

## *Interactions of Poly(hydroxypropyl Acrylate-Co-Tetraethylene Glycol Dimethacrylate) with Aqueous Electrolytes*

### INTRODUCTION

In an earlier investigation on photopolymerization, hydroxypropyl acrylate and tetraethylene glycol dimethacrylate homo- and copolymers were prepared.<sup>1</sup> These materials are similar to those which have been used for nonionic membranes.<sup>2-4</sup> Ionic membranes have also been prepared incorporating poly(acrylic acid),<sup>5-7</sup> a product to be expected from the hydrolysis of poly(hydroxypropyl acrylate). Both types have given good salt rejection in hyperfiltration studies.<sup>2-7</sup>

The photopolymerization product of hydroxypropyl acrylate, 5% tetraethylene glycol dimethacrylate, in cylindrical form offered a convenient means of investigating interactions of this copolymer (hereafter to be simply called polymer) with aqueous electrolytes, including the distribution of sodium chloride at equilibrium. In this work, we report the effects of solution pH and the degree of hydrolysis on the swelling of the polymer and the distribution of solutes between polymer and water.

### EXPERIMENTAL

#### Polymer

A monomer solution 95 parts by weight hydroxypropyl acrylate and 5 parts by weight of the crosslinking agent tetraethylene glycol dimethacrylate was prepared. This was then dissolved in an equal volume of either dimethylformamide or 1:1 water-ethylene glycol solutions containing uranyl nitrate hexahydrate (UNH) to give a final concentration of 0.014M UNH. Vertical, open-ended Pyrex tubes 4 to 6 mm in I.D. were filled to a height of 14 cm and stoppered at the top. The solution was irradiated with light from a 150-W tungsten bulb at a distance of 15 cm for 1 hr. The polymer was then removed and soaked in ~1 liter of distilled water at room temperature (24-26°). The water was changed frequently for a week, then intermittently for an additional two to three weeks before use. Composition of the water-soaked polymer was then determined by weighing blotted cylinder segments in a stoppered vial and drying to constant weight at 100° and 1-2 torr. Duplicate preparations from each solvent gave water-soaked products all having polymer compositions in the range of 55.0-56.6%. The average composition was 55.9% polymer-44.1% H<sub>2</sub>O, or 0.79 g H<sub>2</sub>O per gram dry residue.

#### Distribution Measurements

**Sodium Chloride.** Weighed cylinders of blotted polymer (0.6-1 g) were equilibrated at 25 ± 1° for 14 days in 100 ml volumes of 0.5M NaCl as made up and at different pH's resulting from the addition of NaOH. The cylinders were again blotted and weighed, and the NaCl in the polymer was removed by soaking the cylinder overnight twice in 100-ml portions of distilled water. Chloride was determined potentiometrically using standard 0.05M AgNO<sub>3</sub>. All of the chloride was removed in the first wash except from the swollen cylinder, which had the maximum salt uptake (119 mg); from this cylinder 1.95 meq Cl<sup>-</sup> were removed in the first water wash and 0.08 meq in the second.

**Bases, Acetates, and Phosphates.** The distribution of other chemicals between polymer and water was determined by equilibrating 0.5-1 g polymer cylinder segments in 100 ml volumes of 0.1N aqueous solute. After a nine-day period at 25 ± 1°, the clear cylinders, some greatly swollen as a result of hydrolysis (see Results and Discussion section), were carefully removed, blotted, and weighed. Imbibed solute was removed with two successive 100-ml water soakings. The bases were titrated with standard 0.1N HCl and acetic acid with standard 0.1N NaOH. Sodium dihydrogen phosphate,

cupric acetate, sodium acetate, and disodium hydrogen phosphate were passed through a cation exchange column (Dowex 50 in the hydrogen form); acid in the effluents was titrated with standard base.

### Hydrolysis

The extent of hydrolysis caused by each reagent was determined by measuring the exchange capacity of the polymer cylinder after reagent and water soakings. Standard 0.1*N* HCl, 50 ml, was added. After 24 hr, the solution and subsequent water washes were separated; the excess HCl in the solution and washes was determined by titration with standard base. The weight of dry polymer in the acid form was obtained by heating at 100° while pumping at 1 to 2 torr to constant weight. The exchange capacity in meq/g dry product was the ratio of meq of acid used up by the polymer to the dry polymer weight in the hydrogen form.

### RESULTS AND DISCUSSION

The distribution of NaCl between polymer and water at room temperature is shown in Table I. When soaked in 0.5*M* NaCl at make-up pH, the water-wet polymer shrank slightly (14% by weight). The ratio ( $K_d$ ) of salt concentration (moles NaCl/1000 g H<sub>2</sub>O, measured as moles of the coion Cl<sup>-</sup>) inside the polymer to that in the solution after equilibration was 0.29.

When the pH of the NaCl solution was raised, the behavior of the polymer underwent drastic changes. The addition of small amounts of NaOH to the NaCl solutions caused the polymer cylinders to swell somewhat (columns 2, 3, and 4, Table I), with corresponding increase in the amount of salt in the solution inside the cylinder. When 2.2 meq. NaOH per g water-wet polymer was added to the soak solution (column 5), the cylinder swelled to 6.3 times its original weight, with the NaCl distribution coefficient increasing to >0.8.

Since the slightly basic salt solutions ended up with pH's <7 after the equilibration period, it appeared likely that the poly(hydroxypropyl acrylate) had undergone some saponification, i.e., propanediol and sodium polyacrylate were formed by the hydrolytic action of NaOH on the poly(hydroxypropyl acrylate). The swelling would then be explained by the known swelling of poly(acrylic acid) upon neutralization as observed by Kuhn,<sup>8</sup> Katchalsky,<sup>9</sup> Breitenbach and Karlinger,<sup>10</sup> and others.<sup>11-16</sup> Therefore, the polymer was soaked in 0.1*N* solutions, mostly bases of different base strengths, and the exchange capacity of the polymer was measured after determining the extent of swelling

TABLE I  
Effect of pH on Distribution of NaCl Between Polymer and Aqueous Phases<sup>a</sup>

meq NaOH added/g water-wet polymer	—	0.06	0.08	0.25	2.2
pH of NaCl soln. after equilibration	3.3-4.0	4.5	5.2	6.8	10.5
Swelling factor <sup>b</sup>	0.86 <sup>c</sup>	1.00	1.16	1.58	6.30 <sup>d</sup>
NaCl molality in polymer	0.15 <sup>c</sup>	0.19	0.22	0.30	0.42
Distribution coefficient $K_d$ <sup>e</sup>	0.29 <sup>e</sup>	0.37	0.45	0.59	0.82

<sup>a</sup> After 0.6- to 1-g samples of polymer were equilibrated 14 days at 25 ± 1° in 100 ml volumes of 0.5*M* NaCl solutions, except d.

<sup>b</sup> Weight of polymer after equilibration/original weight of water-wet polymer.

<sup>c</sup> Average of five samples.

<sup>d</sup> Equilibrated four days, polymer about 50% hydrolyzed.

<sup>e</sup>  $K_d$  = Moles NaCl per kg H<sub>2</sub>O in polymer/moles NaCl per kg H<sub>2</sub>O in solution after equilibration (NaCl determined as Cl<sup>-</sup>).

TABLE II  
Reaction of Aqueous Solutes with Polymer<sup>a</sup>

Solute in 0.1 <i>N</i> aqueous solution	Swelling factor <sup>b</sup>	Exchange capacity <sup>c</sup>	Moles solute/ kg water in polymer	Dist. coef. $K_d$ <sup>d</sup>
Acetic acid	1.0	0.04	0.183	1.83
Sodium dihydrogen phosphate	1.0	0.02	0.031	0.31
Cupric acetate	1.1	1.10	0.093	1.84
Pyridine	4.1	—	—	—
Sodium acetate	5.4	0.8	0.067	0.67
Sodium bicarbonate	5.5	0.9	0.059	0.60
Disodium hydrogen phosphate	5.8	0.9	0.022	0.45
Ammonium hydroxide	9.3	1.4	0.085	0.84
Sodium carbonate	11.7	3.1	0.0245	0.51
Tetramethyl ammonium hydroxide	18.4	7.2	0.056	0.65
Sodium hydroxide	18.9	8.8	0.059	0.73
Cesium hydroxide	19.5	9.0	0.055	0.65
Lithium hydroxide	20.0	10.1	0.058	0.71

<sup>a</sup> Polymer samples, 0.5–1 g, equilibrated nine days in 100 ml of 0.1*N* solution at  $25 \pm 1^\circ$ .

<sup>b</sup> Weight of polymer after equilibration/original weight of water-soaked polymer.

<sup>c</sup> Meq per gram dry product in the hydrogen form.

<sup>d</sup>  $K_d$  = Moles solute per kg H<sub>2</sub>O in polymer/moles solute per kg H<sub>2</sub>O in solution after equilibration.

and the amount of solute in each cylinder. In the weak bases, the polymer cylinders swelled 4 to 6 times their original water-soaked weight (Table II). Their exchange capacities were somewhat less than 1 meq per g dry product. The strong bases (tetramethyl ammonium hydroxide, sodium hydroxide, cesium hydroxide, and lithium hydroxide) caused the cylinders to swell 18 to 20 times their original water-soaked weight. The largest exchange capacity, produced by lithium hydroxide, was 10.1 meq per g dry product in the H<sup>+</sup> form. Since the maximum exchange capacity would have been 12.7 if all the poly(hydroxypropyl acrylate) had been converted to poly(acrylic acid), it is apparent that the bulk of such conversion was effected.

The exchange capacity thus was simply a measure of the poly(hydroxypropyl acrylate) hydrolyzed. The extent of hydrolysis depended on the diffusion of the base into the polymer and on the strength of the base; the stronger the base, the greater was the amount of hydrolysis and the greater the swelling resulting from the attraction for water by the carboxylate salt group in the polymer.

Despite the tremendous swelling of the polymer occurring in the basic solutions listed in Table II, the base concentration in the cylinder was less than that of the soak solution. The distribution coefficient for the stronger bases was  $\sim 0.7$ . The  $K_d$  values varied from 0.45 for disodium hydrogen phosphate to 0.84 for ammonium hydroxide.

The distribution coefficients are a result of interactions in the system water–electrolyte–polymer; they reflect the differences in attractive or repulsive forces between each electrolyte and the functional groups in the polymer. The selective preference for water rather than electrolyte is apparent (particularly in the absence of hydrolysis) in all cases except for acetic acid and cupric acetate. Their  $K_d$  values of 1.8 (Table II) are indicative of highly specific interactions between polymer and these solutes. Of the rejected electrolytes, those which caused hydrolysis were not as effectively rejected because of the large volume of water imbibed by the carboxylate salt resulting from the

hydrolysis. The solution volume was so great that a large portion, beyond the range of the functional groups' rejective influence, was essentially composed of aqueous feed.

It should be possible to effectively change the distribution coefficients, particularly in neutral solutions wherein the polymer does not hydrolyze, by controlling the ion exchange capacity and the degree and type of crosslinking in the polymer. If the swelling factor were kept constant as the exchange capacity increased, the concentration of the electrolyte in the polymer should decrease. The swelling of the polymer can be controlled by increasing the number of crosslinks and by changing the type of crosslinker, e.g., ethylene glycol dimethacrylate will permit less swelling than tetraethylene glycol dimethacrylate. Thus, varying the polymer's exchange capacity and crosslinkage should markedly affect both the amount of electrolyte solution imbibed and the distribution coefficient of the electrolyte.

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