

Characterization of Polyelectrolyte Solutions

I. Molecular Fractionating on Ion Exchange Resins

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The screening effect of anion exchange resins upon a polyelectrolyte solution containing anions of varying size is discussed. In experiments with polystyrene sulphonic acid no change in this screening effect has been found when under equilibrium conditions resins of varying degree of cross-linking are used. However, a variation in the porosity of the resin gives a change in the screening properties; a resin of high porosity being able to retain larger ions as compared with a resin of low porosity.

Resins of varying porosity are used in an ion exchange battery for the fractionation, based on differing ion size, of polyelectrolyte solutions. The limitations of the method are pointed out.

Several years ago Samuelson¹ demonstrated that anion exchange resins have a screening effect on the ions in a solution of a polyelectrolyte. When such a solution is passed through a column containing an anion exchange resin, the ions whose size is large enough to prevent penetration into the resin structure will pass through together with any non-ionic components whereas low-molecular-weight anions are retained by the resin. This arbitrary separation into low and high-molecular-weight anions is governed by a number of experimental conditions. There are indications² that this method classifies a low-molecular-weight anion as one with the ionic size equal to or less than 30 Å. The use of this separation has been reported by many authors in later years.

As is pointed out in many papers^{3,4,5}, it would be reasonable to expect a change in the screening effect by varying the degree of cross-linking of the resin, *i. e.* a resin with low degree of cross-linking (highly swollen) should be able to retain larger ions than a resin with a normal degree of cross-linking. In the present paper it is shown that under the conditions obtained in a laboratory ion exchange column with a flow-rate of about 1 ml cm⁻²min⁻¹ there exists no difference in screening properties between anion exchange resins of varying

* The main part of the experimental work was done during 1953 at the College of Forestry in Syracuse, N.Y., U.S.A.

degree of cross-linking as far as a solution of polystyrene sulphonic acid is concerned. This means that under the conditions and in the system in question, a variation in the degree of cross-linking of the resin does not affect the screening properties. On the other hand, under non-equilibrium conditions a difference in screening properties between resins of different degree of cross-linking is obtained as a result of the differences in penetration rate between ions of varying size which are obtained when the degree of cross-linking is altered ⁶.

The above statements seem to be true for all resins of the translucent type. As demonstrated in the present paper, resins of the porous type (obtained from the Chemical Process Company, Redwood City, California, U.S.A., under the special trade name Porous Duolite) show, however, varying screening properties.

The promising results with the porous resins justified investigating them as possible fractionating agents for polyelectrolytes. Provided that a porous resin gives a sharp fractionation based on the degree of polymerisation or preferably the ionic size, the prime requisite for satisfactory fractionation exists.

EXPERIMENTAL

Materials

The resins. All the resins were ground and screened to a particle size 0.25–0.42 mm. The cation exchange resins were regenerated with 3 N hydrochloric acid and the anion exchange resins with a 2 N ammonium hydroxide solution.

The polyelectrolyte solution. The ammonium salt of sulphonated polystyrene, stated by the manufacturer to have an average molecular weight of about 10 000 was obtained from the Monsanto Chemical Company. The salt was dissolved in water and the free acid liberated by passing the solution through a column containing a cation exchange resin of the sulphonic acid type in the hydrogen form.

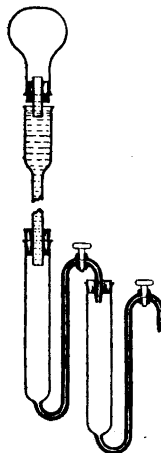


Fig. 1. Apparatus with two columns coupled in series and with arrangement for constant flow-rate through the system.

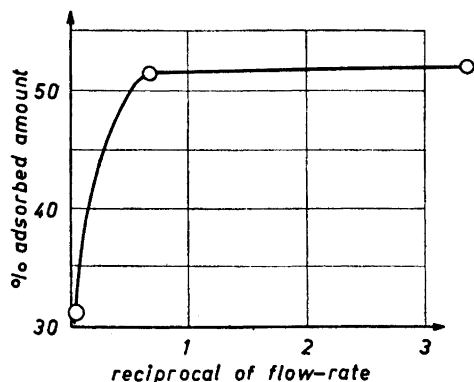


Fig. 2. The adsorbed amount of acid at different flow-rates. Column: Dowex 3.

Experiments

Fractionations with anion exchange resins of the translucent type. The separation of the polyelectrolyte into two fractions by the passage through an anion exchange column was studied under varying experimental conditions. For this study the weakly basic anion exchange resin Dowex 3 was used. The arrangements to get a constant flow-rate and to couple two columns in series are shown in Fig. 1. The polystyrene sulphonic acid liberated in the first column entered the second column, containing the anion exchange resin under study (Dowex 3). Part of the anions was adsorbed and the larger ions that were not adsorbed were found in the effluent. After washing the column with distilled water, the effluent plus the washings were titrated with 0.1 N sodium hydroxide solution using phenolphthalein as indicator. Knowing the amount of acid in the original solution, the adsorbed amount of acid was calculated by

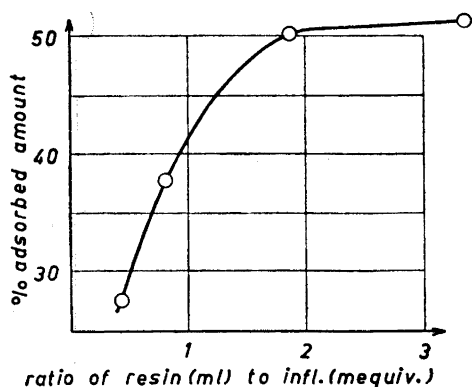


Fig. 3. Variation of the amount of adsorbed acid with varying ratios of resin to influent. Column: Dowex 3.

Table 1. Effect of resin cross linkage on ion adsorption. Influent: 2.8 % solution containing 1.38 mequiv acid; flow-rate: 1 ml min⁻¹; ratio resin (ml) to influent (mequiv): 7.

Type of resin	Degree of cross-linking	Amount of acid in the effluent, mequiv	Adsorbed acid as per cent of acid in influent
Dowex 1	about 8	0.645	53.2
» 1	1	0.652	52.8
» 1	10	0.654	52.6
Amberlite IRA-400	—	0.643	53.4
Amberlite IR-4B	—	0.647	53.1

difference. In some experiments this procedure was checked by elution with 1 N sodium hydroxide solution and estimation of the retained acids, and good agreement was obtained.

As is seen from Fig. 2, a flow-rate of 1 ml per min or lower represents equilibrium conditions. Furthermore, a resin to influent ratio of 2 or higher is needed to give a sharp fractionation, Fig. 3. The exchange capacity of the resin is about 0.5 mequiv/ml for this particular range of ionic size as compared with 2.7 mequiv/ml for really low-molecular-weight ions.

The same experimental technique was used in order to study the influence of the degree of cross-linking of the resin. In Table 1 the fractionation results are given for the strongly basic anion exchange resin (Dowex 1) against varying degrees of cross-linking which is given as per cent and is equal to the amount of divinylbenzene used in the polymerisation step in the preparation of the resin. In Table 1 two Amberlite resins are also included, one strongly basic (Amberlite IRA-400) the other weakly basic (Amberlite IR-4B).

As seen in Table 1 a variation from 1 to 10 in the degree of cross-linking does not give any difference, within experimental error, in the screening properties of the resin.

Fractionation with a combination of anion exchange resins of the translucent and of the porous type. With the same experimental conditions, porous resins adsorb a greater amount of acids from a given polyelectrolyte solution in comparison with translucent ones, and furthermore, there are resins with different acid retaining capacity, representing a variation in porosity. For one and the same resin, however, the capacity changes with the ratio resin (ml) to influent (mequiv) with the range that has been studied (Fig. 4). For fractionating on an absolute basis this is a very great draw-back that cannot be overcome but for comparative purposes, on a qualitative basis, this type of resin can be used to obtain a rapid answer as to the distribution of the degree of polymerisation for a polyelectrolyte.

As an illustration the following experiment was made. An exchange battery of the type illustrated in Fig. 1 was used with four columns coupled in series according to Fig. 5. In the first column the conversion to polystyrene

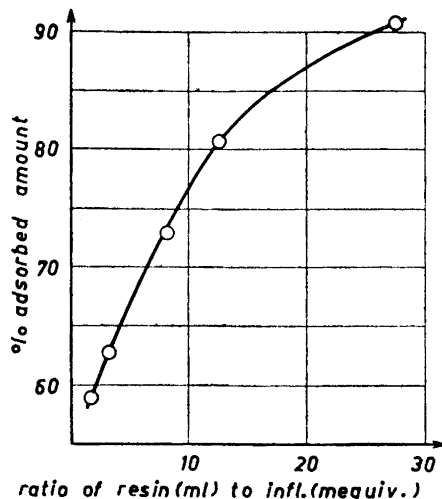


Fig. 4. Variation of the amount of adsorbed acid with varying ratios of resin to influent. Column: Duolite A2.

sulphonic acid occurred and in the last three columns the anions were selectively adsorbed. 50 ml of the polyelectrolyte solution containing 14.11 mequiv were passed through the battery followed by washing with distilled water. The effluent was collected, reference fraction 4, and the columns were separated. Each column was separately eluted with 100 ml 1 N sodium hydroxide solution with subsequent washing with distilled water. In order to remove excess of sodium hydroxide and to convert the salts into the corresponding acids, the collected eluates were passed through columns containing a sulphonic acid cation exchange resin in the hydrogen form. The processed eluate from column 2 was termed fraction 1, that from column 3 fraction 2, and that from column 4 fraction 3. The amount of acid in each fraction was then determined by titration with 0.1 N sodium hydroxide solution against phenolphthalein.

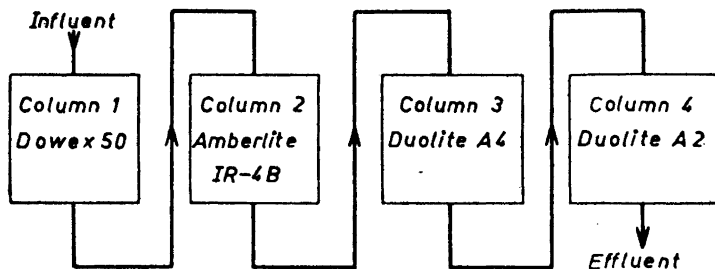


Fig. 5. Ion exchange battery for fractionation.

Table 2. Fractionation of a sample with an average molecular weight of 10 000. Influent: 50 ml containing 14.11 mequiv; flow-rate: 1 ml min⁻¹.

Fraction No.	Amount of acid		Specific viscosity at 25°C of a solution containing 8 mequiv per litre
	mequiv	%	
1	7.26	52.4	0
2	1.278	9.2	0.08
3	1.502	10.8	0.30
4	3.805	27.5	0.71
total	13.85	99.9	

An aliquot of each fraction was diluted to a concentration of 8 mequiv acid per litre and the specific viscosity was measured at 25°C in Ostwald viscometers. The results are given in Table 2.

There is no doubt that the procedure used separated the polystyrene sulphonic acid into fractions with gradually increasing molecular weight. However, as already pointed out, the great disadvantage is that the amount of acid in each fraction depends not only on the properties of the sample and of the resins used but also to a great extent on the experimental conditions.

The fractionating battery according to Fig. 5 gave results as reported in Table 2 for a sulphonated polystyrene with an average molecular weight of 10 000. Another sample of sulphonated polystyrene with a higher average molecular weight (70 000) has been fractionated on the same battery and with the same experimental conditions. The results are given in Table 3. As might be expected the polyelectrolyte with the higher average molecular weight gives smaller amounts of acid in fractions 2 and 3 and higher in fraction 4.

CONCLUSIONS

A variation in the degree of cross-linking from 1 to 10 % for the strongly basic anion exchange resin Dowex I did not cause any change in the screening properties of the resin (Table 1). This means that the various resins when used

Table 3. Fractionation of a sample with an average molecular weight of 70 000. Influent: 60 ml containing 15.60 mequiv acid; flow-rate: 1 ml min⁻¹.

Fraction No.	Amount of acid	
	mequiv	%
1	8.21	53.1
2	0.95	6.15
3	0.50	3.23
4	5.80	37.7
total	15.46	100.2

in excess in column operation, retained the same amount of acid from a given polystyrene sulphonic acid solution. It is further interesting to note that the same amount of acid is taken up also by the strongly basic resin (Amberlite IRA-400) and the weakly basic resin (Amberlite IR-4B).

It should be pointed out that the above observations have been made under equilibrium conditions, *i. e.* at a low flow-rate. Under non-equilibrium conditions, however, the uptake may very well be different for different resins of the translucent type.

As shown in Tables 2 and 3 porous resins with the general trade name Duolite can retain larger ions in comparison with translucent resins. If three columns containing resins of varying porosity are coupled in series, Fig. 5, this ion exchange battery can, as shown in Tables 2 and 3, be used for fractionating the polystyrene sulphonic acid. The solution to be analysed is passed through resins of successively increasing porosity. Each resin retains ions within a specific size range. Hence, a fractionation based on ionic size takes place.

The results from fractionations according to the proposed method can, however, only be used for comparative purposes, because the range of size of retained ions for a particular resin is not constant but varies with the ratio of the amount of resin to the amount of added ions.

REFERENCES

1. Samuelson, O. *Svensk Papperstidning* 46 (1943) 583.
2. Kumin, R. *Anal. Chem.* 21 (1949) 87.
3. Kressman, T. R. E. and Kitchener, J. A. *Discussions Faraday Soc.* 1949 No. 7, 90.
4. Partridge, S. M. *Nature* 169 (1952) 496.
5. Samuelson, O. *Ion exchange resins in analytical chemistry* John Wiley New York 1953.
6. Richardson, R. W. *J. Chem. Soc.* 1951 910.

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