

# Solute-Membrane Interactions in Hyperfiltration

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## Synopsis

The performances of several composite membranes (PEC-1000, Teijin, HR-95, HR-98) and one asymmetric membrane (Solrox SC-200) in hyperfiltration are compared at 25°C using different aqueous feed solutions (0.1M and 0.5M NaCl, 0.5M 1,3- and 1,4-dioxan, 0.1M benzyl alcohol and 2-methoxybenzyl alcohol, 1,2- and 1,4-butandiol, and Triton feed solution). The effects of solute dissociation, polarization, and hydrogen bonding ability on solute permeability are discussed; steric effects are also being considered. Strong solute-membrane interactions are exhibited in hyperfiltration by systems with distinct hydrogen bonding capabilities of the solute with functional sites of the membrane matrix. Knowledge of solute-membrane interactions can be useful for elaborating separation and transport mechanisms.

## INTRODUCTION

In the past, transport processes in hyperfiltration have been described by many authors applying various transport theories and assuming different models characterizing the mechanism of solute separation.<sup>1-6</sup> Distinct experimental phenomena can be explained by use of the corresponding theories and transport models. However, due to the large number of feed solutions, the various hyperfiltration conditions, and the continuously newly prepared membranes, arguments still persist about the validity and applicability of the different theories and models such as solution-diffusion and pore-flow models. For this reason, a study of some additional solution-membrane systems might be appropriate.

In this paper, we will mainly discuss interactions between solutes and membranes in different solute-membrane systems on the basis of recently published work<sup>5,6</sup> and additional experimental results. This might be useful for further elaboration of transport mechanisms of permeants and, in addition, for the preparation of distinct membranes exhibiting high performance. Moreover, the experimental results might contribute to a clarification of the range of applicability of synthetic membranes for separation processes.

## EXPERIMENTAL

Using different aqueous feed solutions (0.1M and 0.5M NaCl, 0.5M 1,3- and 1,4-dioxan, 0.1M benzyl alcohol and 2-methoxybenzyl alcohol, 0.1M Triton, and 0.1M 1,2- and 1,4-butandiol), the hyperfiltration performances of four different composite flat sheet membranes (PEC-1000 manufactured by Toray

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Industries; Teijin-1091 manufactured by Teijin Co. with an active layer made from PBIL; HR-95 and HR-98 manufactured by Film-Tech Co. with an active layer made from an aromatic polyamide), and one asymmetric membrane (Solrox SC-200 manufactured by Sumitomo Chemical Industries and made from a polyacrylnitril copolymer) were determined. The chemical composition of the membranes used, the repeating units of the basic membrane polymers, and the manufacturer of the corresponding membranes are listed in Table I. In addition, the constitutional formulas of the organic solutes used are summarized in Table II. The applied experimental procedure, described in detail elsewhere,<sup>7</sup> was modified in so far as 80 ppm NaHSO<sub>3</sub> were added to each feed solution to remove O<sub>2</sub> and thus to protect the PEC-1000 membranes from oxidation. In addition, the surface tension  $\gamma$  and the kinematic viscosity  $\nu$  of aqueous Triton solutions were measured as functions of the concentration  $c'_s$  ( $0.0001M \leq c'_s \leq 0.3M$  Triton).

The NaCl concentrations were determined by AAS and the concentrations of organic solutes by use of a differential refractometer (manufactured by Waters). The experimental setup and procedure were described in detail elsewhere.<sup>1,8</sup>

The surface tension of aqueous Triton solutions as a function of the Triton concentration was measured by use of a du Nouy surface tensiometer and the viscosity of the corresponding solutions by use of an Ubbelohde viscosimeter.

TABLE I  
Membrane Manufacturers, Membrane Compositions, and Repeating Units of Polymers Used to Prepare the Corresponding Active Layer or Membrane

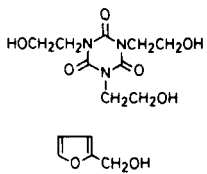
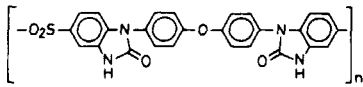
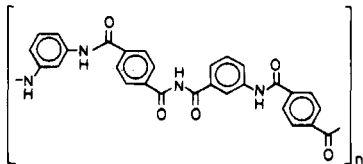
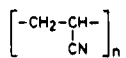



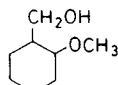
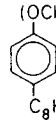
Membrane	Chemical composition	Repeating unit	Manufacturer
PEC-1000	Copolymer of 1,3,5-tris (2-hydroxyethyl) isocyanurate and  Furfuryl alcohol		Toray Industries
Teijin-1091	Polybenzimidazole (PBIL)		Teijin Company
HR-95 HR-98	Aromatic polyamide		Film-Tech. Company
SOLROX SC-200	Polyacrylnitril with small amount of additives		Sumitomo Chemical Industries

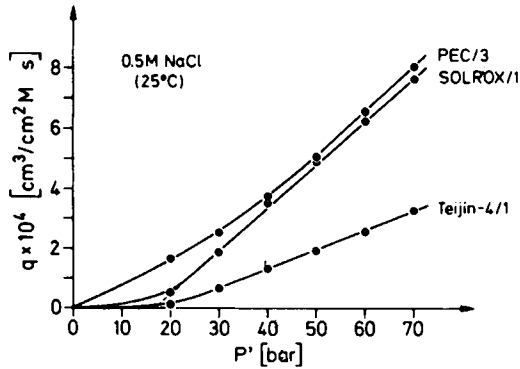
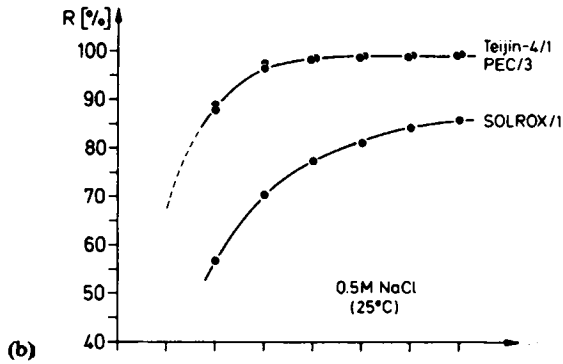
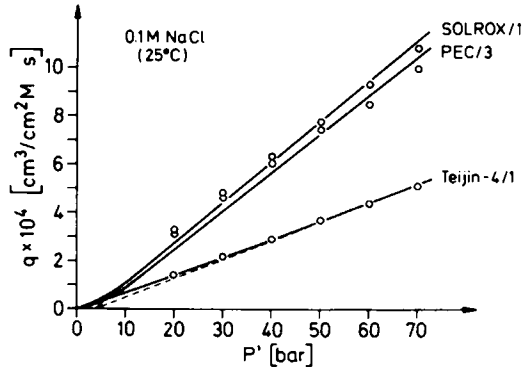
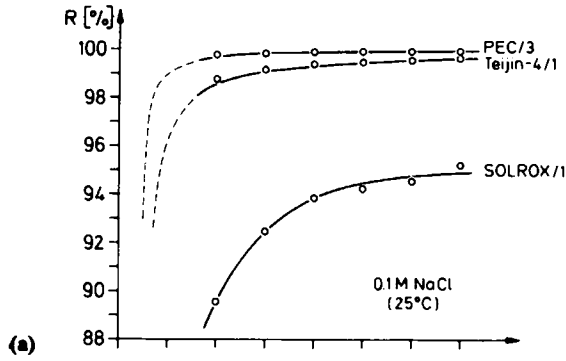
TABLE II  
Chemical Constitutional Formulas of Solutes Used

Compound	Formula
1,4-Dioxan	
1,3-Dioxan	
Benzylalkohol	
2-Methoxybenzylalkohol	
1,2-Butandiol	$C_2H_5CHOHCH_2OH$
1,4-Butandiol	$CH_2OHCH_2CH_2CH_2OH$
Triton	 $(OCH_2CH_2)_{9-10}OH$

## RESULTS AND DISCUSSION

First, the rejection  $R$  and the volume flux  $q$  as functions of the feed pressure  $P'$ , measured with 0.1M and 0.5M NaCl brine solutions at 25°C, are graphically shown in Figures 1(a) and 1(b).

As can be seen from Figure 1(a), the PEC-1000 membrane exhibits the highest rejection towards 0.1M NaCl in comparison to all other membranes used. Furthermore, it possesses a comparably large production rate (about 850 L/m<sup>2</sup>d. at 70 bar). Rejection and volume flux decreases with decreasing feed pressure. The decay of  $R$  and  $q$  with increasing feed concentration (0.1–0.5M NaCl) is due to the raising osmotic pressure. It should be noted that the volume flux decay with increasing NaCl brine concentration is much less for the Solrox membrane than for the Teijin and PEC-1000 membranes due to the comparably low NaCl rejection of the Solrox membrane in the presence of a 0.5M NaCl brine solution. This low rejection results in a lower osmotic pressure difference across the membrane. At a brine concentration of 0.5M NaCl, the volume flux of the Solrox membrane even exceeds the fluxes of the two other membranes. In comparison to the volume flux decay with increasing NaCl brine concentration,  $q$  decreases much less with increasing feed concentration when the feed concentration of organic solutes is raised to a concentration of 0.5 mol/L since the osmotic pressure of a 0.5M NaCl



Figs. 1(a) and 1(b). Solute rejection  $R$  and volume flux  $q$  as functions of the feed pressure  $P'$ , using PEC-1000, Teijin 1091, SolroX SC-200 membranes with 0.1M (a) and 0.5M (b) NaCl feed solution at 25°C. The numbers after the solidus denote different membrane samples punched out of a larger membrane sheet.

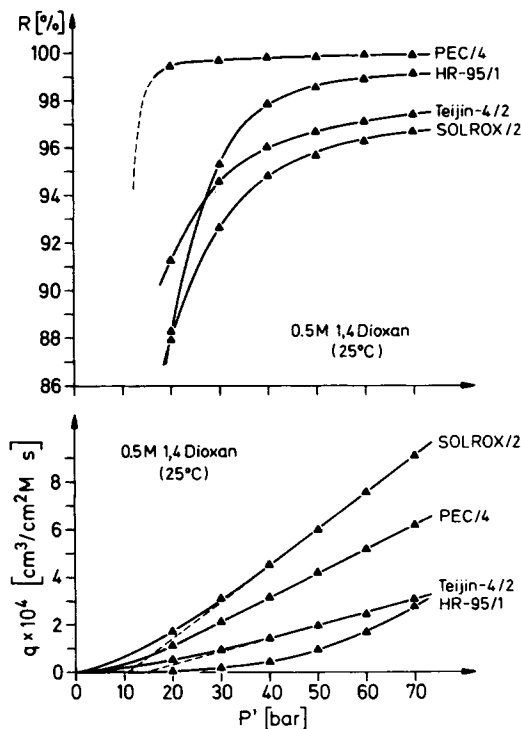


Fig. 2(a). Solute rejection  $R$  and volume flux  $q$  as functions of the feed pressure  $P'$ , using PEC-1000, HR-98, Teijin, and Solrox membranes with 0.5M 1,4-dioxan feed solution at 25°C. The numbers after the solidus denote different membrane samples punched out of a larger membrane sheet.

solution is about twice as large as that of a 0.5M dioxan feed solution, for instance.

### Effect of a Dipole Moment of Solute on Rejection

As can be seen from Figures 2(a) and 2(b), a change of the polarity of a solute (nonpolar 1,4-dioxan to polar 1,3-dioxan) results in quite different variations of  $R$  for different membranes. In case of the solrox membrane,  $R$  and  $q$  decrease when 1,4-dioxan is exchanged for 1,3-dioxan whereas the opposite effect is observed with the HR-95 membrane where the rejection for 1,3-dioxan is larger than that for 1,4-dioxan. Nearly no effect of the polarity on the solute rejection is observed with the Teijin and PEC-1000 membranes where the values of  $R$  and  $q$  are nearly the same for 1,4-dioxan and 1,3-dioxan.

### Effect of Hydrogen Bonding Ability of Solutes on Rejection

Alcohol separation by hyperfiltration has already been studied<sup>9,10</sup> several times, but mostly with the same membrane. In contrast to those investigations, the hyperfiltration performance of different kinds of membranes in the presence of different organic solutes is considered in this paper. In addition to dioxan, benzyl alcohol, 1,2- and 1,4-butandiol were selected to further clarify the effect of possible hydrogen bond formation on the permeation of organic

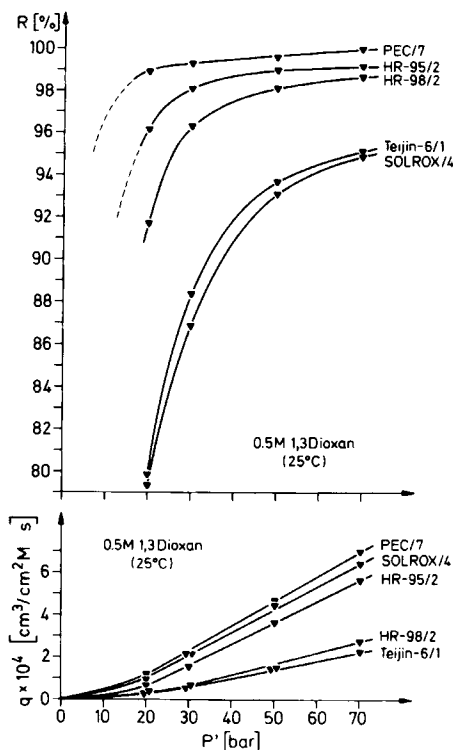


Fig. 2(b). Solute rejection  $R$  and volume flux  $q$  as functions of the feed pressure  $P'$ , using PEC-1000, HR-95, HR-98, Teijin, and Solrox membranes with 0.5M 1,3-dioxan feed solution at 25°C. The numbers after the solidus denote different membrane samples punched out of a larger membrane sheet.

solutes through membranes. Since an internal hydrogen bond between the two OH—groups of 1,2-butandiol might be formed,<sup>11</sup> the OH—groups of this substance might not form intermolecular hydrogen bonds with the corresponding sorption sites of a membrane. In comparison to 1,2- and 1,4-butandiol, benzyl alcohol possesses only one OH—group whereas its geometric molecular size is similar to that of dioxan.

It is obvious from Figure 3(a) that the values of  $R$  and  $q$  obtained with PEC-1000, HR-98 and Solrox membranes and benzyl alcohol feed solutions are similar to those obtained with 1,4- and 1,3-dioxan feed solutions. The hyperfiltration performance of the Teijin membrane in the presence of a benzyl alcohol feed solution, however, differs drastically from its performance in the presence of 1,4- and 1,3-dioxan feed solutions. The Teijin membrane exhibits, for instance, an essentially higher rejection for dioxan ( $R_{\infty} = 98.82\%$ ) than for benzyl alcohol ( $R_{\infty} = 68.14\%$ ). In addition, the hydrodynamic permeability of the membrane decreases from  $l_p = 5.21 \times 10^{-6} \text{ cm}^3/\text{cm}^2 \text{ M s atm}$  to  $l_p = 4.8 \times 10^{-7} \text{ cm}^3/\text{cm}^2 \text{ M s atm}$  ( $\text{cm}^2 \text{ M} = \text{cm}^2 \text{ wet membrane}$ ) for dioxan and benzyl alcohol, respectively. In agreement with the higher rejection of dioxan compared to that of benzyl alcohol, the osmotic permeability and thus the value  $l_{\pi}/l_p$  are smaller for dioxan than for benzyl alcohol ( $l_{\pi} = 5.45 \times 10^{-6} \text{ cm}^3/\text{cm}^2 \text{ M s atm}$ ,  $l_{\pi}/l_p = 1.045$  for dioxan and  $l_{\pi} = 6.36 \times 10^{-5} \text{ cm}^3/\text{cm}^2 \text{ M s}$

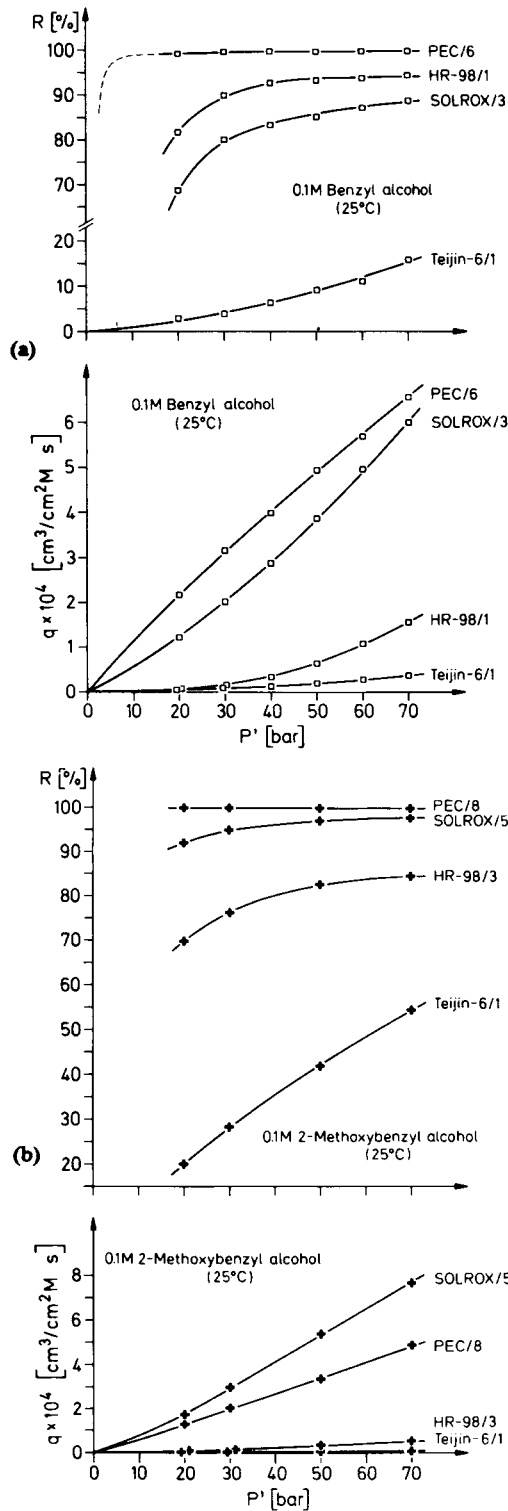


Fig. 3(a-d). Solute rejection  $R$  and volume flux  $q$  as functions of the feed pressure  $P'$ , using PEC-1000, HR-98, Teijin, and Solrox membranes with 0.1M feed solutions of benzyl alcohol (a), 2-methoxybenzyl alcohol (b), 1,2-butandiol (c), and 1,4-butandiol (d) at 25°C. The numbers after the solidus denote different membrane samples punched out of a larger membrane sheet.

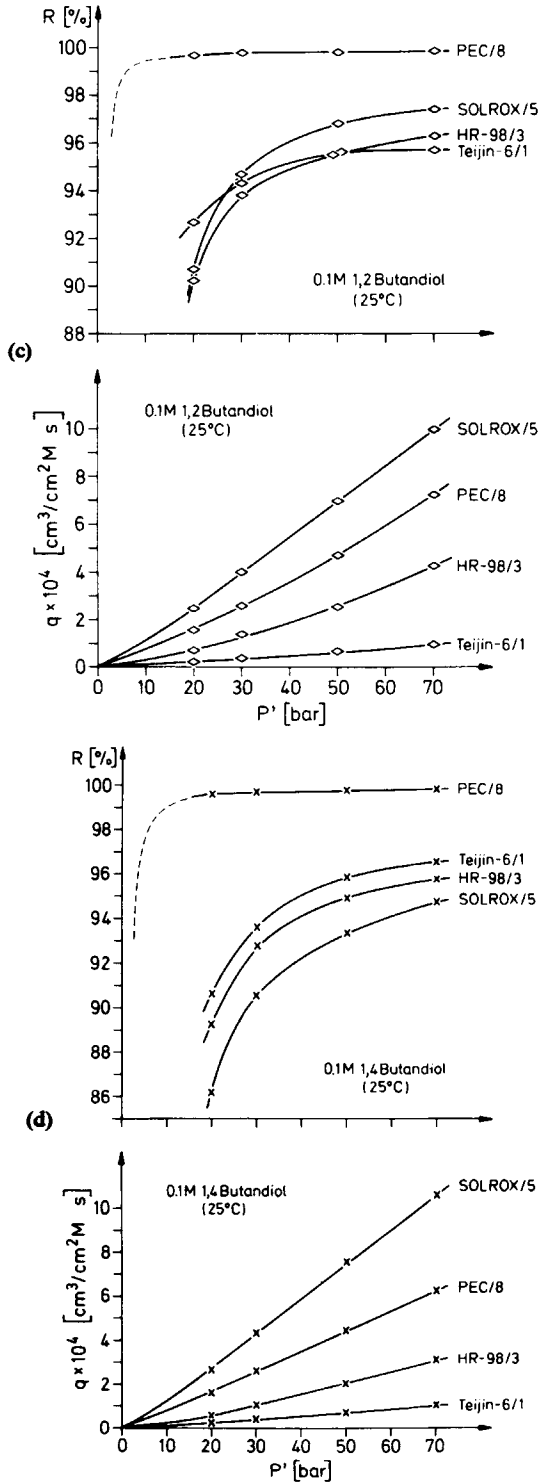


Fig. 3. (Continued from the previous page.)



atm,  $l_{\pi}/l_p = 133$  for benzyl alcohol). The substantial flux decline of the Teijin membrane in the presence of benzyl alcohol is, in addition to compaction effects, essentially due to a strong interaction between the membrane and the solute. This is obvious from the reversible recovery of the permeability. The permeability returns to its original value when benzyl alcohol feed solution is again exchanged for pure water or another inorganic feed solution.

As can be seen from Figure 3(b), 2-methoxybenzyl alcohol behaves similar to benzyl alcohol, although it is still better rejected than benzyl alcohol by the Solrox and Teijin membrane. In contrast, 2-methoxybenzyl alcohol is less rejected than benzyl alcohol by the HR-98 membrane. These experimental findings indicate again that very specific interactions between solute and membrane govern the solute permeability.

Furthermore, it is obvious from Figures 3(a)–(d), that the Solrox, HR-98, and Teijin membrane exhibit higher rejections for 1,2- and 1,4-butandiol than for benzyl alcohol, although the butandiol molecules are smaller than the benzyl alcohol molecule.

The experimental findings might indicate that hydrogen bond formation is not contributory to interactions of butandiol with the membranes as there exists no difference in the rejections of 1,2- and 1,4-butandiol. In addition, considering that a higher solute rejection correlates with a smaller solute partition coefficient, this conclusion is also consistent with the observation that butandiol is better rejected by the Solrox, HR-98, and Teijin membrane than benzyl alcohol, although butandiol is more likely made for hydrogen bond formation due to its two OH—groups compared to benzyl alcohol with its single OH—group.

On the other hand, H-bond formation seems to contribute to the interaction of benzyl and 2-methoxybenzyl alcohol with the membranes used, especially the Teijin membrane. This might be due to the effect of the aromatic benzyl ring on the OH—group. In contrast to the aliphatic chain of butandiol, the aromatic benzyl ring attracts the electron of the OH—group more strongly, resulting in a more positively charged OH—group, which then interacts more strongly with the membrane sites. Comparing, in addition, the constitutional formulas of the membrane materials (Table I), it is obvious that only the Teijin membrane possesses strong negative charges (SO<sub>2</sub>—groups). Thus, the OH—group of benzyl alcohol might easily form a hydrogen bond with those SO<sub>2</sub>—groups whereas no such interaction sites are present in the other membranes.

### Effect of Geometric Molecular Size on Solute Rejection

In order to further demonstrate the effect of the molecular size on the rejection of the respective solute, Triton instead of benzyl alcohol was used in additional experiments. In comparison to the molecular size of benzyl alcohol, the molecular size of Triton is enlarged by the hydrophobic side chain which is attached to the benzyl ring containing the OH—group. Figure 4 summarizes the experimental findings obtained for  $R$  and  $q$  as functions of the feed pressure  $P'$ . Comparing the experimental results, obtained with Triton (Fig. 4), with those, obtained with benzyl alcohol [Fig. 3(a)], shows clearly that an enlargement of the molecular size beyond a limiting value leads to a

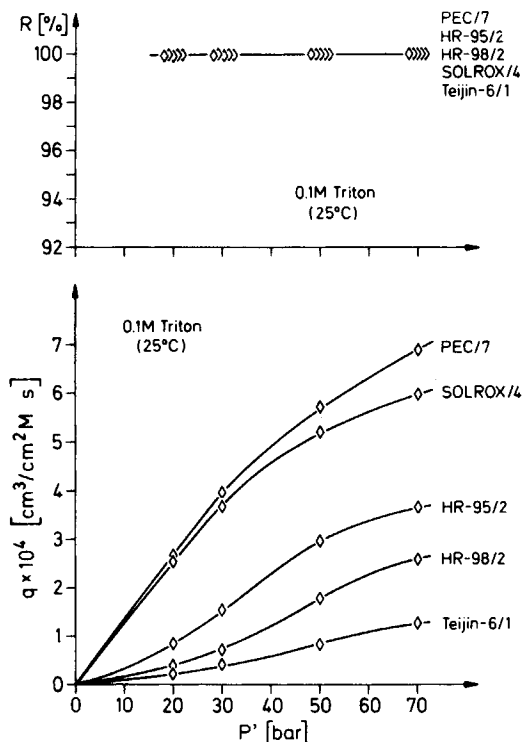


Fig. 4. Triton rejection  $R$  and volume flux  $q$  as functions of the feed pressure  $P'$ , using PEC-1000, HR-95, HR-98, Teijin, and Solrox membranes with 0.1M Triton feed solution at 25°C. The numbers after the solidus denote different membrane samples punched out of a larger membrane sheet.

situation where the molecular size determines the solute permeability. As a consequence of its molecular size, Triton is nearly completely rejected at all feed pressures between 20 and 70 bar ( $R \approx 100\%$ ). Thus, the Triton concentration within the membrane remains nearly zero, and no interaction of Triton with the membrane matrix can occur. Therefore, the volume flux of most membranes is much less reduced in the presence of Triton than in the presence of benzyl alcohol, for instance.

Moreover, Figure 5 exhibits  $R$  and  $q$  as functions of the Triton feed concentration. The volume fluxes of the HR-95, HR-98, and Teijin membrane decrease by 10–30% whereas those of the PEC-1000 and Solrox membrane decrease only by 2–3% when the Triton feed concentration is increased from  $2.9 \times 10^{-4}M$  to  $4 \times 10^{-3}M$ . At Triton feed concentrations beyond  $4 \times 10^{-3}M$ , the volume fluxes of the HR-95, HR-98, and Teijin membrane still decrease, slowly approaching a flux value of about 50% of the original flux value at a Triton feed concentration of 0.28M. On the other hand, the volume fluxes of the PEC-1000 and Solrox membranes start to decrease drastically beyond a Triton feed concentration of  $4 \times 10^{-2}M$ , reaching a volume flux value of about 20% of their original values and that again at 0.28M Triton feed concentration. Regarding the rejection as a function of the Triton feed concentration, it should be noted that at very low Triton feed concentrations

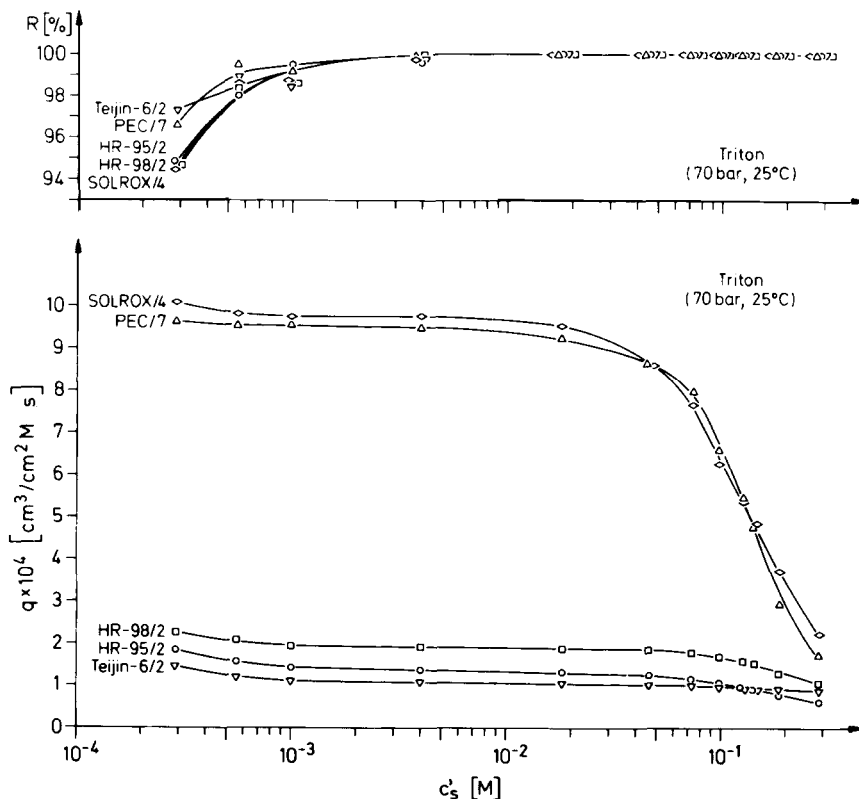


Fig. 5. Triton rejection  $R$  and volume flux  $q$  as functions of Triton feed concentration  $c'_s$ , using PEC-1000, HR-95, HR-98, Teijin, and Solrox membranes at  $P' = 70$  bar and  $25^\circ\text{C}$ . The numbers after the solidus denote different membrane samples punched out of a larger membrane sheet.

( $c'_s \leq 0.004M$ ) the rejection is smaller than 100% ( $R \approx 95\%$ ). At  $c'_s > 0.04M$ ,  $R$  approaches nearly 100% where the permeant concentration remains practically stable at about 10–20 ppm. The increase of  $R$  with increasing feed concentration might be due to so-called micelle formation as the rejection of larger aggregates of Triton molecules will still be higher than the rejection of the monomeric units.

In order to correlate the hyperfiltration performance of the membranes in the presence of Triton feed solutions with physicochemical properties of the solutions, the surface tension  $\gamma$  and the kinematic viscosity  $\nu$  of the solutions were measured as functions of the Triton concentration. The corresponding experimental results are graphically reproduced in Figure 6 where, in addition to  $\gamma$  and the reciprocal kinematic viscosity  $1/\nu$ , also the effective pressure ( $\Delta P - \Delta \Pi$ ) is plotted as a function of the Triton concentration  $c'_s$ . As is evident from this figure, the variations of ( $\Delta P - \Delta \Pi$ ) and  $\gamma$  with  $c'_s$  do not correspond with the variations of  $q$ . However, it is possible to correlate the variation of  $q$  with that of  $1/\nu$  at larger Triton feed concentrations at least for the PEC-1000 and Solrox membranes. It should be mentioned that the variation of  $R$  with  $c'_s$  at very low Triton concentrations is essentially a consequence of the variation of  $q$  with  $c'_s$ .

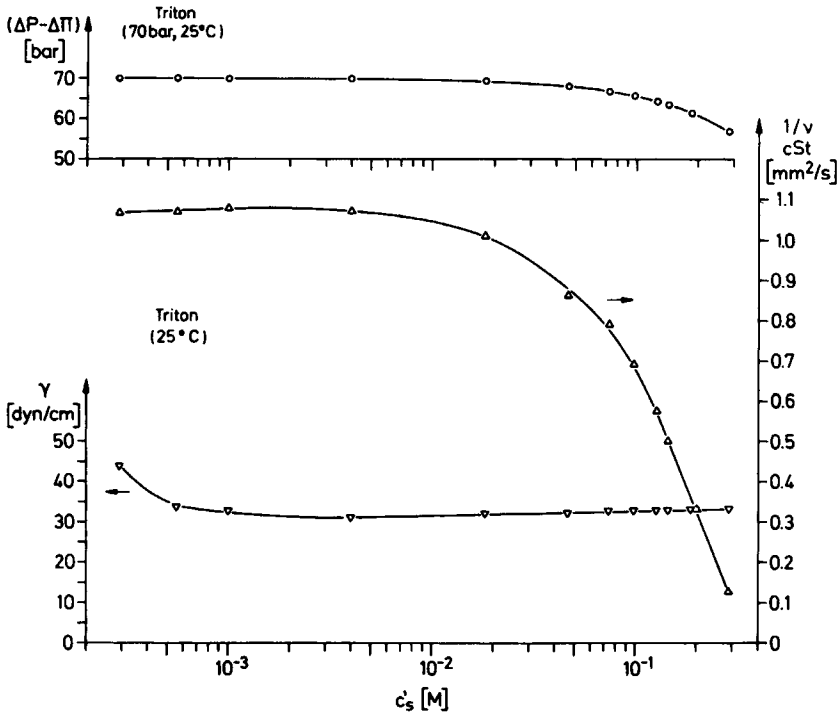


Fig. 6. Effective pressure difference at  $P' = 70$  bar,  $(\Delta P - \Delta \Pi)$ , surface tension  $\gamma$ , and reciprocal kinematic viscosity  $1/\nu$ , of Triton solutions as functions of the Triton concentration  $c'_s$  at 25°C.

## CONCLUSIONS

Figure 7 summarizes the experimental results obtained with a Teijin membrane and all the different feed solutions. First, the experimental results, reported in this paper, completely support the idea that solute transport across fine porous and dense membranes is essentially governed by the solubility of the solute within the membrane phase. In addition to membrane model-independent transport relationships (e.g., linear phenomenological relationships, Kedem-Spiegler relationship), the following two- and three-parametric membrane model-dependent relationships can thus be applied to analyze solute transport across such membranes: (1) solution-diffusion model; (2) fine-porous membrane model; (3) combined viscous-flow frictional model. Second, the hyperfiltration performance of different synthetic membranes in the presence of different aqueous organic feed solutions exhibits that very specific interactions between organic solutes and membranes generally govern the permeation of the solutes through the membranes. Therefore, it is nearly impossible to apply experiences obtained with a specific aqueous organic feed solution and a distinct membrane to another distinct membrane/feed solution system. This might be possible only if the chemical structure of the membranes under consideration is nearly the same at least to some extent (e.g., aliphatic polyamides, aromatic polyamides, and cellulose acetates).

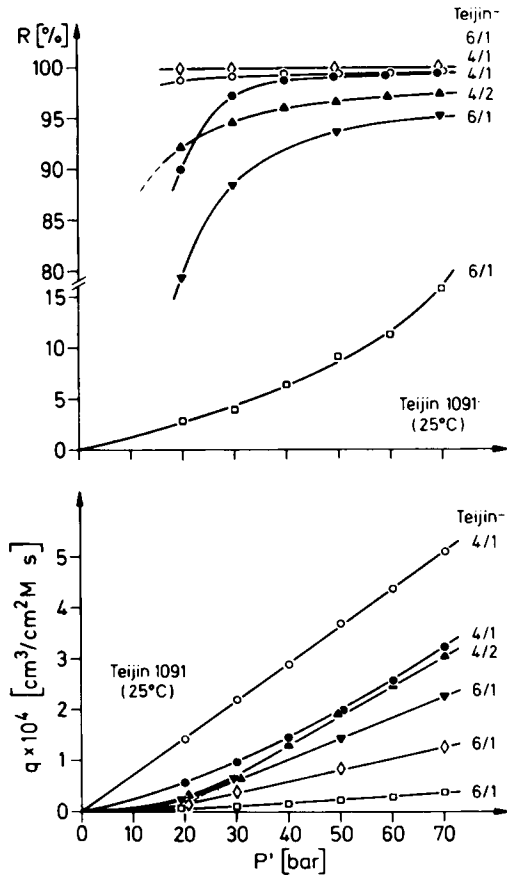


Fig. 7. Solute rejection  $R$  and volume flux  $q$  as functions of the feed pressure  $P'$ , using a Teijin membrane with different feed solutions at 25°C. The numbers after the solidus denote different membrane samples punched out of a larger membrane sheet: ( $\diamond$ ) 0.1M Triton; ( $\circ$ ) 0.1M NaCl; ( $\bullet$ ) 0.5M NaCl; ( $\blacktriangle$ ) 0.5M 1,4-dioxan; ( $\blacktriangledown$ ) 0.5M 1,3-dioxan; ( $\square$ ) 0.1M benzylalcohol.

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