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Reverse Osmosis Separation of Phenols in Aqueous Solutions Using Porous Cellulose Acetate Membranes

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Synopsis

Reverse osmosis separations of phenol (9.4 to 108 ppm), *p*-cresol (108 ppm), and *p*-chlorophenol (129 ppm) were studied using Loeb-Sourirajan-type porous cellulose acetate membranes, and single-solute aqueous feed solutions at 500 psig and the indicated solute concentrations. It was found that, by dissociating the solute by changing the pH of the feed solution, all the above phenols could be separated by reverse osmosis. Solute separation increased with increase in the degree of dissociation of the solute in the feed solution; and, by the appropriate choice of pore size on the membrane surface, separations of phenol approaching the degree of dissociation of phenol in the feed solution could be obtained under the operating conditions used. Similar experiments using aniline (93 ppm) as the solute showed that dissociation of solute molecules in the feed solution could be a technique generally applicable for the reverse osmosis separation of nonionic solutes in aqueous solution. The effects of operating pressure in the range 250 to 1500 psig and pore size on the membrane surface on the separation of un-ionized phenol and *p*-chlorophenol showed that, with respect to single-solute aqueous feed solutions of phenols, the component whose relative acidity was greater was preferentially sorbed at the cellulose acetate membrane–aqueous solution interface, and the solute concentration in the membrane-permeated product solution was a function of the extent and mobility of each of the sorbed species.

INTRODUCTION

The reverse osmosis separation of low concentrations (<100 ppm) of phenols in aqueous solutions is of practical interest from the point of view of water pollution control. Using Loeb-Sourirajan-type porous cellulose acetate membranes and aqueous feed solutions containing 70 to 80 ppm of phenol, Lonsdale et al.[1] reported negative separations (i.e., phenol enrichment in permeate) of 10% to 20% in the operating pressure range of 34 to 104 atm at 30°C; the negative separations increased with increase in operating pressure. Recent work[2] on the physicochemical criteria for the reverse osmosis separation of alcohols, phenols, and monocarboxylic acids showed that, with similar cellulose acetate membranes at 23–25°C and an operating pressure of 250 psig (17 atm), negligible or slightly negative separations were obtained, and the high acidity (proton-donating character-

istic) of the essentially undissociated phenol molecule was responsible for its low separations. This work[2] also showed that dissociation of the solute molecule favored its separation under reverse osmosis operating conditions because of the electrostatic repulsion of ions at the membrane–solution interface,[3,4] indicating the possibility of increasing the reverse osmosis separation of phenols by ionizing the solute molecules which can be brought about by increasing the pH of the feed solution. The success of this technique of separating phenols is illustrated in this paper, using phenol, *p*-cresol, and *p*-chlorophenol as solutes; the generality of the technique is also illustrated using aniline as the solute.

EXPERIMENTAL

Reverse Osmosis Experiments

Reagent-grade phenol (9.4 to 108 ppm), *p*-cresol (108 ppm), *p*-chlorophenol (129 ppm), and aniline (93 ppm) were used as solutes at the concentrations indicated. Sodium hydroxide or hydrochloric acid was used for adjusting the pH of the feed solutions. Laboratory-made Batch 316-type porous cellulose acetate membranes were used in the reverse osmosis experiments. The apparatus, experimental procedure, and membrane details have been reported.[2,5,6] As usual, the membranes were subjected to an initial temperature and pressure treatment prior to reverse osmosis experiments. Membranes preshrunk at different temperatures were used to give different levels of solute separation at a given set of operating conditions. The effective film area was 7.6 cm^2 in all cases. Most of the experiments were done at 500 psig, and some studies were also made in the operating pressure range of 250 to 1500 psig. The membranes used in the former experiments were initially subjected to a pure-water pressure of 600 psig for 1 to 2 hr, and those used in the latter studies were subjected to similar pressure treatment at 1700 psig. All experiments were carried out at laboratory temperature (23–25°C). Since the solute concentrations used were very small, the osmotic pressure and other effects[7] on membrane performance were essentially eliminated. All experiments in this work were of the short-run type, each lasting for about 2 hr.

In all experiments, the terms "product" and "product rate" refer to membrane-permeated solutions. In each experiment, the per cent solute separation, defined as

$$\left[\frac{\text{solute ppm in feed} - \text{solute ppm in product}}{\text{solute ppm in feed}}\right] \times 100,$$

the product rate [PR], and the pure-water permeation rate [PWP] in grams per hour per given area of film surface (7.6 cm^2) were determined at the specified operating pressure, feed concentration, and feed flow rate. The reported [PR] and [PWP] data are those corrected to 25°C using the

TABLE I
Film Specifications and Performance Data for
Aqueous Sodium Chloride Feed Solutions

Film no.	Operating, pressure, psig	Specifications: $A \times 10^6$, g mole/cm²·sec·atm	Specifications: $(D_{AM}/K\delta) \times 10^5$, cm/sec	Performance data[a]: Solute sepn., %	Performance data[a]: Product rate, gal/day·ft²
1	500	2.41	3.72	94.8	37.9
2	500	3.64	9.75	91.5	57.3
3	500	4.97	20.74	86.1	78.0
4	500	6.65	68.22	68.9	104.9
21	500	3.31	2.37	95.6	49.0
23	500	6.14	30.99	82.4	95.2
51	500	2.21	3.96	95.9	35.3
55	500	4.23	15.60	86.1	65.6
82	1500	2.17	13.16	94.0	106.9
84	1500	2.68	39.66	84.9	131.8
85	1500	3.58	142.8	68.1	177.4

[a] Feed concentration: 1500 ppm NaCl; $k = 57 \times 10^{-4}$ cm/sec.

relative viscosity and density of pure water. Table I gives data on the specifications of the membranes used, expressed in terms of pure-water permeability constant A and the solute transport parameter $D_{AM}/K\delta$ for sodium chloride; these data were obtained from the experimental [PWP], [PR], and solute separation data for the reference solution system sodium chloride–water.[8a] A feed flow rate of 400 cc/min was used in most experiments; at this feed rate, the mass transfer coefficient on the high-pressure side of the membrane was 57×10^{-4} cm/sec for the reference solution system 1500 ppm NaCl–H_2O.[8a] Table I also gives some data on membrane performance for the latter system.

Analysis

The analysis for sodium chloride in aqueous solutions was done using a conductivity bridge. A Beckman total carbon analyzer Model 915, described earlier,[2] was used to measure the concentrations of *p*-cresol and *p*-chlorophenol. The concentrations of undissociated and dissociated phenol, aniline, and, in some experiments, *p*-chlorophenol were measured by determining the ultraviolet absorption maxima characteristic for each chemical species; for this purpose, a Beckman Model D-1 double-beam recording ultraviolet spectrophotometer was used. Absorption spectra were scanned downward from 350 millimicrons (mμ) to find the exact wavelength for maximum absorption. Quartz cells of lengths 1 cm and 0.1 cm were used depending on solute concentration. Dilution of sample solution was avoided in order not to change the degree of dissociation of solute molecules.

RESULTS AND DISCUSSION

Dissociation of Phenol in Aqueous Solutions and Their pH

Calculation of Degree of Dissociation. The dissociation of phenol may be represented by the equation

$$C_6H_5OH \rightleftharpoons C_6H_5O^- + H^+.$$

The dissociation constant K_a of phenol is the equilibrium constant for the above reaction:

$$\therefore K_a = \frac{[C_6H_5O^-][H^+]}{[C_6H_5OH]}. \tag{1}$$

Since the ionization constant of water K_w is given by

$$K_w = [H^+][OH^-], \tag{2}$$

$$\frac{K_w}{K_a} = \frac{[C_6H_5OH][OH^-]}{[C_6H_5O^-]}. \tag{3}$$

Let x_0 be the initial concentration of phenol in solution and x be the equilibrium concentration of $C_6H_5O^-$ in solution; also let $x_{OH,0}$ and x_{OH} be the initial and equilibrium concentrations, respectively, of OH^- in solution; x_0 represents the concentration of phenol initially added to water, and $x_{OH,0}$ represents the concentration of NaOH initially added to solution. Since the amount of OH^- consumed for dissociation equals the amount of $C_6H_5O^-$ formed, eq. (3) can be written as

$$\frac{K_w}{K_a} = \frac{(x_0 - x)(x_{OH,0} - x)}{x}. \tag{4}$$

Solving eq. (4) for x, the expression for the degree of dissociation x/x_0 can be obtained as

$$\frac{x}{x_0} = {}^1/_2\left[\frac{K_w}{K_a x_0} + 1 + \frac{x_{OH,0}}{x_0}\right] - \sqrt{{}^1/_4\left[\frac{K_w}{K_a x_0} + 1 + \frac{x_{OH,0}}{x_0}\right]^2 - \frac{x_{OH,0}}{x_0}}. \tag{5}$$

[The other solution to eq. (4) is inadmissible since it gives x/x_0 always greater than 1]. From data on K_a, K_w, and the initial concentrations x_0 and $x_{OH,0}$ the degree of dissociation of phenol in aqueous solutions can be calculated using eq. (5).

The above equation shows that when $x_{OH,0} = x_0$,

$$\frac{x}{x_0} = {}^1/_2\left[\frac{K_w}{K_a x_0} + 2\right] - \sqrt{{}^1/_4\left(\frac{K_w}{K_a x_0}\right)^2 + \frac{K_w}{K_a x_0}} \tag{6}$$

and the degree of dissociation of phenol is practically complete when $x_{OH,0} \gg x_0$, and practically zero when $x_{OH,0} \ll x_0$.

Calculation of pH of Solution. The equilibrium concentration of OH^- in solution is given by

$$x_{OH} = x_{OH,0} - x. \tag{7}$$

Defining

$$pOH = -\log x_{OH}, \tag{8}$$

the pH of the solution is given by

$$pH = pK_w - pOH. \tag{9}$$

Using data on K_w, K_a, and initial concentrations x_0, $x_{OH,0}$, the quantities x, x_{OH}, and pH can be calculated from eq. (5), (7), and (9), respectively.

Experimental Determination of Degree of Dissociation. Un-ionized phenol and phenoxide ion have different values for the absorption maxima of secondary bands at wavelengths of 269 mμ and 286 mμ, respectively. The concentrations of the above two components in solution can hence be determined by assuming the additivity of absorbencies,[9] so that

$$c_{phenol}\,(a_s)_{phenol,269} + c_{phenoxide}\,(a_s)_{phenoxide,269} = (k_s)_{sample,269} \tag{10}$$

$$c_{phenol}\,(a_s)_{phenol,286} + c_{phenoxide}\,(a_s)_{phenoxide,286} = (k_s)_{sample,286} \tag{11}$$

where c_{phenol} and $c_{phenoxide}$ are concentrations of undissociated phenol and phenoxide ion, respectively, in solution; $(a_s)_{phenol,269}$ and $(a_s)_{phenol,286}$ are absorbency indices of undissociated phenol at 269 mμ and 286 mμ, respectively; $(a_s)_{phenoxide,269}$ and $(a_s)_{phenoxide,286}$ are absorbency indices of phenoxide ion at 269 mμ and 286 mμ, respectively; and $(k_s)_{sample,269}$ and $(k_s)_{sample,286}$ are absorbency coefficients of the solution at 269 mμ and 286 mμ, respectively.

The values of the above absorbency indices at the indicated wavelengths were calculated from experimental data on transmittancies of standard phenol and phenoxide solutions, $(T_s)_{phenol\ standard}$ and $(T_s)_{phenoxide\ standard}$, at the respective wavelengths, using the following relationships:

$$(a_s)_{phenol} = \frac{\log_{10}[1/(T_s)_{phenol\ standard}]}{b_m c} \tag{12a}$$

$$(a_s)_{phenoxide} = \frac{\log_{10}[1/(T_s)_{phenoxide\ standard}]}{b_m c} \tag{12b}$$

where b_m = thickness of cell used, and c = standard concentrations of phenol or phenoxide ion as the case may be. The absorbency coefficients were calculated from transmittancies of samples of unknown composition, $(T_s)_{sample}$, at the respective wavelengths, using the relation

$$(k_s)_{sample} = \frac{\log_{10}[1/(T_s)_{sample}]}{b_m}. \tag{13}$$

Defining the determinant $|D|$ as

$$|D| = \begin{vmatrix} (a_s)_{\text{phenol},269} & (a_s)_{\text{phenoxide},269} \\ (a_s)_{\text{phenol},286} & (a_s)_{\text{phenoxide},286} \end{vmatrix} \tag{14}$$

Equations (10) and (11) may be solved simultaneously to give

$$c_{\text{phenol}} = \frac{(a_s)_{\text{phenoxide},286}}{|D|} (k_s)_{\text{sample},269} - \frac{(a_s)_{\text{phenoxide},269}}{|D|} (k_s)_{\text{sample},286} \tag{15}$$

$$c_{\text{phenoxide}} = \frac{(a_s)_{\text{phenol},269}}{|D|} (k_s)_{\text{sample},286} - \frac{(a_s)_{\text{phenol},286}}{|D|} (k_s)_{\text{sample},269} \tag{16}$$

The applicability of eqs. (15) and (16) for the experimental determination of the concentrations of un-ionized phenol and phenoxide ion in aqueous solutions was verified in this work.

An aqueous standard solution of phenol at a concentration of 0.0003177 g mole/l. (phenol standard) and another standard solution of 0.000254 g mole/l. of 0.1*N* sodium hydroxide solution (phenoxide standard) were used to obtain data on transmittancies for use in eqs. (12a) and (12b); in the former solution, phenol was practically un-ionized, and in the latter, phenol was practically completely ionized. The above solute concentrations were chosen so that peak absorption of each band fell on the density scale between 0.4 and 0.8[10]. For the verification of the analytical technique, total phenol concentrations in the range 0.00025 to 0.001 g mole/l. with molar ratios of NaOH to phenol in the range 0.1 to 3.0 were used. The results obtained are given in Tables II and III.

The data given in Table II show that the experimental values on the wavelengths and absorbency indices corresponding to maximum absorption of un-ionized phenol and phenoxide ion are in reasonable agreement with the literature values.[10,11] For the sake of consistency, the experimental values obtained in this work were used in eqs. (15) and (16) for the calculation of phenol and phenoxide ion concentrations. The data given in Table III show that the total concentrations of phenol ($c_{\text{phenol}} + c_{\text{phenoxide}}$) calculated using eqs. (15) and (16) agree with the experimental values within

TABLE II
Wavelengths for Absorption Maxima and Absorbency Indices of Phenol and Phenoxide Ion

	Phenol	Phenoxide ion
Wavelength for absorption maximum, mμ		
Experimental	269	286
Reference 10	270	287
Absorbency index[a] at 269 mμ (exptl.)	1452	24.8
Absorbency index at 270 mμ (ref. 10)	1450	—
Absorbency index at 286 mμ (exptl.)	108.2	2535
Absorbency index at 287 mμ (ref. 10)	—	2600

[a] In units of l./cm·g mole.

TABLE III
Experimenal Determination of Phenol and Phenoxide Ion Concentrations in Solution by Additivity of Absorbencies

Solution no.	Total phenol concn. in solution, g mole/l.	Molar ratio of NaOH to phenol	pH of solution, exptl.	Calcd. values by additivity of absorbencies			
				Phenol concn., g mole/l.	Phenoxide ion concn., g mole/l.	Total phenol concn., g mole/l.	Error, %
1	0.000249	0.1	6.3	0.000250	0.000004	0.000254	+2.0
2	0.000254	0.5	8.7	0.000211	0.000043	0.000253	−0.4
3	0.000249	1.0	9.1	0.000154	0.000101	0.000255	+2.4
4	0.001	2.0	11.2	0.000129	0.000885	0.001014	+1.4
5	0.001	3.0	11.5	0.000050	0.000931	0.000981	−1.9

2%. The above results show that the concentrations of phenol and phenoxide ions in solution can be determined experimentally with reasonable accuracy by spectrophotometric analysis on the basis of the additivity of absorbencies. This technique was followed in this work for the experimental determination of the degree of dissociation of phenol.

Experimental Determination of pH. The pH of solutions was experimentally determined within an accuracy of ±0.1 using Corning pH meter Model 12.

Comparison of Calculated and Experimental Values. Literature values of pK_a for phenol at 25°C range from 9.88 to 10.08[12]. The ionization constant of water is affected by temperature.[13] There is always some difference in the temperature of the solutions during spectrophotometric measurements and that during pH measurements. Consequently there is some question regarding the choice of pK_a and pK_w values to be used in theoretical calculations for comparison with experimental data. Using the values of 10.08 for pK_a for phenol and 14 for pK_w for water, and values of 0.0005 and 0.001 g mole/l. for x_0 for phenol together with $x_{OH,0}$ for NaOH in the range 0.0003 to 0.01 g mole/l., the degree of dissociation of phenol, x/x_0, and the pH of the solution were calculated using eqs. (5) and (9). The pH of solution versus degree of dissociation correlation was essentially the same for the phenol concentrations used. Such correlation obtained by theoretical calculations is given by the solid line in Figure 1. Using the same values of x_0 and $x_{OH,0}$, the degree of dissociation of phenol was experimentally determined by the spectrophotometric technique described above, and the pH of the solution was measured in each case. These experimental data are also plotted in Figure 1, where the dashed line represents the correlation of experimental data. The agreement between the calculated and experimental data is sufficiently good to confirm the essential validity of the methods employed here for the calculation and the experimental determination of the degree of dissociation of phenol. The experimental results show that phenol is practically undissociated at pH < 7 and almost completely dissociated at pH > 12.3. The effect of pH

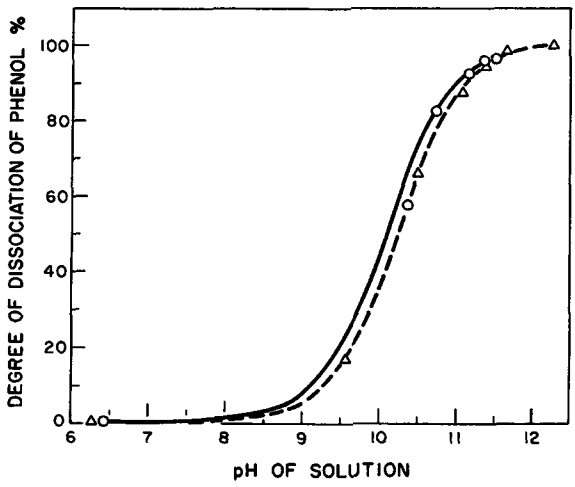

Fig. 1. Effect of pH of solution on degree of dissociation of phenol. Total phenol concentration in solution: (O) 0.005 g mole/l.; (Δ) 0.001 g mole/l.; (- -) experimental; (——) calculated using $pK_a = 10.08$ and $pK_w = 14.0$.

of solution on the degree of dissociation of phenol is particularly steep in the pH range 9.2 to 11.2 where the degree of dissociation changes from 10% to 91%.

Effect of pH of Feed Solution on Solute Separation

Separation of Phenol. By the addition of 0, 0.0003, 0.001, 0.002, 0.003, or 0.01 g mole of NaOH per liter of aqueous solutions containing 0.001 g mole of phenol in the same volume, feed solutions of pH equal to 6.3, 9.7, 10.6, 11.2, 11.5, and 12.3, respectively, were prepared. Reverse osmosis experiments were then carried out with the above feed solutions at 500 psig. The results obtained with four different samples of the membrane are given in Figure 2, which shows the effect of pH of feed solution (and hence the degree of dissociation of phenol in the feed solution) on solute separation, product rate, and the pH of the product solution under reverse osmosis operating conditions. The pH versus degree of dissociation correlation given by the dashed line in Figure 2 is the same as the one given in Figure 1 corresponding to the experimental data.

At pH 6.3, when phenol was practically undissociated in the feed solution used, negative solute separations of ~−5% (i.e., ~5% phenol enrichment in the product solution) were obtained with the films tested. These data are consistent with those reported earlier.[1,2]

In the pH range 9.7 to 12.3, phenol is dissociated from 19% to ~100%; in the above range of pH, phenol was positively separated with all the films tested. The extent of phenol separation increased with increase in pH of feed solution. With respect to each film, the form of pH versus solute separation correlation is exactly similar to that of pH versus degree of dissociation correlation, which shows that there exists a direct corre-

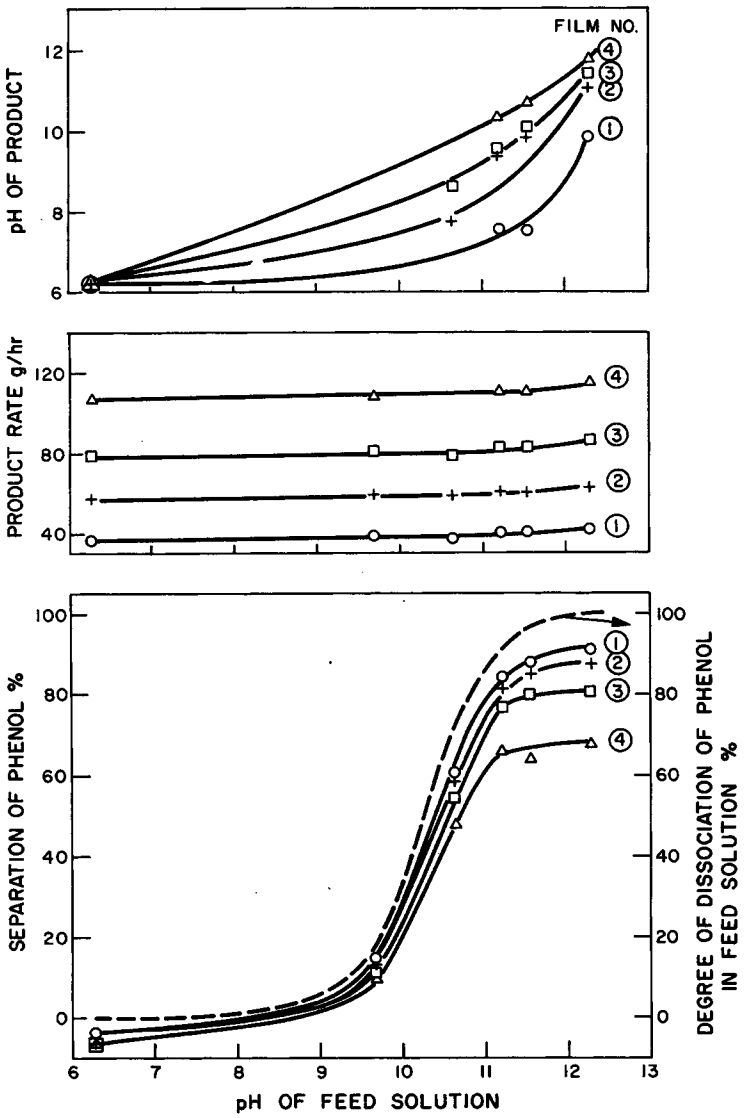

Fig. 2. Effect of pH of feed solution and degree of dissociation on separation of phenol, product rate, and pH of product solution. Film, Batch 316 type cellulose acetate membranes; total phenol concentration in feed, 0.001 g mole/l.; operating pressure, 500 psig; feed flow rate, 400 cc/min; effective film area, 7.6 cm^2.

spondence between degree of dissociation and solute separation, and the reverse osmosis separation of phenol increases with increase in its degree of dissociation in feed solution.

At any given pH of feed solution, phenol separation was highest with film 1, lowest with film 4, and intermediate with films 2 and 3. The increasing order of phenol separation corresponds exactly to the decreasing

order of average pore size on the membrane surface, as represented by the data on $D_{AM}/K\delta$ for NaCl (Table I) for the films tested. This correlation is the same as that obtained for the separation of completely ionized inorganic solutes in aqueous solution[3a] and hence indicates that the general mechanism of separation involved is the same for both organic and inorganic ions.

The separation data with films 1 to 4 show that at any feed solution pH, phenol separation is always less than the degree of dissociation, but the former approaches the latter with decrease in the average size of pores on the membrane surface. These data indicate the possibility that, with appropriate choice of the porous structure on the membrane surface, phenol separations virtually identical to its degree of dissociation can be obtained, which means that at a feed solution pH of ~12.3 or above, close to complete separation of phenol is attainable by reverse osmosis. In any case, it is of practical interest to note that 92% separation of phenol was actually obtained with film 1 when the feed pH was 12.3.

The experimental separation data presented in Figure 2 constitute further evidence that electrostatic repulsion of ions at the membrane–solution interface is a governing criterion in reverse osmosis separation when the solute molecule is partially or completely dissociated. The successful application of the above criterion for the reverse osmosis separation of phenol confirms the basic validity and practical utility of the physicochemical criteria developed earlier[2] for the reverse osmosis separation of alcohols, phenols, and monocarboxylic acids.

The data on product rates show that an increase in phenol separation was always accompanied by an increase in product rate with each one of the films studied. Similar results have been reported before.[2] Such results could be explained, as before,[2] on the basis that an increase in degree of dissociation decreased phenol–polymer intermolecular hydrogen bonding effects affecting the porous structure of the membrane. However, in the particular experiments reported in Figure 2, there was the added obvious possibility of the hydrolytic degradation of the membrane material because of its contact with high-pH feed solutions. This possibility was confirmed by the data presented in Table IV on the performance of the membranes with aqueous sodium chloride feed solutions before and after each of the experiments with aqueous phenol feed solutions of different pH. The relative decrease in sodium chloride separations accompanied by a relative increase in product rates obtained after experiments with high-pH (>11) feed solutions is typical of the effect of hydrolysis of membrane material on membrane performance.[3b] Even in short-run experiments, the effect of the above hydrolysis on membrane performance is significant when the pH of the feed solution was greater than 11. On the basis of the above data, it should be concluded that hydrolysis of the membrane material was primarily responsible for the increase in product rates obtained with increase in the pH of the phenolic feed solutions; and, but for this hydrolysis, phenol separations could have been better with feed solutions of pH >11.

TABLE IV
Membrane Performance with Aqueous Sodium Chloride Feed Solutions Before and After Experiments with Aqueous Phenol Feed Solutions of Different pH[a]

	Solute separation, %				Product rate, g/hr			
Order of experiment	1[b]	2	3	4	1	2	3	4
Initial (before any expt. with aqueous phenol feed solution)	94.8	91.5	86.1	68.9	37.9	57.3	78.0	104.9
After expt. with aqueous phenol feed solution of given pH								
pH 6.3	94.8	91.5	86.1	68.9	37.9	57.3	78.0	104.9
pH 9.7	94.7	91.6	85.0	68.6	39.3	59.6	81.2	108.0
pH 10.6	94.9	92.4	85.8	69.4	38.6	58.2	79.3	106.1
pH 11.2	94.6	91.7	85.4	68.8	39.0	59.1	80.4	106.7
pH 11.5	93.9	91.1	84.9	68.0	39.3	59.4	81.1	107.7
pH 12.3	92.5	87.1	77.9	53.9	42.0	63.6	88.7	114.3

[a] Feed concentration, 1500 ppm NaCl; feed flow rate, 400 cc/min; operating pressure, 500 psig; membrane rea, 7.6 cm^2.
[b] Film number.

The pH of the product solution was always less than the pH of the feed solution with respect to each membrane tested. The relative values of the product solutions decreased in the same order of the decrease in the values of $D_{AM}/K\delta$ for sodium chloride for the membranes used. These results are understandable on the basis of the differences in the average size of pores on the surfaces of the respective membranes. Figure 2 also shows that a product pH of 7 could be obtained with feed pH of 10.75, 9, 7.8, and 7.25 in conjunction with films 1, 2, 3, and 4, respectively. Since a higher pH of feed solution also results in a higher degree of dissociation of phenol, both high phenol separation and low pH of the product solution can be obtained simultaneously with appropriate choice of the porous structure of the membrane surface. However, with a high-pH feed solution, the useful life of the membrane should be expected to be curtailed drastically owing to hydrolytic degradation of the cellulose acetate material on the membrane surface.

Separation of Substituted Phenols. The effect of pH on the reverse osmosis separations of *p*-chlorophenol and *p*-cresol, each present as single organic solute in aqueous solution containing 0.001 g mole/l. (129 and 108 ppm, respectively) was also studied using six different samples of cellulose acetate membranes. The results obtained with two of them (films 21 and 23) are given in Figure 3; the other films gave similar results.

The choice of the above solutes for study in this work was influenced by the following factors. Both the above substituted phenols are common constituents of many wastewaters[14]; consequently, the results on their separation are of practical interest. At 500 psig, both solutes were separated either negligibly or negatively under operating conditions when the

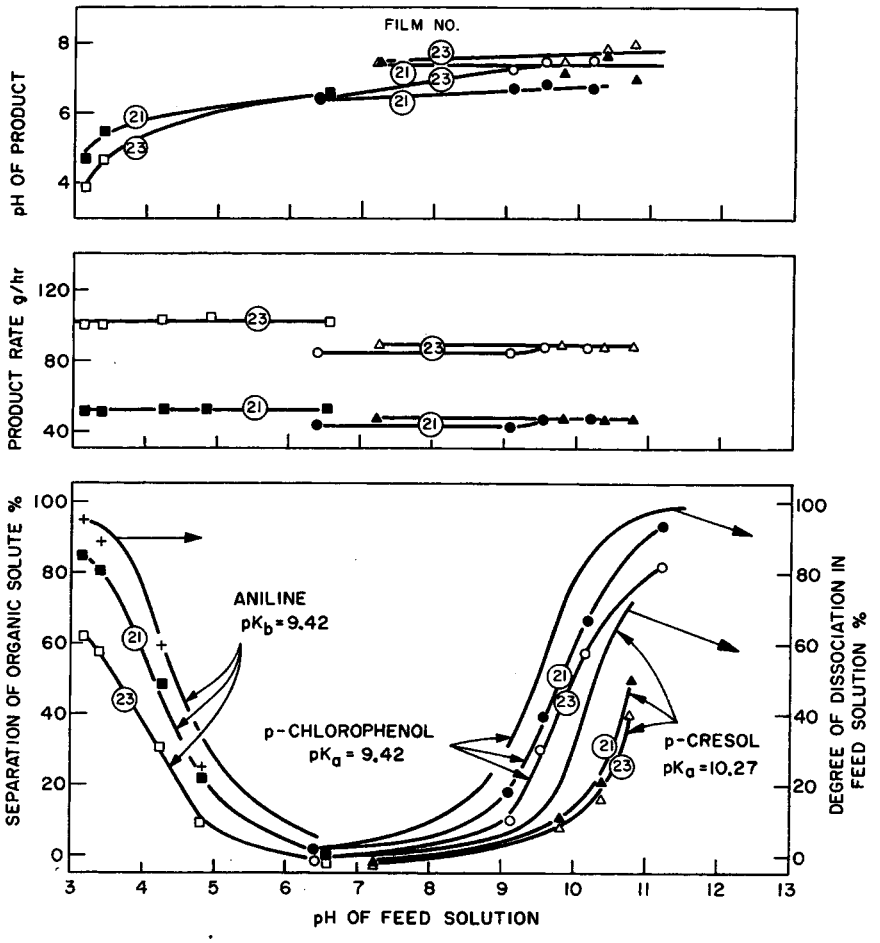

Fig. 3. Effect of pH of feed solution and degree of dissociation on the separations of *p*-chlorophenol, *p*-cresol, and aniline, and the corresponding product rates and pH of feed solutions. Film, Batch 316 type cellulose acetate membranes; total concentration in feed, 0.001 g mole/l. for each of the solutes *p*-chlorophenol, *p*-cresol, and aniline; opdrating pressure, 500 psig; feed flow rate, 400 cc/min; effective film area, 7.6 cm^2. (+) Degree of dissociation of aniline, experimental data.

solute molecules remained essentially un-ionized. On the basis of the foregoing discussion on the governing influence of dissociation on reverse osmosis separation, one would expect that both *p*-chlorophenol and *p*-cresol could be separated by dissociating the solute molecules by changing the pH of the feed solution. The pK_a values[12] for *p*-chlorophenol and *p*-cresol are respectively 9.42 and 10.27, which lie on either side of the pK_a value (10.08) for phenol. Consequently, at any given pH and total concentration of organic solute, the degree of dissociation of *p*-chlorophenol is higher and that of *p*-cresol is lower than that of phenol. One would then expect the order of solute separation in reverse osmosis to correspond to the

order of solute dissociation in the feed solution. The experimental results, illustrated in Figure 3, did confirm the above expectations.

The pH of feed solution versus degree of dissociation correlations given in Figure 3 were obtained by calculations using eqs. 5, 7, and 9. The calculations showed that, with respect to each solute, the degree of dissociation was practically negligible at feed pH of 7, and dissociation increased steeply with increase in pH of the feed solution. The experimental results showed direct correspondence between increase in degree of dissociation of solute in the feed solution and solute separation in reverse osmosis. Further, under the experimental conditions used, solute separation was always less than the degree of dissociation of solute in the feed solution for all the films tested, and solute separation was always relatively higher for the membrane whose $D_{AM}/K\delta$ for the reference solute (sodium chloride) was lower. These results showed that both *p*-chlorophenol and *p*-cresol could be separated by reverse osmosis by the dissociation of solute molecules by changing the pH of the feed solution; and, by appropriate choice of the porous structure of the membrane surface, solute separations approaching the degree of dissociation could be obtained at the operating conditions of pressure and feed concentration used in this work. With film 21, *p*-chlorophenol separation of 94% and *p*-cresol separation of 50% were actually obtained in this work using feed solutions of pH 11.2 and 10.8, respectively; the calculated degrees of dissociation of solutes in the feed solutions were 98% for *p*-chlorophenol and 71% for *p*-cresol.

In terms of separation of the reference solute, sodium chloride (Table I), the porous structure of the membrane surfaces for films 1 and 21 were comparable. Comparing the data on the separation of *p*-chlorophenol and *p*-cresol obtained with film 21 with those of phenol obtained with film 1, it could be seen that the separation of phenol was in between those of *p*-chlorophenol and *p*-cresol at any given pH of the feed solution, and so was the corresponding degree of dissociation of the organic solute in the feed solution. For example, at a feed pH of 10.5, the degrees of dissociation of *p*-chlorophenol, phenol, and *p*-cresol in the feed solutions were 91%, 66%, 60%, respectively; the corresponding solute separations were 78%, 55%, and 28%, which illustrate the existence of direct correspondence between the order of degree of dissociation and that of solute separation. These results again illustrate the governing significance of dissociation of solute molecules in the feed solution and hence the electrostatic repulsion of ions at the membrane–solution interface on solute separation in reverse osmosis.

The data on product rates show that an increase in solute separation was also accompanied by an increase in product rate. With significant levels of solute separation, the pH values of the product solutions were less than those of the corresponding feed solutions. These results were similar to those obtained for aqueous phenol feed solutions (Fig. 2). While the comments made earlier with reference to similar data in Figure 2 are applicable to the data presented in Figure 3, it should be added that there was no noticeable hydrolysis of the membrane material in the latter experi-

ments, as shown by the essential identity of solute separation and product rate data obtained for the reference solution system (1500 ppm NaCl–H_2O) before and after the experiments with the phenolic feed solutions.

Separation of Aniline. Aniline is a base, while phenol and substituted phenols are acids. The physicochemical criteria for the reverse osmosis separation of bases have been extensively discussed.[15] The object of including a few experiments on aniline separation in this work was to examine the general applicability of the technique used for the successful reverse osmosis separation of nonionic solutes.

The concentration of aniline used in the feed solution was 0.001 g mole/l. (93 ppm) in all cases. At neutral pH, aniline exists essentially as unionized molecules in aqueous solution. The molecules, however, can be ionized to different extents by decreasing the pH of the feed solution by the addition of the required amount of hydrochloric acid. The change in pH of the feed solution, and the corresponding change in the degree of dissociation of aniline, can be calculated using eqs. (5) and (7) in which K_a is replaced by the dissociation constant for the base K_b ($= K_w/K_a$); $x_{OH,0}$ and x_{OH} are replaced by $x_{H,0}$ and x_H representing the initial and equilibrium concentration, respectively, of hydrochloric acid in the feed solution; and x represents the equilibrium concentration of ionized aniline. The pH-versus-degree of dissociation correlation obtained from such calculations is given in Figure 3. The above correlation was also established experimentally following the procedure similar to that used for the case of phenol. The experimental data obtained are also given in Figure 3, which shows good agreement between experimental and calculated values. These results show that the degree of dissociation of aniline increases steeply with decrease in pH of the feed solution. Further, the pH-versus-degree of dissociation correlations for aniline and *p*-chlorophenol are symmetrical on either side of the neutral pH, which is not surprising in view of the fact that the pK_a value for *p*-chlorophenol and the pK_b value for aniline are the same (9.42).

The reverse osmosis data obtained with films 21 and 23 with aqueous solutions of aniline in the pH range of 6.5 to 3.2 are also given in Figure 3. At the pH of 6.5, when the degree of dissociation of aniline in the feed solution was negligible, the solute separations obtained with films 21 and 23 were either negligible or slightly negative. With a decrease in pH and the consequent increase in the degree of dissociation of aniline in the feed solution, solute separation increased correspondingly with both films 21 and 23. At pH of 3.2, when the degree of dissociation of aniline in the feed solution was 95%, positive aniline separations of 85% and 62% were obtained with films 21 and 23, respectively. Again, the form of the pH versus-degree of dissociation and solute separation correlations were similar. These results establish beyond question that changing pH is just a means for changing the degree of dissociation of the solute in the feed solution, and it is the latter change that governs the separation of ionizable solutes in reverse osmosis. The results also establish the general applicability of the

technique of dissociation of the solute molecules in the feed solution for the reverse osmosis separation of nonionic solutes; and as such, the technique has a wide scope in practical reverse osmosis operations.

In the pH range of 6.5 to 3.2, there was practically no change in the product rates and also in the reverse osmosis performance of films for the reference solution system (sodium chloride–water) before and after the experiments with aniline feed solutions. These results showed that the membrane material was not affected by hydrolysis in the above pH range under the conditions of the experiments.

At significant levels of solute separation, the pH of the product solution was always more than the pH of the corresponding feed solution, and the former was closer to neutral pH, indicating that the quality of the product water was approaching that of pure water. These results are consistent with those obtained in the case of phenolic feed solutions.

Separation of Phenols—Effect of Operating Conditions

The effects of total phenol concentration in the feed, feed flow rate, and operating pressure on the reverse osmosis separation of phenol in aqueous solutions were examined using six different samples of films for each set of experiments. The results obtained with two films in each set are reported in Figures 4 to 7; the results obtained with the other films were similar. The degree of dissociation of phenol in the feed solution was determined experimentally for each run.

Figure 4 illustrates the effect of total phenol concentration in feed in the range 0.1×10^{-3} to 1.15×10^{-3} g mole/l. (9.4 to 108 ppm) on solute separation, product rate, and pH of the product solution. In these experiments, the pH of the feed solution was kept constant at 11.2 by the addition of the required amount of NaOH to the feed solution. In the above concentration range at pH 11.2, the degree of dissociation of phenol in the feed solution increased from 86% to 91%; under the same conditions, solute separation increased from 76% to 85% with film 51 and from 62% to 77% with film 55. These data again illustrate the correspondence between degree of dissociation and solute separation and show that, in the feed concentration range studied, solute separation in reverse osmosis is a function of the degree of dissociation of solute in the feed solution under otherwise identical operating conditions of pressure and feed flow rate. Since the feed concentrations involved were very small, the osmotic pressure effects on transport were negligible as shown by the product rate data which remained essentially constant with respect to each film. The pH of the product solution was always less than the pH of the feed solution, and the former was relatively more for the product solution obtained with film 55, which gave relatively less solute separation. These results are similar to those given in Figure 2. The abrupt increase in pH obtained with the product solution from the last experiment in the series indicated that the membrane was then significantly affected by hydrolysis.

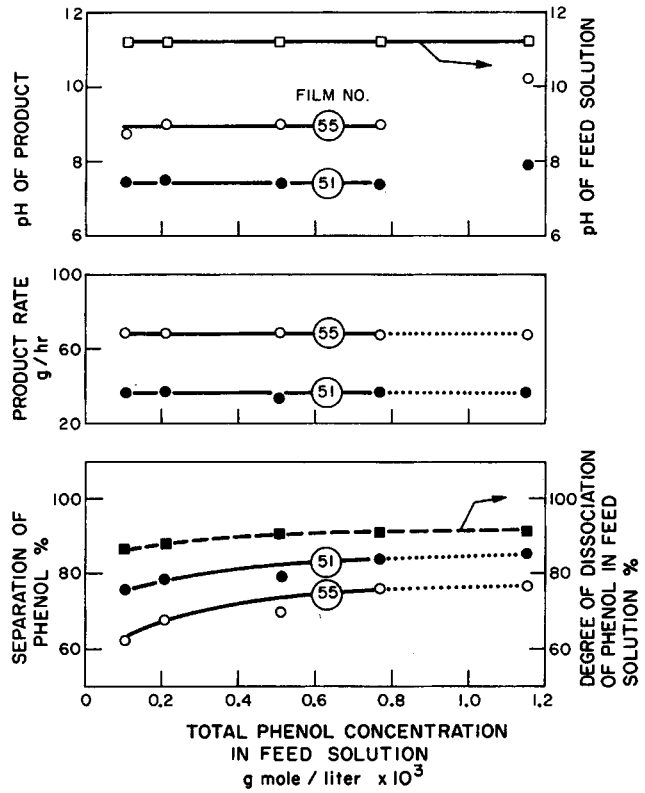

Fig. 4. Effect of feed concentration on the separation of phenol, product rate, and pH of product solution. Film, Batch 316 type cellulose acetate membranes; operating pressure, 500 psig; feed flow rate, 400 cc/min; effective film area, 7.6 cm². (■) Degree of dissociation of phenol, experimental data.

Figure 5 illustrates the effect of feed flow rate on the separation of phenol. In these experiments, the total concentration of phenol in the feed solution was 0.001 g mole/l. (94 ppm), and the pH of the feed solution was kept constant at 11.2 as before, under which condition the degree of dissociation of phenol in the feed was 91%. The increase of feed flow rate from 200 to 600 cc/min in the particular apparatus used made practically no change in solute separations and product rates. Such results have been predicted before[7] for dilute aqueous sodium chloride feed solutions using the same apparatus. The pH of the product solutions showed a tendency to decrease with increase in feed flow rate, which showed the sensitivity of the pH of the solution even to small changes in the concentration of the alkali ions.

Figures 6 and 7 illustrate, respectively, the separation of un-ionized and partially ionized phenol in the operating pressure range 250 to 1500 psig. In both sets of experiments, the overall concentration of phenol in the feed solution was 0.001 g mole/l. (94 ppm).

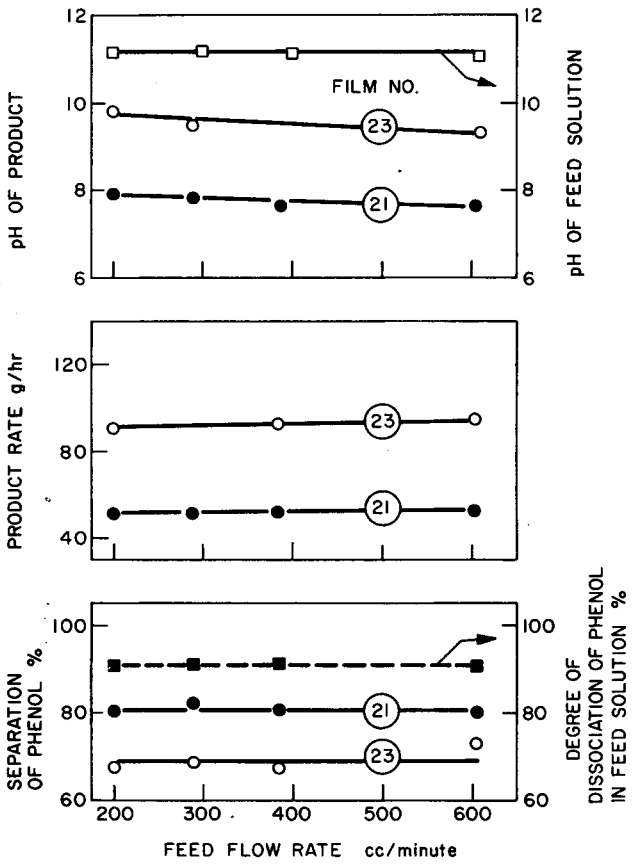

Fig. 5. Effect of feed flow rate on the separation of phenol, product rate, and pH of product solution. Film, Batch 316 type cellulose acetate membranes; total phenol concentration in feed solution, 0.001 g mole/l.; operating pressure, 500 psig; effective film area, 7.6 cm². (■) Degree of dissociation of phenol, experimental data.

In the first set of experiments (Fig. 6), no alkali was added to the feed solution; consequently the pH of the feed solution was 6.4, under which condition phenol existed essentially completely as un-ionized molecules. With this feed solution, negative separations of phenol were obtained in reverse osmosis experiments, i.e., there was phenol enrichment in the product solution. The negative separation was relatively more with the membrane whose average pore size on the membrane surface was relatively less. Further, the negative separation increased with increase in operating pressure, particularly in the range of 250 to 1000 psig. For example, phenol enrichment in the product increased from 3.5% to 10.5% in the operating pressure range of 250 to 1500 psig for film 82. Similar negative separations have been reported before.[1,2]

In the second set of experiments (Fig. 7), NaOH was added to the feed solution to bring its pH to 11.2, so that the phenol molecules were partially

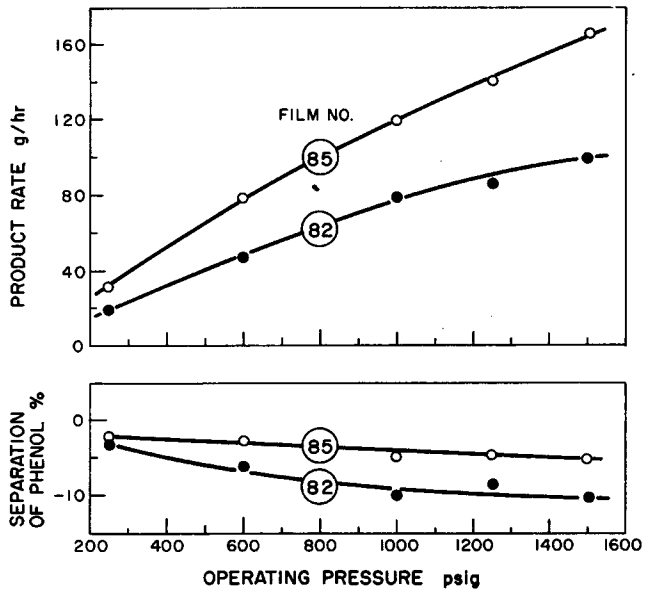

Fig. 6. Effect of operating pressure on the separation of undissociated phenol and product rate. Film, Batch 316 type cellulose acetate membranes; total phenol concentration in feed solution, 0.001 g mole/l.; feed flow rate, 400 cc/min; effective film area, 7.6 cm^2.

(91%) ionized in solution. With such feed solutions, positive overall separations of phenol were obtained in the product solutions in reverse osmosis; further, the overall phenol separation either decreased slightly with increase in operating pressure (film 82) or passed through a slight maxium (film 84) in the operating pressure range of 250 to 1500 psig. These results showed the combined effects of pressure on the positive separation of ionized phenol and the negative separation of un-ionized phenol in the feed solution.

In both sets of experiments (Figs. 6 and 7), product rates increased with increase in operating pressure, and the nonlinearity in the operating pressure-versus-product rate relationship is apparently due to membrane compaction at higher operating pressures. Since solute separations varied only in a small range with the films tested, no significant change in the pH of the product solutions was encountered.

Criteria for Reverse Osmosis Separation

The governing significance of $\Delta\nu_s$ (shift in the OH band maximum in the IR spectra) and the Taft number (σ^*) for the reverse osmosis separation of alcohols and phenols in aqueous solution using porous cellulose acetate membranes has been discussed.[2] The relevant value of σ^* for water is 0.49; from Figure 2 in reference 2, the corresponding value of $\Delta\nu_s$ is $\sim$250 cm^{-1} It was suggested earlier[2] that, with respect to the systems con-

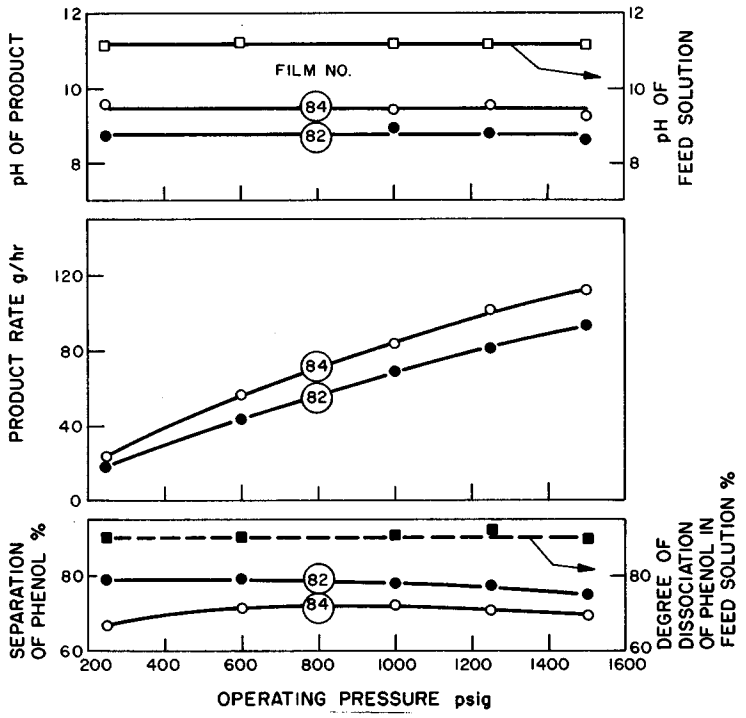

Fig. 7. Effect of operating pressure on the overall separation of phenol from aqueous solution containing partially dissociated phenol, product rate, and pH of product solution. Film, Batch 316 type celulose acetate membranes; total phenol concentration in feed solution, 0.001 g mole/l.; feed flow rate, 400 cc/min; effective film area, 7.6 cm^2. (■) Degree of dissociation of phenol, experimental data.

sidered, positive separations were obtainable in reverse osmosis for all alcohols and phenols whose $\Delta\nu_s$ values were less than that of water, and negative separations were obtainable for those whose $\Delta\nu_s$ values were greater than that of water. This suggestion was based on the criterion that, for the solute–water system under discussion, that component which had a greater value of $\Delta\nu_s$ was preferentially sorbed at the membrane–solution interface. This criterion seemed reasonable since the chemical nature of the cellulose acetate membrane had been shown to have a net proton acceptor character.[15] The validity of the above criterion was examined further in this work.

The $\Delta\nu_s$ value for phenol (288 cm^{-1}) is greater than that of water; on the basis of the above criterion, phenol should be preferentially sorbed at the cellulose acetate–aqueous solution interface. The experimental separation data presented in Figure 6 show that phenol was preferentially transported through the membrane under the test conditions, that increase of operating pressure increased the preferential transport of phenol through the membrane, and that the enrichment of phenol in the product solution was relatively more for the film whose average surface pore size was rela-

tively less. All these results support the validity of the above criterion for preferential sorption in reverse osmosis.

The $\Delta\nu_s$ value for *p*-chlorophenol (313 cm^{-1}) is even higher than that of phenol. In the previous work[2] it was found that *p*-chlorophenol was positively separated at 250 psig, and this result appeared as an exception to the given $\Delta\nu_s$ versus solute separation correlation. Since the data on the separation of *p*-chlorophenol appeared to offer a test case for the above criterion, a set of further experiments were carried out with aqueous feed solutions containing *p*-chlorophenol. The solute concentration used was 0.001 g mole/l. (129 ppm). No alkali was added to the feed solution; consequently, the degree of dissociation of the solute in the feed solution was practically zero. The effects of operating pressure and average pore size on the membrane surface on solute separation were investigated. The operating pressure used was in the range 250 to 1500 psig. The average pore size on the membrane surface used was represented in the arbitrary scale of data on reverse osmosis separation of sodium chloride at 1500 psig using an aqueous feed solution containing 1500 ppm of NaCl, at the same feed flow rate (400 cc/min) as that used in all the experiments in this series. Thus, an increase in sodium chloride separation would represent a decrease in the average pore size on the membrane surface. Five different samples of the membrane were used with average pore sizes corresponding to sodium chloride separations in the range of 53% to 96%. The results obtained with aqueous *p*-chlorophenol feed solutions are given in Figure 8, which shows data on solute separation and the ratio [PR]/[PWP] as a function of operating pressure and average size of pores on the membrane surface.

The results obtained were extremely interesting. With respect to *p*-chlorophenol separation, the data ranged from −11% to +42.9% depending upon operating pressure and pore size on the membrane surface. For any given membrane, solute separation decreased with increase in operating pressure. At 250 psig, positive separations were obtained with all the membranes tested, and solute separation increased with decrease in pore size; *p*-chlorophenol separations were 5.4% and 42.9%, respectively, with membranes whose surface pores were the biggest and the smallest used. In the operating pressure range of 600 to 1500 psig, both negative and positive separations were obtained depending on membrane pore size; and at each pressure, the negative separations passed through a maximum. At 600 psig, solute separation was negligible with the membrane whose pore size was the biggest used, and separation decreased to −4% with a membrane of intermediate pore size and then increased to +20% with the membrane whose pore size was the smallest one used. At 1000 psig and 1500 psig, the corresponding solute separation data were −1.4%, −7.8%, and +19%, and −3%, −11%, and −1%, respectively. With respect to product rate data, the results showed that the ratio [PR]/[PWP] decreased with increase in operating pressure for any given membrane and also decreased with decrease in pore size at any given operating pressure.

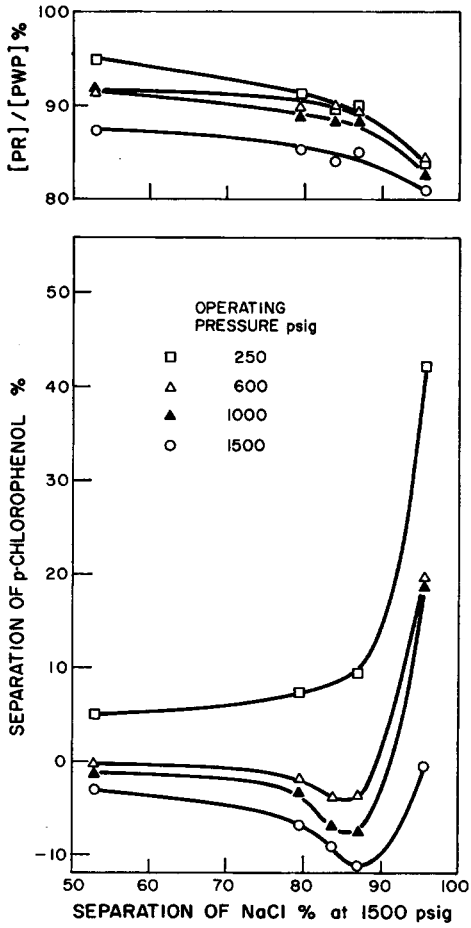

Fig. 8. Effect of operating pressure and pore size of membrane surface on the separation of undissociated *p*-chlorophenol in aqueous solution. Film, Batch 316 type cellulose acetate membranes; total *p*-chlorophenol concentration in feed solution, 0.001 g mole/l.; feed flow rate, 400 cc/min.

The above results are understandable on the following basis:

1. At the membrane–solution interface, both *p*-chlorophenol and water are attracted toward the membrane surfaces since the membrane material has a net proton acceptor character.

2. Since $\Delta\nu_s$ for *p*-chlorophenol is greater than that for water, *p*-chlorophenol is more attracted to the membrane surface than water, i.e., *p*-chlorophenol is preferentially sorbed at the interface.

3. In the sorbed layer, the mobility of water is more than that of *p*-chlorophenol as a consequence of (2) above.

4. The mobility of the preferentially sorbed *p*-chlorophenol decreases as the membrane surface is approached; thus, in general, the preferentially sorbed layer consists of both immobile and mobile layers.

5. Increase of operating pressure increases the sorption of both *p*-chlorophenol and water at the interface.

6. Increase of operating pressure also increases the degree of mobility of the preferentially sorbed layer, i.e., a greater proportion of the preferentially sorbed layer is mobile at higher operating pressures.

The existence of mobile and immobile sorbed layers and the effect of pressure on the mobility of the sorbed species postulated above (items 4, 5, and 6) have been established before in gas permeation and separation experiments using similar membranes.[16]

Solute separation in the product solution is governed by the relative fluxes of the more concentrated interfacial fluid and the bulk (boundary) fluid through the membrane pores. For any given membrane, while the transport of the more concentrated interfacial fluid through the membrane pores tends to result in solute enrichment (or negative solute separation) in the product solution, a decrease in the mobility of the preferentially sorbed species during such transport tends to decrease the above solute enrichment; further, if the preferentially sorbed *p*-chlorophenol consists partly or totally of immobile layers, a net positive solute separation can result in the product solution because of the flux of the relatively more mobile water in the sorbed region. Therefore, the flow of the interfacial fluid through the membrane pores can result in an overall positive, negative, and/or negligible solute separation in the product solution, depending on the extent of preferential sorption, number of immobile layers, and the relative mobility of the sorbed species under the conditions of the experiment.

Since the extent and mobility of the preferentially sorbed species increases with pressure, solute separation decreases with increase in operating pressure for any given membrane. At any given pressure, decrease in membrane pore size decreases the effective area available for the flow of the bulk fluid, which increases the net effect of the flow of the interfacial fluid on solute separation. This latter change should be expected to become progressively steeper as the membrane pore size is progressively reduced to a critical pore size characteristic of the membrane–solution system under consideration.

Referring to the experimental results presented in Figure 8, the small positive separation obtained at 250 psig with the membrane whose average pore size was the biggest one used and the increase in separation obtained with decrease in average pore size at the same operating pressure indicate that the mobility of *p*-chlorophenol was less than that of water in the sorbed layer at the above operating pressure. The increase in the mobility of *p*-chlorophenol in the sorbed layer with increase in operating pressure is illustrated by the corresponding decrease in solute separation. Referring to experiments in the operating pressure range of 600 to 1500 psig, the initial increase in negative separation with decrease in membrane pore size, and the subsequent decrease in such negative separation (which, in some cases, turned into considerable positive separation) with further decrease in membrane pore size, illustrate the effect of the flux of the interfacial fluid

on solute separation as the pore area available for fluid flow decreased progressively. At any given operating pressure, the steep decrease in [PR]/[PWP] ratio with decrease in pore size indicates the possible existence of immobile layers in the preferentially sorbed region, which tend to block the pore area available for fluid flow. Consequently, when the pore size is sufficiently small and the number of immobile layers is sufficiently high, solute separation tends to increase significantly, as seen in Figure 8. Also, the decrease in [PR]/[PWP] ratio obtained with increase in operating pressure for any given membrane indicates that the number of immobile layers in the preferentially sorbed region increases with increase in operating pressure.

The above results with the *p*-chlorophenol–water system (Fig. 8) are significant from several points of view. They establish the essential validity of the criterion for preferential sorption stated earlier for the separation of alcohols and phenols in aqueous solution using porous cellulose acetate membranes; namely, that the component whose $\Delta\nu_s$ value is greater is preferentially sorbed at the membrane–solution interface. The results further illustrate that solute concentration in the product solution is a function of the mobility of the preferentially sorbed species, and hence the product solution is not necessarily always concentrated with the preferentially sorbed species. The results bring out specifically the importance of operating pressure and pore size on the membrane surface on solute separation in reverse osmosis, and hence open up new avenues for further investigations on criteria for reverse osmosis separation.

CONCLUSIONS

Electrostatic repulsion of ions at the membrane–solution interface, with the consequent preferential sorption of water at the interface, is a governing criterion in reverse osmosis separation when the solute molecule is partially or completely dissociated in the aqueous feed solution. This criterion offers a useful means for the reverse osmosis separation of nonionic solutes in aqueous solution using porous cellulose acetate and similar membranes.

Preferential sorption of water resulting from the preferential repulsion of solute molecules at the interface and that resulting from the preferential attraction for water at the interface seem distinguishable. For example, with particular reference to work reported already on the separation of acids and bases using porous cellulose acetate membranes,[2,15] the former is the case when the solute molecules are ionized or when the solute is a base; and the latter is the case when the solute is an un-ionized acid whose acidity is less than that of water. While the membrane pore structure is generally unaffected in the former case, it is affected in the latter case as seen in the respective product rate data.

Preferential sorption of solute at the interface, the possible existence of both mobile and immobile layers in the sorbed region, and the difference in the mobility of the sorbed species give rise to unique possibilities of bringing

about positive separation of such solutes in reverse osmosis operations by suitable choice of operating conditions.

In view of the fact that complete ionization of phenols require high pH of feed solutions, the data presented in this paper reinforce the practical need for suitable membranes resistant to hydrolytic degradation.

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