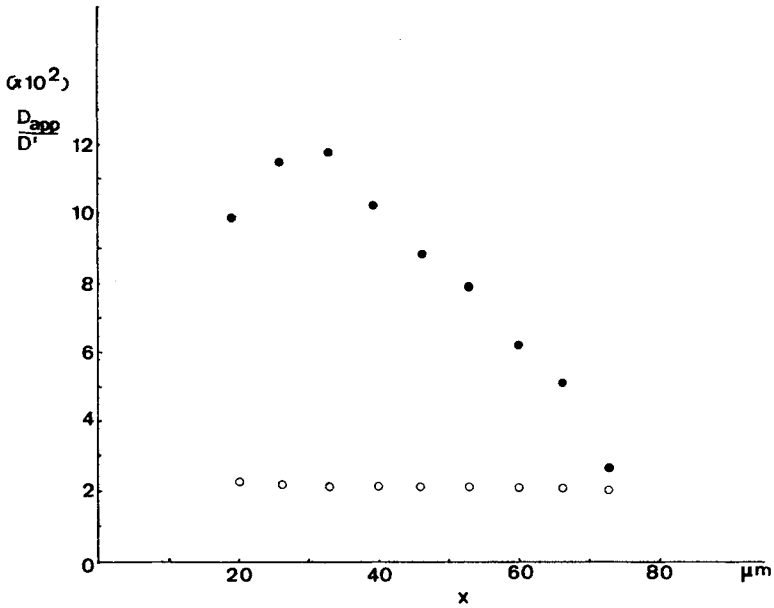
Fig. 5. Calculated $dc^\phi_m/dc^\phi$ for simultaneous diffusion of two penetrants at $S^\phi = 5 \times 10^{-4}$ mole/g and $K = 10^5$ g/mole for both from experimental values of $c^\phi$ of salicylic acid and 1-aminoanthraquinone.
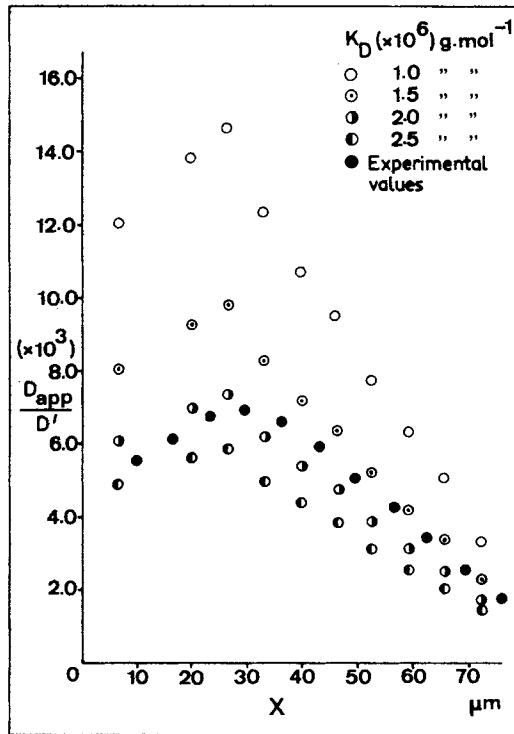


Fig. 6. Experimental $dc^\phi_m/dc^\phi$ for simultaneous diffusion of salicylic acid and 1-aminoanthraquinone and calculated values at $S^\phi = 5 \times 10^{-4}$ mole/g, $K_C = 10^5$ moles/g and $K_D = 10^6$–2.5 $\times$ $10^6$ moles/g.

and

$$c^{\phi}{}_{mD} = \frac{c^{\phi}{}_{D}[-1 - K(S^{\phi} - c^{\phi}{}_{C} - c\phi_{D}) + \{[1 + K(S^{\phi} - c^{\phi}{}_{C} - c^{\phi}{}_{D})]^2 + 4K(c^{\phi}{}_{C} + c^{\phi}{}_{D})\}^{1/2}]}{2K(c^{\phi}{}_{C} + c^{\phi}{}_{D})}. \qquad (15)$$

Differentiation of $c^{\phi}{}_{mD}$ with respect to $c^{\phi}{}_{D}$ and $c^{\phi}{}_{C}$ and numerical differentiation of $c^{\phi}{}_{C}$ with respect to $c^{\phi}{}_{D}$ and substitution of experimental data in eq. (16)

$$\frac{dc^{\phi}{}_{mD}}{dc^{\phi}{}_{D}} = \frac{\partial c^{\phi}{}_{mD}}{\partial c^{\phi}} + \left(\frac{\partial c^{\phi}{}_{mD}}{\partial c^{\phi}{}_{C}}\right)\left(\frac{dc^{\phi}{}_{C}}{dc^{\phi}{}_{D}}\right) \qquad (16)$$

gives values for $dc^{\phi}{}_{mD}/dc^{\phi}{}_{D}$ which, when plotted against $x$ (for $S^{\phi} = 5 \times 10^{-4}$ mole/g and $K = 10^5$ g/mole), give the curves shown in Figure 5. When $c^{\phi}{}_{C} > 0$, $D_{app}$ rises to a maximum and then descends in the direction of $x$, whereas, when $c^{\phi}{}_{C} = 0$, $D_{app}$ is constant.

**Case 2.** Let us take $S^{\phi} = 5 \times 10^4$ mole/g and $K_C = 10^5$ g/mole, which are realistic values derived from Figure 4b, and let us substitute in eq. (14) the values $10^6$, $1.5 \times 10^6$, $2.0 \times 10^6$, and $2.5 \times 10^6$ for $K_D$. Solution of this equation by Newton's method will give us $dc^{\phi}{}_{m}/dc^{\phi}$. Curves were obtained in this way by using experimental values $c^{\phi}{}_{C}$ for salicylic acid and $c^{\phi}{}_{D}$ for 1-aminoanthraquinone from profiles of these two penetrants after simultaneous diffusion; these are shown in Figure 6. This figure illustrates the change in the apparent diffusion coefficient along $x$, since $dc^{\phi}{}_{m}/dc^{\phi} = D_{app}/D'$, where $D'$ is a constant. The corresponding curve obtained by the use of the same values for $c^{\phi}{}_{C}$ and $c^{\phi}{}_{D}$ from eq. (5b) is shown on the same figure and is very similar to the theoretical curve for $K_D = 2.0 \times 10^6$ g/mole.

To obtain $D_{app}/D'$ for this purpose, $D'$ has to be known. This is obtained from eq. (2) which requires a knowledge of the diffusivity $D$ of 1-aminoanthraquinone in salicylic acid and of the porosity of the polyester film. The diffusivity in water at 90° was $2.3 \times 10^{-5}$ cm²/sec, and this value was used because in the presence of salicylic acid the determination of $D$ at 90° presented insurmountable difficulties. The porosity was assumed to be[7] 0.01, and therefore $D' = 1.32 \times 10^{-7}$ cm²/sec, since $b = 3^{1/2}$.

The above analysis supports the view expressed in the previous paper[1] that salicylic acid affects the rate of diffusion of 1-aminoanthraquinone by competing with it for the same adsorption sites in the substrate.

## Nomenclature

| | |
|---|---|
| $D$ | diffusivity (cm²/sec) |
| $D'$ | effective diffusion coefficient (cm²/sec) |
| $D_{app}$ | apparent diffusion coefficient (cm²/sec) |
| $P$ | porosity (nondimensional) |
| $b$ | tortuosity factor (nondimensional) |
| $c_m$ | concentration of mobile molecules of penetrant (moles/g) |
| $c_{im}$ | concentration of immobilized (adsorbed) molecules (moles/g) |
| $c$ | total concentration of molecules of penetrant (moles/g) |
| $c_e$ | $c$ in equilibrium with $c$ (moles/g) |
| $x$ | distance of penetration along radius of roll ($\mu$m) |
| $t$ | duration of experiment (min) |

| | |
|---|---|
| $\eta$ | Boltzmann variable $(= x/2t^{1/2})$ |
| $k_{im}$ | rate constant of immobilization (adsorption (g/mol $\cdot$ sec) |
| $k_m$ | rate constant of mobilization (desorption) (sec$^{-1}$) |
| $S^{\phi}$ | total concentration of immobilization (adsorption) sites (moles/g) |
| $K = k_{im}/k_m$ | equilibrium constant (g/mole) |
| subscript D | 1-aminoanthraquinone |
| subscript C | salicylic acid |
| superscript $\phi$ | substrate |
| superscript $\sigma$ | solution |

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