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Regulatory aspects of permeation through ordinary and modified nylon films

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Summary

Permeation through ordinary and modified nylon 66 films was studied in order to devise means by which the permeation rate could be regulated. Three types of film matrix were used: unmodified nylon film, nylon film where the amino end groups were blocked to about 75%, and nylon film with blocked amino groups (75%) where also a quaternary ammonium compound (cetyl trimethyl ammonium bromide, CTAB) was added to the film. The permeation rate of *p*-toluene sulfonate and *β*-naphthalene sulfonate through these films were studied with special emphasis on the pH dependence. Especially at high pH and in agreement with the higher partitioning to the film for naphthalene sulfonate, this salt gave a higher permeation rate than did toluene sulfonate. The permeation rate through unmodified nylon film varied with pH. The blocking of the amino groups decreased the pH dependence and addition of CTAB increased the level of the permeation rate within the whole pH range studied. Very low or high permeation rates could be achieved by means of different pHs in the water solutions on either side of the film.

Introduction

In order to enhance the rate of permeation through films and membranes, various additives have been used both in the membrane (film) phase and in the surrounding water phase, for synthetic (Fürst et al., 1980; Cianetti and Danesi, 1983; Strzelbicki et al., 1984) as well as biological (Irwin et al., 1969; Gibaldi and Grundhofer, 1973; Walkling et al., 1978a and b) systems. These additives could, for example, act by disturbing the structure of a synthetic film by a leaking additive (Lippold et al., 1980; Lippold and Förster, 1981), by complex formation with the permeating species (Tsukube, 1983a and b), or by ion pair formation with the permeating species (Walkling et al., 1978a and b; Ågren et al., 1974; Duffey et al., 1978; Mothes et al., 1983). In this paper some results with reference to the permeation through nylon 66 films with and without additive will be presented where *p*-toluene sulfonic acid and *β*-naphthalene sulfonic acid have been used as test substances. The main aim has been to explore various regulatory mechanisms.

Nylon 66, being a polyamide, contains free amino and carboxylic end groups. In order to try to further delineate the role of the end groups as well as the effect of interacting additives as mediators of facilitated transport, three types of films

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have been used. The rate of transport has been studied as a function of pH, concentration of the mediator, and, to some extent, also the buffer composition.

Materials and Methods

Nylon 66 was obtained from BDH Chemicals (Poole, U.K.). β-Naphthalene sulphonic acid was obtained from Eastman-Kodak (Rochester, NY, USA). Other chemicals used were of analytical quality.

Three types of film were used in the studies: (a) ordinary nylon film; (b) a film where the amino end groups had been blocked to about 75% of their initial amount; and (c) a film with a quaternary ammonium compound (cetyl trimethyl ammonium bromide, CTAB) incorporated and blocked amino groups according to (b). The amounts of free amino end groups in nylon were determined by titration of dissolved samples of the film. Blocking of the amino groups was achieved by addition of caproic acid chloride as in a previous work (Sjökvist et al., 1978). After blocking, the amount of free amino groups was found to be about 1.3×10^{-2} M, which is approximately 25% of their initial amount. Film preparation, measurement of film thickness, and permeation studies have been described elsewhere (Sjökvist et al., 1978).

In the studies of the permeation characteristics of sulfonic acids through films containing CTAB, the same film was used in a series of permeation tests. Between the runs, the film was carefully washed with a 0.1 M solution of $NaClO_4$ to remove any trace of sulfonic acid and to retain CTAB in the membrane phase. Different pieces of the same film were analyzed for the ammonium compound, one sample before the permeation experiments and the other after, according to a method (Gustavii and Schill, 1966) modified for determination in nylon film. The samples were dissolved in formic acid and pH adjusted to 6.6 with NaOH and phosphate buffer. The ammonium compound was extracted into methylene chloride as a complex with picrate and the concentration measured spectrophotometrically.

The permeability coefficient, P, was calculated according to:

$$\frac{dc_1}{dt} = -\frac{P \cdot A}{V \cdot \ell}(c_1 - c_2) \qquad (1)$$

where c_1 and c_2 are the concentrations in the aqueous acceptor and donor solutions, respectively, ℓ is the film thickness, A the film area, and V the volume of the aqueous acceptor solution. The time of the calculation was set at zero some hours after the actual start of the experiment. Eqn. 1 was used in a simulation program, DARE P, connected to a system for function minimization, MINUIT (Wait and Clarke, 1977; James and Roos, 1976). The computation was performed on a NORD-10 computer system.

Results and Discussion

The possibility of regulating the transport rate was examined by variation of the following parameters: (1) varying concentrations of additive in the film; (2) study of different permeants through the film matrix; (3) modification of the film matrix; and (4) use of the pH-dependent permeability to achieve very low or high permeation rate by means of different pH values in the water solutions on either side of the film.

Varying additive concentrations

A number of runs were performed in order to determine the effect of the concentration of quaternary ammonium compound in the film. Naphthalene sulfonic acid and toluene sulfonic acid were to permeate nylon film with blocked amino end groups and containing different amounts of CTAB at pH 8.1. The resulting permeability coefficient is seen from Fig. 1 to increase with increasing concentration of CTAB. The effect of CTAB on the permeation rate was supposed to be due to ionic interaction between sulfonate ions and quaternary ammonium compound, which increases the distribution of sulfonate ions to the film. Formation of ion pairs between quaternary ammonium compounds and naphthalene sulfonate has earlier been found to be

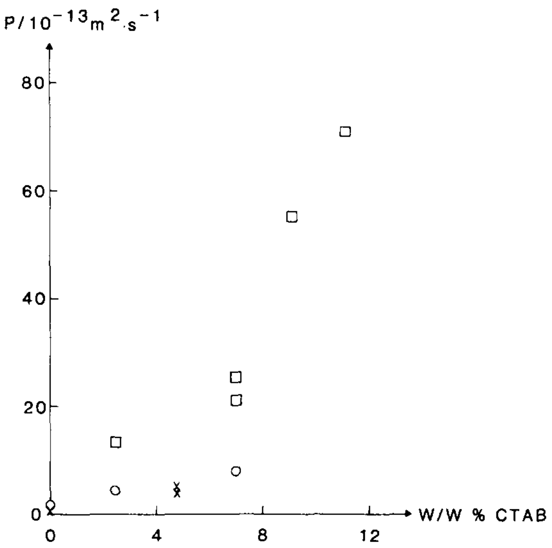

Fig. 1. Permeability coefficient versus concentration of CTAB in blocked nylon film. □, naphthalene sulfonic acid at an initial concentration of donor solution of 2×10^{-4} M; ○, naphthalene sulfonic acid 3×10^{-3} M; ×, toluene sulfonic acid 3×10^{-3} M. pH of aqueous phase = 8.1.

a possible explanation of their distribution between different aqueous–organic systems (Gröningsson and Weimers, 1975; Hackzell and Schill, 1981).

Comparison of permeants

The permeability coefficients for toluene sulfonic acid and naphthalene sulfonic acid in nylon film with blocked amino groups are presented in Fig. 2. The permeability coefficient for naphthalene sulfonic acid is higher than that for toluene sulfonic acid in this film, especially at high pH values. Naphthalene sulfonic acid is a larger molecule and is expected to have a lower diffusion coefficient due to the higher film resistance. This phenomenon was seen in earlier works on unmodified film (Wirbrant and Sundelöf, 1985a and b). On the other hand, the partitioning to the film is higher for naphthalene sulfonic acid, as was seen in the permeation experiments directly from the equilibrium distribution between the film and the aqueous phase, and this probably explains the higher permeation rate. The permeation rates of the solutes differed in a similar way for films containing CTAB.

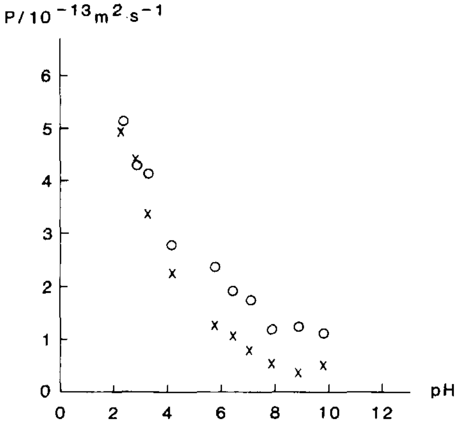

Fig. 2. Permeability coefficients in nylon film with blocked amino end groups versus pH. ×, toluene sulfonic acid; ○, naphthalene sulfonic acid; both acids with an initial concentration of the donor solution of 3×10^{-3} M.

Modification of film matrix

A number of runs were performed with toluene sulfonic acid as the solute at an initial concentration of the donor solution of 3×10^{-3} M and at varying pH values (Fig. 3A). This is a very strong acid ($pK_a = -1.34$) (Dinius and Choppin, 1962) which is ionized throughout the entire interval studied. The permeation coefficient for this salt through unmodified nylon film shows an increase with a factor of about 17 between pH 10 and pH 3. This increase might be explained by interaction between the anions and the protonated amino groups of nylon, in combination with a counteracting effect from ionized carboxyl end groups, which decreases the rate at high pH. The pH dependence is in agreement with the results presented for nylon 212, with reference to ionized substances (Seki and Okahata, 1984).

For a film where the amino end groups have been blocked, the pH dependence of P is reduced (Fig. 3A), and this also supports the theory of interaction between the amino groups and sulfonate ions. The pH dependence seen for this film might be due to the amino groups that are still present to 25% of their initial amount. The ratio between the permeability coefficient for an unmodified film and a film with blocked amino groups (○ in Fig. 3B) is about 3.5 at pH < 8. The ratio between the number of protonated amino

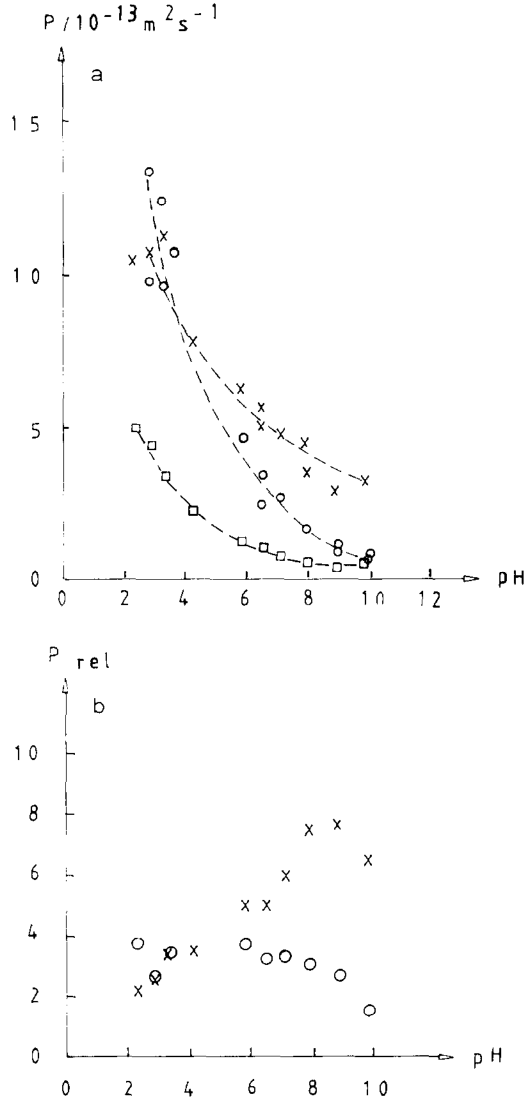

Fig. 3. A: permeability coefficient for toluene sulfonic acid versus pH. Initial concentration of the donor solution: 3×10^{-3} M. ○, Nylon 66 film; □, nylon film with blocked amino end groups; ×, nylon film with blocked amino end groups containing 5 w/w% CTAB. The lines are drawn freehand to illustrate the data. B: relative permeability of toluene sulfonic acid versus pH. ○, (permeability through nylon film)/(permeability through nylon film with blocked amino groups); ×, (permeability through nylon film with blocked amino groups containing CTAB)/(permeability through nylon film with blocked amino groups).

end groups in these films remains unchanged throughout the pH interval, and a constant factor is to be expected if the protonated amino groups are of the greatest importance for the permeability process. The factor 3.5, also, is of the same magnitude as the ratio between the number of amino groups in the films. At high pH the amino end groups are not protonated, and if their number is the only difference between the film, the relative permeability ought to approach one.

When 5 w/w% CTAB is added to a film with blocked amino groups, the pH dependence of the permeability coefficient is of the same magnitude as in blocked films without CTAB, but the level increases throughout the interval (Fig. 3A). This is in agreement with an interaction between CTAB and sulfonate ions, which ought to be of the same magnitude within the entire pH interval. The ratio between the permeability coefficient in this film and in a film with blocked amino groups (× in Fig. 3B) increases with pH. At low pH values the quaternary ammonium compound has only a small influence on the permeability, if the main increase in rate is due to the protonated amino groups. At increasing pH values, first the carboxyl end groups get ionized, and at still higher values the amino groups will be neutralized. Both these facts decrease the permeability rate and the influence of CTAB gets more pronounced.

The present results, as shown in Fig. 3A, indicate certain regulation possibilities. On the one hand it seems feasible to reduce the pH dependence of the permeation considerably by blocking the amino end groups. On the other hand, the level of the permeation rate can be increased by adding a substance capable of interacting with the permeating species.

The buffer system used in the aqueous solutions also appeared to have some influence on the permeation rate. For the data shown in Fig. 3A, phosphate buffers were used at pH 1.8–8 and borax buffers at pH 8.8–10 (Britton, 1956; Bates, 1964), all solutions having an ionic strength of 0.1. Experiments with hydrogen chloride buffers at pH 1–2.2 (Handbook of Chemistry and Physics, 1974–75), also adjusted to an ionic strength of 0.1, gave a clear discontinuity in the curve, the *P* values being about one-third of the corresponding values with phosphate buffer.

Since a concentration dependence of the distribution coefficient for the permeant is expected

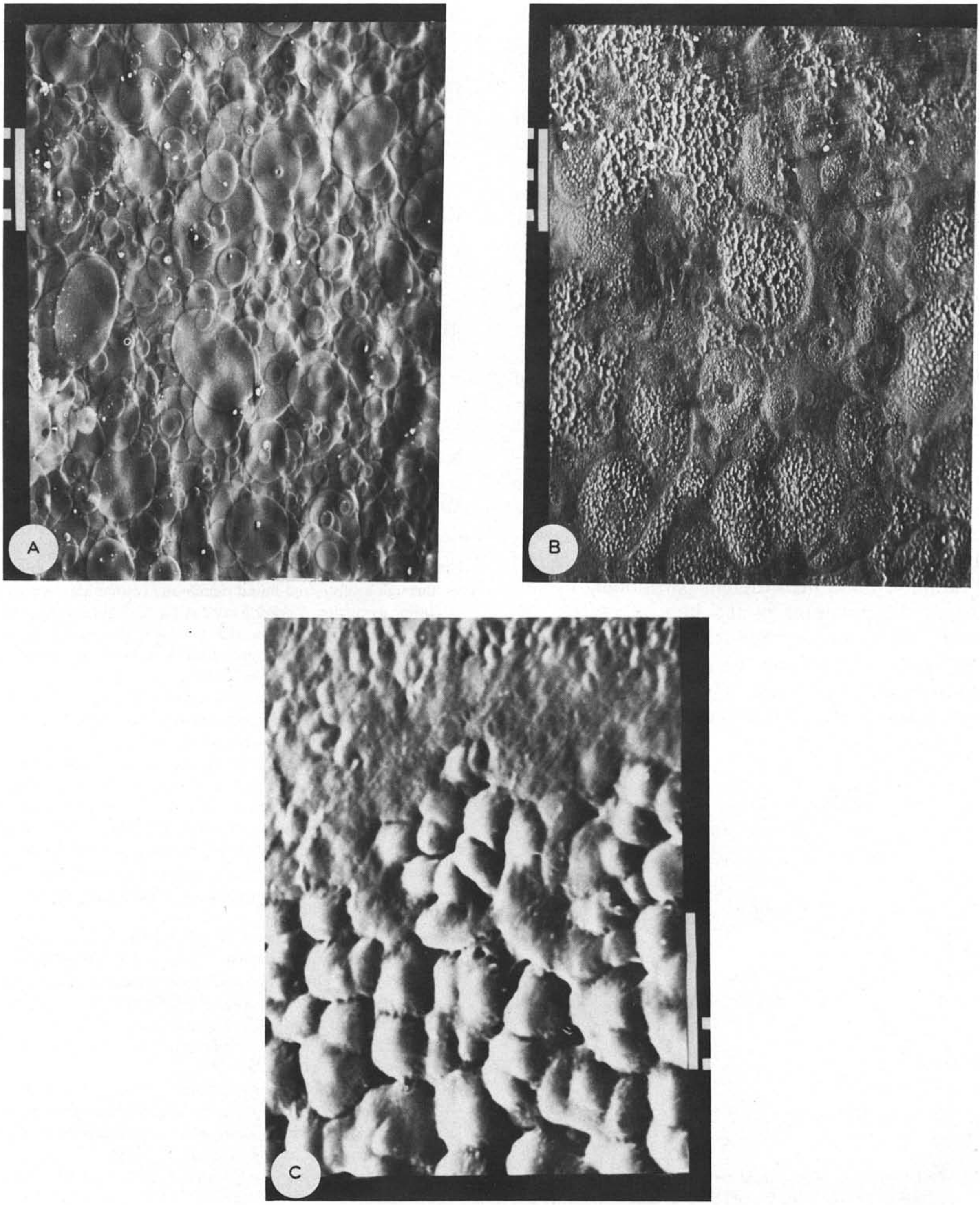

Fig. 4. Electronic microscopy photograph of nylon film. A: unmodified nylon film; magnification 200 ×. B: nylon film with blocked amino end groups containing CTAB; magnification 200 ×. C: same film as B; magnification 3000 ×.

even in these systems (Wirbrant and Sundelöf, 1983), the pH dependence also reflects different concentrations in the membrane phase at varying pH values. Another factor which might influence the permeation characteristics is a difference in structure between unmodified nylon films and films containing CTAB. Electron microscopy photographs of these films, Fig. 4A–C, do show a clear difference in structure, but this point has not been pursued further.

Regulation by pH dependence

Another way of regulating the rate of permeation by the pH dependence is shown in Fig. 5. High pH in the donor solution and low pH in the acceptor solution gives almost no permeation whatsoever. The opposite condition gives a high permeation rate, where the acceptor solution attains a higher concentration than does the donor solution, and the transport continues against the concentration gradient (cf. Barker and Hadgraft, 1981; Babcock et al., 1980). This is a logical result, bearing in mind the different partitioning behavior of the permeant in the film at various pH values (Wirbrant and Sundelöf, 1985b), considering at a low pH value the permeant has a high partitioning to the film, whereas at a high pH value there is much less partitioning.

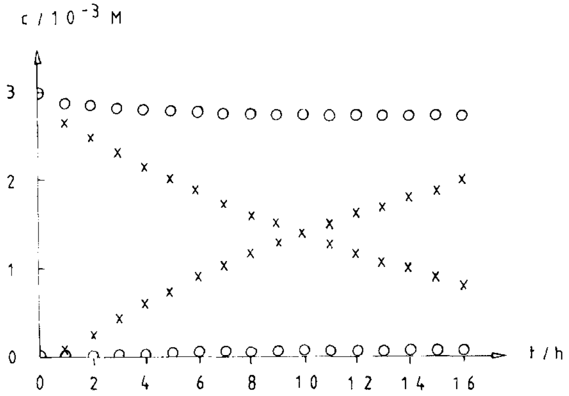

Fig. 5. Permeation of naphthalene sulfonic acid with initial concentration 3×10^{-3} M. ○, pH 9.75 in donor solution, pH 2.32 in acceptor solution; ×, pH 2.31 in donor solution, pH 9.90 in acceptor solution.

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