

Diffusion of Toluene Sulfonic Acid in Nylon Film

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Synopsis

The permeation of *p*-toluene sulfonic acid through nylon 66 film has been studied at different concentrations of sulfonic acid. The ordinary diffusion coefficient in the membrane was found to increase with increasing concentration in nylon, moderately at low concentration but very rapidly when approaching the Langmuir saturation concentration.

INTRODUCTION

Several studies can be found in the literature concerning permeation through polymer films. This subject is of special pharmaceutical interest, e.g., for establishing sustained release delivery of drugs, and for choosing suitable polymeric packaging material. In the case of nylon film, the sorption of many substances show a specific behavior.¹⁻⁶ Both Langmuir and Freundlich sorption isotherms have been found to fit the experimental data, but some substances also show ideal solution behavior in the sense that Henry's law is followed.^{7,8} A combination of concentration-dependent sorption and Henry's law behavior sometimes gives the best fit. Naturally the permeation behavior depends on the sorption characteristics, and theories based on dual sorption mode have been developed and used to estimate diffusion coefficients.⁹⁻¹¹ Experimentally it is often difficult, however, to differentiate between these models. In the specific system to be discussed here, anions could, for instance, interact with protonated amine end groups in the nylon matrix, and in this way to some extent get immobilized for diffusion.

In this work the permeation characteristics of *p*-toluene sulfonic acid in nylon 66 film have been investigated through chemical experiments where the concentration in the external solutions have been monitored. The results will be discussed assuming a Langmuir adsorption isotherm to be applicable. It is clear from this investigation that other techniques such as direct spectroscopic and dynamic studies in the film matrix itself would be necessary to delineate the molecular cause of the Langmuir behavior.

THEORY

In an earlier investigation¹² the partitioning of *p*-toluene sulfonic acid to nylon 66 film from a buffer solution was found to follow a Langmuir adsorption isotherm in a certain concentration interval. No significant difference was found between the amount of sulfonic acid sorbed per unit volume nylon for films of different thicknesses, and so the sorption was

assumed to be a volume effect, with a difference in concentration at the surface and in the bulk of the film that is negligible for calculation of partitioning ratio.

The relationship between concentration in membrane phase and in aqueous phase according to this theory is given by

$$y = y_m c / (c + k') \quad (1)$$

where y is the concentration of sulfonic acid in the nylon phase (expressed as M), y_m the corresponding maximum concentration possible, c the concentration in aqueous phase, and k' a constant. The flow through the membrane is governed by Fick's first law

$$J = -D \cdot A \cdot (\text{grad } y) \quad (2)$$

where J is the total flow. Seen from the receptor solution with concentration c_1 and volume V_1

$$J = V_1 (dc_1/dt) \quad (3)$$

After a sufficiently long time there will be a constant value of grad y throughout the membrane given by

$$\text{grad } y = \frac{y_2 - y_1}{l} = k_d \cdot \frac{c_2 - c_1}{l} \quad (4)$$

where y_1 and y_2 are the concentrations at the surfaces of the film in contact with the receptor resp donor solutions. Here it is assumed that equilibrium is established between the solutions and the membrane phase at the two phase boundaries, the distribution coefficient k_d according to (1) being given by

$$k_d = y_i / c_i = y_m / (c_i + k') \quad (i = 1, 2) \quad (5)$$

Due to the Langmuir sorption effect the distribution coefficient is not a constant, but varies with concentration in the aqueous phase. Figure 1 shows this variation of k_d with concentration. The values of y_m and k' were determined from the intercept and slope, respectively, of the straight line obtained when $1/y$ was plotted vs. $1/c$ at different pH values.¹² The good linearity of these plots supports the plausibility of the Langmuir approach. The values of y_m and k' were inserted into (5), and the dotted lines are according to this. This means that k_d has different values at the two phase boundaries, and these values also vary with time. The difference between these two values of k_d depends upon the concentration interval in accordance with the Langmuir adsorption isotherm.

Combining (2), (3), (4), and (5) gives

$$\frac{dc_1}{dt} = D \cdot \frac{A y_m}{V_1 l} \left(\frac{c_2}{c_2 + k'} - \frac{c_1}{c_1 + k'} \right) \quad (6)$$

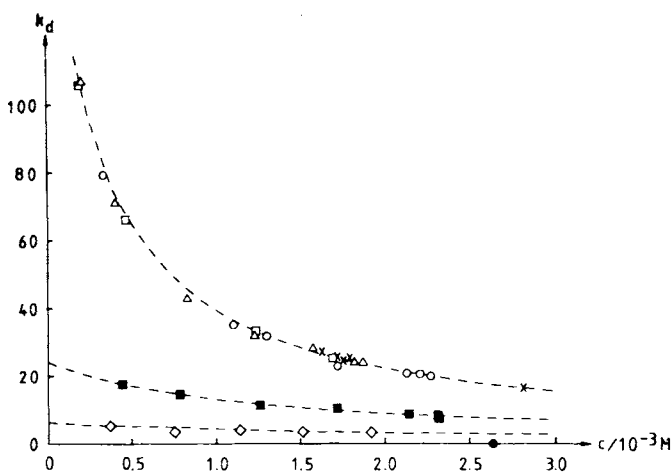


Fig. 1. Partition coefficient for *p*-toluene sulfonic acid to nylon 66 film vs. concentration in aqueous phase: (×) pH 1.83; (□) pH 2.33; (○) pH 2.82; (△) pH 3.75; (■) pH 5.94; (◇) pH 7.13; (●) pH 10.74.

This equation has been used to determine D from the permeation experiment primary data of c_1 as a function of time. c_2 is taken to be some starting concentration minus c_1 and an empirical time dependent term due to the Langmuir adsorption.

EXPERIMENTAL

Chemicals

The chemicals used were of analytical grade. Granular nylon 66 was purchased from BDH Chemicals Ltd. The water used was freshly redistilled.

Methods

Nylon films were made by the same method as earlier.^{13,14} A solution of nylon 66 in formic acid was sprayed onto a rotating glass cylinder. The film thickness was determined from the absorbance of β -rays. For the permeation experiments the film was clamped between two lucite blocks in which channels had been cut. The two solutions were circulated in these channels by an external pump, and the concentration was measured continuously by a spectrophotometer.¹³

The diffusion coefficient was evaluated from eq. (6) utilizing a digital computer and a nonlinear least square curve fitting method. The time was arbitrarily set to zero when a couple of hours had passed since the actual start of the experiment (individual zero time trials for the different experiments).

RESULTS AND DISCUSSION

In Figure 2 is shown an example of a permeation experiment and the corresponding theoretical curve for c_1 as a function of t . The values of diffusion coefficients calculated from eq. (6) in this way for different pH

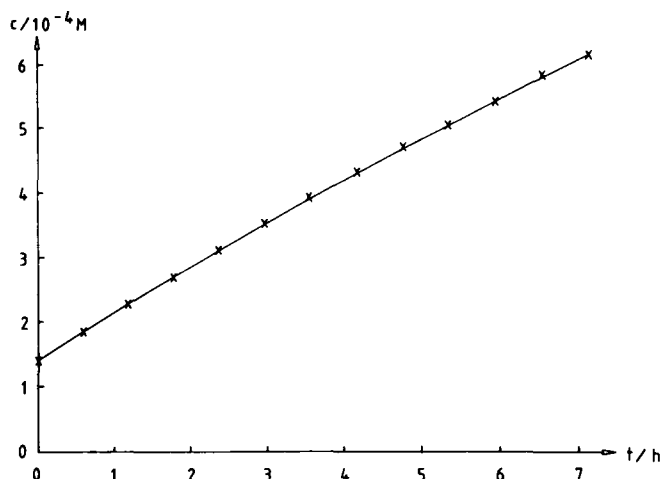


Fig. 2. Typical diffusion experiment for *p*-toluene sulfonic acid through nylon film: (×) experimental values, drawn line: theoretical curve calculated from Eq. (6).

values at varying initial concentrations in the aqueous phase are given in Figure 3. The diffusion coefficient is obviously dependent on concentration in the aqueous phase, with the most drastic rise in D at low concentrations. There also seems to be a pH dependence. The dashed line is drawn to satisfy the points of pH values 2.9 and 3.4, for which the partitioning behavior to nylon is identical, and for which also similar values of diffusion coefficients seem to apply. The plotted values of diffusion coefficients are mean values, integrated between the concentrations at the two sides of the nylon film during the calculation. This introduces an uncertainty in D , the values being the more accurate the smaller is concentration gradient, especially in the region of strong concentration dependence.

In Figure 4(a) the diffusion coefficient is plotted vs. mean concentration in nylon phase. Mean concentration is here defined as the mean of the four concentrations at the film surfaces at the time set to zero and at the time of the end of the experiment. Obviously the concentration profile gets rather

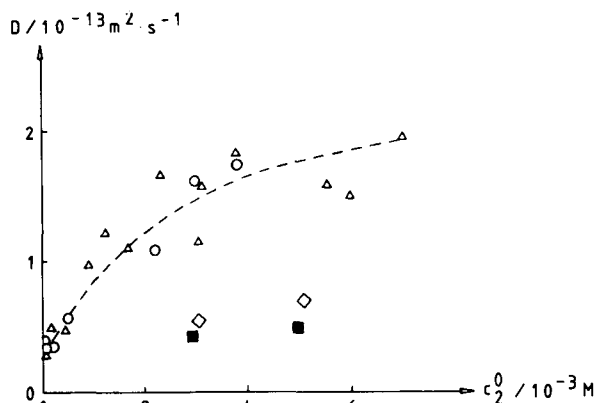


Fig. 3. Diffusion coefficient for *p*-toluene sulfonic acid in nylon film vs. initial concentration in aqueous phase: (○) pH 2.9; (△) pH 3.4; (■) pH 6.0; (◇) pH 7.2.

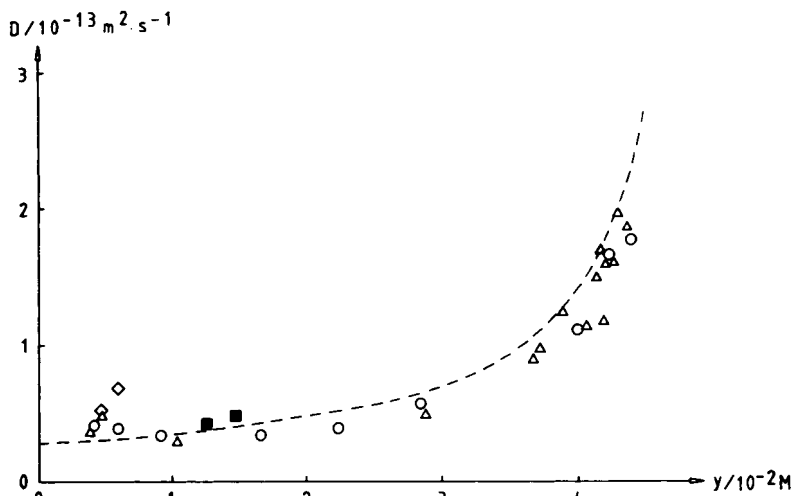


Fig. 4(a). Diffusion coefficient for *p*-toluene sulfonic acid through nylon film vs. mean concentration in nylon phase. Symbols have the same meaning as in Figure 3. The line is drawn according to (7).

different from that corresponding to concentrations in the aqueous phase. The most direct way to understand this is to think of the concentration scale in the aqueous phase as being transferred into the concentration scale in nylon phase through the nonlinear Langmuir equilibrium relationship (see Fig. 1 and ref. 12).

The shape of the D vs. y curve is the same as found by Datyner et al. for diffusion of dye into polyamide 6 films.¹⁵ This type of concentration profile might be due to immobilization of solute in the polymer.¹⁶ The acid anion shows strong interaction with the protonated amine end groups of the nylon. This is borne out experimentally since the maximum amount of sulfonic acid sorbed to nylon at low pH values is approximately equal to the amount of amine end groups obtained by titration of a nylon sample dissolved in a mixture of phenol and methanol with methanolic hydrochloric acid.^{13,17} A line is drawn in the figure according to the relation

$$D(y) = D(0)/(1 - y/y_m) \quad (7)$$

which has been suggested to be valid for diffusion in a film with Langmuir type distribution.¹⁸ In Figure 4(b), D is plotted vs. y/y_m . Here the pH dependence has almost completely disappeared. At high pH values, such as pH 7, the flux through the film is very low, and the uncertainty in D values high, and this might explain why these points deviate somewhat. *p*-Toluene sulfonic acid is a very strong acid, which is completely ionized throughout the entire pH scale studied ($pK_a = -1.34$ ¹⁹), and so the pH dependence that exists for sorption and permeation related to aqueous concentrations are thought to be due to ionization of the carboxyl and amino end groups in nylon. For this it seems difficult to provide reliable data due to the complex surrounding (high concentration of nylon chains) in which the ionization takes place.

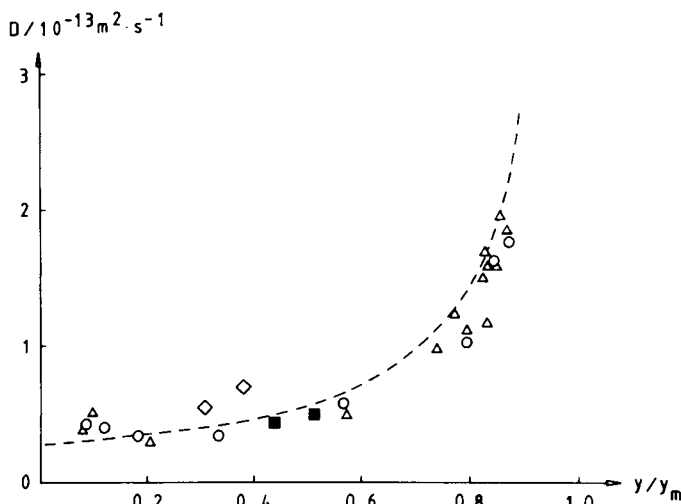


Fig. 4(b). Diffusion coefficient for *p*-toluene sulfonic acid through nylon film vs. normalized concentration in nylon phase. Symbols have the same meaning as in Figure 3. The line is drawn according to (7).

The type of concentration dependence profile observed [Figs. 4(a) and 4(b)] can be anticipated from a thermodynamic discussion of the driving force for diffusion in the membrane when a Langmuir type distribution applies. The following arguments will show this.

For a binary system the diffusion coefficient is given by

$$D = (c/f) (\partial \mu / \partial c)_{P,T} \quad (8)$$

where c = solute concentration and f = frictional coefficient. For the free solution (α -phase) the chemical potential is given by

$$\mu_{i\alpha} = \mu_{i\alpha}^0 + RT \ln a_{i\alpha} \quad (9a)$$

and for the membrane (β -phase)

$$\mu_{i\beta} = \mu_{i\beta}^0 + RT \ln a_{i\beta} \quad (9b)$$

For the dilute solutions studied in this work, $a_{i\alpha}$ could be approximated by $c_{i\alpha}$. At phase equilibrium

$$\mu_{i\alpha} = \mu_{i\beta} \quad (10)$$

and for the thermodynamic part of (8) one has

$$c_{i\beta} \left(\frac{\partial \mu_{i\beta}}{\partial c_{i\beta}} \right)_{P,T} = c_{i\beta} \frac{\partial \mu_{i\alpha}}{\partial c_{i\beta}} = c_{i\beta} RT \frac{1}{c_{i\alpha}} \frac{dc_{i\alpha}}{dc_{i\beta}} \quad (11)$$

where $c_{i\beta} = y$ (concentration in membrane phase). But from (5)

$$\frac{dc_{i\beta}}{dc_{i\alpha}} = \frac{y_m(c_{i\alpha} + k') - y_m c_{i\alpha}}{(c_{i\alpha} + k')^2} = \frac{k' y_m}{(c_{i\alpha} + k')^2} \quad (12)$$

Combining (11) and (12) gives

$$c_{i\beta} \left(\frac{\partial \mu_{i\beta}}{\partial c_{i\beta}} \right)_{P,T} = RT \left(1 + \frac{c_{i\alpha}}{k'} \right) \quad (13)$$

But again from (5)

$$c_{i\alpha} = \frac{k' c_{i\beta}}{y_m - c_{i\beta}} \quad (14)$$

Substituting into (13) then gives

$$c_{i\beta} \left(\frac{\partial \mu_{i\beta}}{\partial c_{i\beta}} \right)_{P,T} = RT \left(1 + \frac{c_{i\beta}}{y_m - c_{i\beta}} \right) \quad (15)$$

From (8) and (15) it is obvious that $D \rightarrow \infty$ when $c_{i\beta} \rightarrow y_m$, since the frictional coefficient f always stays finite.

The detailed relationship between D and y (i.e., $c_{i\beta}$) depends also on the concentration dependence of f . Equation (15) in combination with (8) allows an estimation of the concentration dependence of f to be performed. Such data have been collected in Table I. Comparison of the numerical values of f so obtained with values of f from similar systems in (a) dilute solutions ($f = 6.9 \times 10^{12} \text{ kg mol}^{-1} \text{ s}^{-1}$ for sucrose in aqueous solution, estimated from $f = RT/D^{20}$) and (b) concentrated background of macromolecules ($f = 2.9 \times 10^{13} \text{ kg mol}^{-1} \text{ s}^{-1}$ for fluorescein in aqueous solution also containing 20% w/w dextran T-10²¹) shows that the frictional coefficient is very high in this polymer film. Furthermore, the frictional coefficient seems to be almost independent of pH for a given concentration y in the nylon (membrane) phase. This is an important observation since y_m in the film varies markedly over the pH range from 2.9 to 7.2. For a given pH, using eq. (15), the frictional coefficient is found to increase as y increases. However, in the vicinity of $y = y_m$ this increase is sensitive to variations in the values of the parameters in eq. (15). These findings could be indications of a transport mechanism that depends on the number of "free sites" available, this number being decreased as the concentration in the membrane phase increases.

The results and discussion above deal with the phenomenological aspects of the transport properties in the film phase when a Langmuir sorption process applies. In an earlier publication¹² it was indicated how such systems could be utilized for regulated flow applications. However, the underlying molecular mechanism cannot be elucidated with the experimental methods used so far. To further the molecular understanding, direct spectroscopic and dynamic studies might be helpful.

TABLE I
Frictional Coefficient of *p*-Toluene Sulfonic Acid in Nylon Film at Different Concentration in the Film and Different pH Values of Aqueous Solutions.

$\gamma/10^{-2}M$	pH	$f/10^{16} \text{ kg mol}^{-1} \text{ s}^{-1}$
0.426	2.9	6.45
0.603	2.9	7.34
0.926	2.9	9.04
1.68	2.9	11.1
2.86	2.9	10.2
4.01	2.9	11.2
4.26	2.9	9.99
4.41	2.9	11.6
0.327	3.4	7.89
0.403	3.4	7.02
0.481	3.4	5.44
1.03	3.4	10.8
1.81	3.4	7.68
2.88	3.4	12.1
3.74	3.4	10.1
3.81	3.4	7.99
4.01	3.4	11.1
4.10	3.4	8.13
4.19	3.4	13.0
4.22	3.4	9.81
4.38	3.4	10.6
4.45	3.4	12.4
4.49	3.4	13.8
4.56	3.4	12.6
1.27	6.0	10.4
1.48	6.0	10.5
0.487	7.2	6.62
0.612	7.2	5.83

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