

Diffusion of an Acid Dye in Nylon—in Relation to Sorption and Diffusion of a Gas in Glassy Polymers

EIZO SADA and HIDEHIRO KUMAZAWA, *Department of Chemical Engineering, Kyoto University, Kyoto, Japan*

Synopsis

The steady-state permeation rate data of an acid dye in a nylon film were analyzed via dual-mode sorption and mobility model based on gradients of concentration. The model used incorporates diffusion in a porelike region, unlike diffusion of a gas in a glassy polymer. There was some possibilities of the Nernst to the Langmuir mode diffusion jump, and the diffusivity was estimated.

The sorption isotherm for a gas in glassy polymers has been found to be satisfactorily described by the mathematical form (dual-mode sorption model)¹

$$q = C_D + C_H = k_D p + \frac{C'_H b p}{1 + b p} \quad (1)$$

where k_D , C'_H and b are adjustable parameters, which imply the Henry's law constant, the total sorption capacity of the polymer for penetrant gas in the Langmuir mode, and the affinity constant of the gas for the Langmuir site. Both the sorbed populations, which are termed Henry's law population and Langmuir population, respectively, can contribute to the total flux. This approach has been called dual-mode mobility model, and the diffusion flux can be written as

$$J = -D_D \frac{\partial C_D}{\partial x} - D_H \frac{\partial C_H}{\partial x} \quad (2)$$

where D_D and D_H are the respective diffusion coefficients of the two sorbed populations. In the dual-mode sorption and mobility model, it has also been postulated that there is always local equilibrium between C_D and C_H , viz.,

$$q = C_D + \frac{K C_D}{1 + \alpha C_D} \quad (3)$$

where $K = C'_H b / k_D$ and $\alpha = b / k_D$. Figure 1(a) gives a plausible sketch for diffusion based on the dual-mode sorption and mobility model.

Similarly, the isotherm for sorption of an acid dye in nylon can be described as either

$$q = k_D C + \frac{C'_H b C}{1 + b C} \quad (4)$$

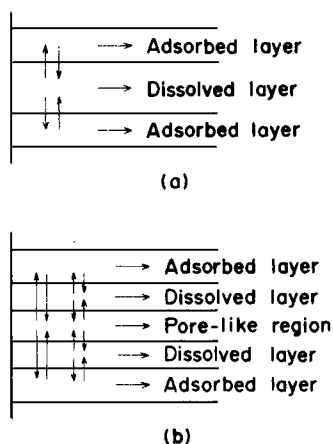


Fig. 1. Conceptual sketch for (a) diffusion of a gas in glassy polymers and (b) diffusion of an acid dye in nylon.

or

$$q = \frac{C'_H b C}{1 + b C} \quad (5)$$

The first term on the right-hand side of eq. (4) should be termed Nernst population, and the second term or the right-hand-side member of eq. (5) should be termed Langmuir population. It should be noted that there is not always the Nernst population for sorption of an acid dye in nylon, whereas the Henry's law population always exists for sorption of a gas in glassy polymer. Nevertheless, the sorbed acid dye still has some mobility, and the diffusion mechanism cannot be followed by simple Fick's law. If only the Langmuir population exists in the polymer phase, the adsorbed layer can be regarded as homogeneous phase. The process of diffusion in the polymer phase may be controlled by simple Fick's law with a concentration-independent diffusivity, that is, the solution-diffusion model may be valid. In fact, however, it has been well known that the diffusion coefficient of an acid dye in nylon is strongly dependent on the concentration of the dye in the polymer phase. Thus, the dual-mode sorption and mobility model, which has been originally derived in diffusion of a gas in glassy polymers, should be modified.

Then, the diffusion in the porelike region will be conveniently invoked when the dual-mode sorption and mobility model is applied to diffusion of an acid dye in nylon. In the earlier article,² the concept was termed parallel transport mechanism. Figure 1(b) depicts a conceptual sketch for the parallel transport mechanism. It is assumed that an acid dye diffuses in the porelike region and there are always local equilibria between C and C_D and between C_D (or C) and C_H , viz.,

$$C_D = k_D C \quad (6)$$

$$C_H = \frac{K C_D}{1 + \alpha C_D} \quad (7)$$

where C denotes the concentration of dye in the porelike region, C_D the concentration of dye in the dissolved layer (i.e., Nernst population), and C_H the concentration of dye in the adsorbed layer (i.e., Langmuir population). The total concentration of dye inside the polymer phase, C_T , which can be experimentally measured, comprises the concentrations of dye in the porelike region, the dissolved layer, and the adsorbed layer. When the sorption equilibrium is attained, the amount of dye in the porelike region is negligibly little compared to that of sorbed dye (less than 0.4% judging from the measured sorption equilibria^{3,4}). Thus, the total uptake of dye at the sorption equilibrium can be regarded as the total amount of sorbed dye, that is, $C_T = q = C_D + C_H$.

In the dual-mode sorption and mobility model modified above, the diffusive flux of an acid dye in nylon can be described as

$$J = -D_p \frac{\partial C}{\partial x} - D_D \frac{\partial C_D}{\partial x} - D_H \frac{\partial C_H}{\partial x} \quad (8)$$

Substitution of eqs. (6) and (7) into eq. (8) leads to

$$J = - \left[D_T + \frac{KD_H}{(1 + \alpha C_D)^2} \right] \frac{\partial C_D}{\partial x} \quad (9)$$

where $D_T = D_p/k_D + D_D$. After integrating eq. (9) over C_D from C_{Dh} to C_{Dl} with J constant under the steady state, one gets

$$Jl = D_T(C_{Dh} - C_{Dl}) + \frac{KD_H(C_{Dh} - C_{Dl})}{(1 + \alpha C_{Dh})(1 + \alpha C_{Dl})} \quad (10)$$

When C_D is replaced with $k_D C$, eq. (10) reduces to

$$Jl = k_D D_T (C_h - C_l) + \frac{C'_H b D_H (C_h - C_l)}{(1 + b C_h)(1 + b C_l)} \quad (11)$$

Therefore, the integral diffusion coefficient \bar{D}_C , which is defined by $Jl/(C_h - C_l)$, can be given as

$$\bar{D}_C = k_D D_T + \frac{C'_H b D_H}{(1 + b C_h)(1 + b C_l)} \quad (12)$$

The above equation predicts a linear relationship between \bar{D}_C and $b/(1 + b C_h)(1 + b C_l)$.

The corresponding expression for permeability P of a gas in a glassy polymer based on dual-mode sorption and mobility model can be derived as follows:

$$\bar{P} = k_D D_D + \frac{C'_H b D_H}{(1 + b p_h)(1 + b p_l)} \quad (13)$$

DISCUSSION

Typical examples of integral diffusion coefficients⁴ are illustrated as a function of the term $b/(1 + bC_h)(1 + bC_l)$ in Figure 2 on the basis of eq. (12). The plots at pH 2.3 do not give an essentially straight line, though a straight line can be approximately drawn through the data at pH 3.05.

On the other hand, the permeability data⁴ for carbon dioxide in polystyrene film sample and methane in polycarbonate film sample were plotted against $b/(1 + bp_h)(1 + bp_l)$ in Figures 3 and 4 on the basis of eq. (13), and essentially linear relationships between the two factors were obtained. From the slope and intercept of the straight line, the diffusion parameters in eq. (13) can be determined. The diffusion coefficients determined thus including the other systems were illustrated in the form of Arrhenius plots in Figure 5. The activation energies from such plots were given in Table I.

As the integral diffusion coefficients of an acid dye in the nylon film sample cannot be predicted by eq. (12), the process of diffusion will be reconsidered using Barrer's suggestion⁷ on diffusion of a gas in a glassy polymer.

If two sorbed penetrants exist in a polymer in the Henry's law and Langmuir modes designated D and H , respectively, then four kinds of unit diffusion step are possible, such as diffusive movements with the two respective modes ($D \rightarrow D$ and $H \rightarrow H$) and diffusive jumps between the modes ($D \rightarrow H$ and $H \rightarrow D$). The total diffusive flux can be given by summing the contribution of each kind of diffusive step, viz.,

$$J = J_{DD} + J_{HD} + J_{DH} + J_{HH} \quad (14)$$

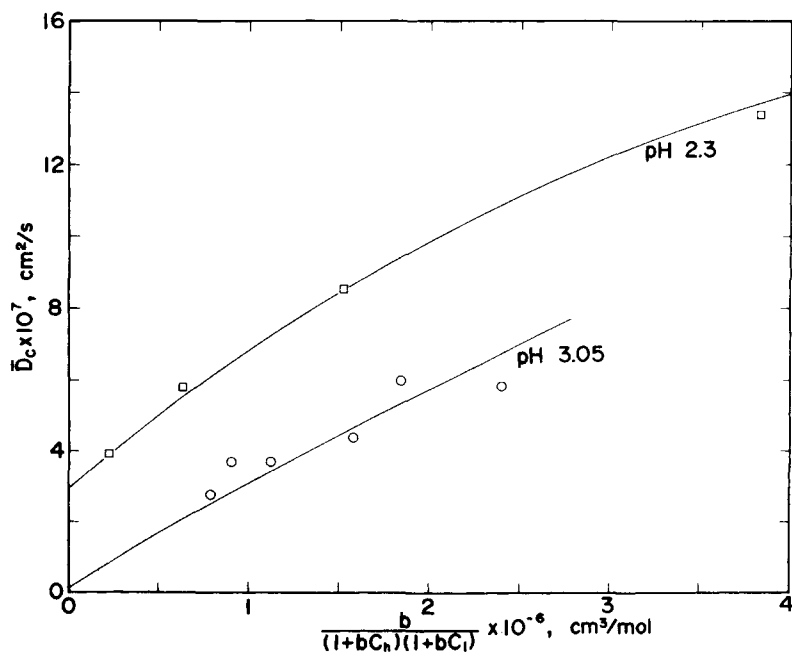


Fig. 2. Integral diffusion coefficients of C.I. Acid Blue 40 in nylon film; test of eqs. (12) and (18).

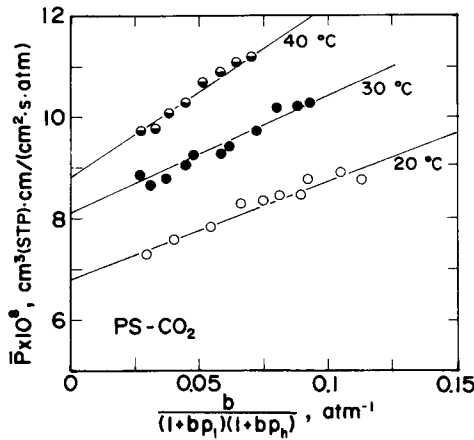


Fig. 3. Permeabilities of carbon dioxide in polystyrene film; test of eq. (13).

Recently, Barrer⁷ derived the flux expression for each kind of diffusive step. The total flux is written as

$$\begin{aligned}
 J = & -D_{DD} \frac{\partial C_D}{\partial x} - D_{HD} \frac{\partial C_H}{\partial x} - D_{DH} \\
 & \times \left[\frac{\partial C_D}{\partial x} \left(1 - \frac{C_H}{C'_H} \right) + \frac{C_D}{C'_H} \frac{\partial C_H}{\partial x} \right] - D_{HH} \frac{\partial C_H}{\partial x}
 \end{aligned} \tag{15}$$

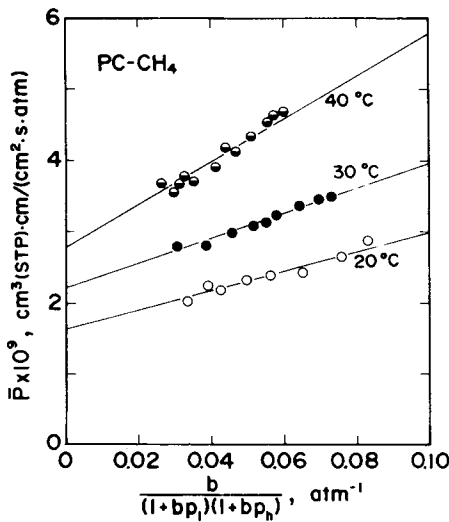


Fig. 4. Permeabilities of methane in polycarbonate film; test of eq. (13).

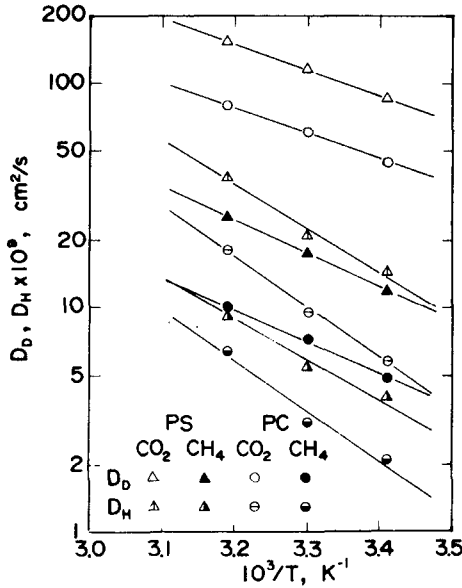


Fig. 5. Arrhenius plots of D_D and D_H .

The permeability \bar{P} , which is defined by $Jl/(p_h - p_l)$, is derived as follows:

$$\bar{P} = k_D D_{DD} + \frac{2k_D D_{DH}}{b(p_h - p_l)} \ln \frac{1 + bp_h}{1 + bp_l} + \frac{C'_H b(D_{HH} + D_{HD}) - k_D D_{DH}}{(1 + bp_h)(1 + bp_l)} \tag{16}$$

As D_{DH} declines to zero, eq. (16) reduces to

$$\bar{P} = k_D D_{DD} + \frac{C'_H b(D_{HH} + D_{HD})}{(1 + bp_h)(1 + bp_l)} \tag{17}$$

and agrees with the permeability expression of eq. (13).

TABLE I
Activation Energies of Diffusion for the Henry's Law and Langmuir Modes

System	E_D (kJ/mol), Henry's law mode	E_H (kJ/mol), Langmuir mode
PS-CO ₂	21.8	35.9
PS-CH ₄	28.5	35.1
PC-CO ₂	21.8	41.8
PS-CH ₄	27.0	42.7
PET-CO ₂ (Koros and Paul) ⁶	35.6	46.0

TABLE II
Sorption and Diffusion Parameters for C.I. Acid Blue 40 in Nylon Film

Item	pH	
	2.30	3.05
k_D	2.72	5.31
b (cm ³ /mol)	2.41×10^8	8.34×10^7
C'_H (mol/cm ³)	5.59×10^{-5}	5.71×10^{-5}
$k_D D_{DD}$ (cm ² /s)	2.95×10^{-7}	6.0×10^{-9}
$D_{HH} + D_{HD}$ (cm ² /s)	3.0×10^{-9}	4.0×10^{-9}
D_{DH} (cm ² /s)	3.0×10^{-9}	4.0×10^{-8}

The corresponding expression for the integral diffusion coefficient \bar{D}_C based on Barrer's concept can be derived as follows:

$$\bar{D}_C = k_D D_{DD} + \frac{2k_D D_{DH}}{b(C_h - C_l)} \ln \frac{1 + bC_h}{1 + bC_l} + \frac{C'_H b(D_{HH} + D_{HD}) - k_D D_{DH}}{(1 + bC_h)(1 + bC_l)} \quad (18)$$

The solid curves in Figure 2 represent the theoretical predictions calculated by eq. (18), using the measured sorption parameters in our previous work.⁴ The assumed values of diffusion parameters are presented in Table II along with the measured values of sorption parameters. The diffusion coefficient D_{DH} , which implies Nernst to Langmuir mode diffusive jump, is larger by an order of magnitude at pH 3.05.

CONCLUSION

The steady-state permeation rate data of an acid dye in a nylon film were analyzed via dual-mode sorption and the mobility model based on gradients of concentration by comparing with the permeability data of gases in glassy polymers. The integral diffusion coefficient expression was derived incorporating a contribution of intermode diffusion jumps. For the acid-dye transport there was an indication of diffusion jumps from the Nernst to the Langmuir mode but not for gas diffusion in glassy polymers.

APPENDIX: NOMENCLATURE

- b Langmuir affinity parameter
- C concentration of dye in porelike region or in outer solution
- C_D concentration of Nernst or Henry's law population
- C_H concentration of Langmuir population
- C'_H Langmuir capacity constant
- C_T total concentration of dye inside the polymer phase
- D diffusion coefficient in polymer phase
- \bar{D}_C integral diffusion coefficient
- $D_T = D_p/k_D + D_D$
- E activation energy for diffusion
- J diffusive flux

K	$= C'_H b / k_D$
k_D	Nernst or Henry's law constant
l	thickness of polymer film
\bar{P}	permeability
p	pressure of penetrant gas
q	total sorbed concentration
T	temperature
x	distance coordinate

Greek symbol

α	$= b / k_D$
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Subscripts

D	Nernst or Henry's law mode
DD	within Nernst or Henry's law mode
DH	from Nernst or Henry's law mode to Langmuir mode
H	Langmuir mode
HD	from Langmuir mode to Nernst or Henry's law mode
HH	within Langmuir mode
h	upstream of permeation cell
l	downstream of permeation cell
p	in porelike region

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