Characterization of Polyelectrolyte Solutions

II. Separation of Strong and Weak Acids by means of Ion Exclusion

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Ion exclusion as applied to quantitative separation on a laboratory scale is described in detail. A separation based on ionic size of the acid components in sulphite waste liquor by means of ion exchange and on the basis of acid strength by means of ion exclusion reveals interesting facts as regards the composition of such a liquor.

The method as applied to a mixture of weak and strong acids gives information as to whether the weak acid groups are attached to the same or to separate molecules as the strong acid groups.

When an electrolyte solution is brought into contact with an ion exchange resin and the counter ions in the resin and in the solution are the same, no ion exchange takes place but a redistribution of the ions between the outer solution and the inner resin phase results. A strong electrolyte is excluded from the resin phase (usually by as much as a factor of 10), whereas a weak electrolyte will be almost evenly distributed. These phenomena have formed a basis for the development of a new technique termed ion exclusion ¹. The method is used for the separation of strong electrolytes from weak or non-electrolytes. As is evident, the main feature with ion exclusion as compared with ion exchange chromatography is that no regeneration of the resin is needed.

EXPERIMENTAL

A. Experiment to establish suitable experimental conditions

A mixture of hydrochloric and acetic acid was passed at constant flow-rate through an ion exchange column containing a cation exchange resin of the sulphonic acid type in the hydrogen form. The mixture was followed immediately by distilled water. The effluent was collected in small fractions and each fraction analysed for the total acid content by titration with sodium hydroxide solution. Furthermore, each fraction was tested for the presence of chloride ions.

¹ The main part of the work was done during 1953—54 at the College of Forestry in Syracuse, N.Y., U.S.A.

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A number of resins with varying degree of cross-linking and of varying particle size were tested, the effect of varying the ratio of influent volume to resin volume was examined and the flow-rate varied. Only with one type of resin and with one set of variables was the separation found to operate satisfactorily. These were: Dowex 50 with 4 % cross-linking and a particle size 50—100 mesh, a ratio of influent volume to resin volume of 1 : 7, and a flow-rate of 1 ml min⁻¹ cm⁻². A column was charged with 70 ml of such a resin in the hydrogen form and 10 ml of a solution containing 0.542 mequiv of hydrochloric acid and 0.528 mequiv of acetic acid was passed through, followed by distilled water. Fractions of 5 ml were collected and the acid concentration was plotted against the effluent volume, Fig. 1. After 50 ml had passed through the column, i.e. after the first peak in the curve, Fig. 1, no chloride was detected in the subsequent fractions. The total amount of acid between 25 and 50 ml effluent volume corresponded within experimental error, to the amount of hydrochloric acid in the influent, and a similar correspondence was found between the total amount of acid between 50 and 100 ml effluent volume and the amount of acetic acid in the influent.

Other mixtures of a strong and a weak acid have been tested and in all instances the strong acids have been found in the effluent fraction between 25—50 ml and the weak acids between 50—100 ml with the intermediate 50—10 ml containing no acid at all.

B. Ion exclusion and ion exchange as applied to the analysis of sulphite waste liquor

A mixture of strong and weak acid polyelectrolytes can be analysed both by means of ion exchange based on ionic size and by means of ion exclusion as described above. These methods were applied to a waste liquor from a laboratory sulphite paper pulp cook

Table 1. Analytical data for the various fractions. All measurements of optical density were made at a dilution of 1 : 5000.

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Description</th>
<th>Acidity</th>
<th>Optical density at 280 m(\nu)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Strong acids mequiv/ml</td>
<td>Weak acids mequiv/ml</td>
</tr>
<tr>
<td>a</td>
<td>Original liquor</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>b</td>
<td>Hydrogen ion exchanged liquor</td>
<td>0.315</td>
<td>0.113</td>
</tr>
<tr>
<td>c</td>
<td>Strong acids in fraction b</td>
<td>0.317</td>
<td>0.042</td>
</tr>
<tr>
<td>d</td>
<td>Weak acids in fraction b</td>
<td>—</td>
<td>0.063</td>
</tr>
<tr>
<td>e</td>
<td>High polymer acids in fraction b</td>
<td>0.169</td>
<td>0.063</td>
</tr>
<tr>
<td></td>
<td>after &quot;screening&quot; by ion exchange</td>
<td></td>
<td></td>
</tr>
<tr>
<td>f</td>
<td>Strong acids in fraction e</td>
<td>0.170</td>
<td>0.032</td>
</tr>
<tr>
<td>g</td>
<td>Weak acids in fraction e</td>
<td>—</td>
<td>0.055</td>
</tr>
</tbody>
</table>

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Fig. 2. Potentiometric titration plot according to Gran for fraction c (Table 1).

on spruce. The metal cations in the liquor were first replaced by hydrogen ions by using a cation exchange resin of the sulphonie acid type (resulting in fraction b, Table 1). Part of this acid fraction was passed through a column containing the weakly basic anion exchange resin, Amberlite IR-4B. The high polymer acids were found in the effluent (fraction e, Table 1), whereas the low-molecular-weight acids were adsorbed by the resin. By means of the ion exclusion technique described above the original hydrogen ion exchanged liquor (fraction b) and the high polymer acid fraction (fraction e) were each separated into two fractions, viz. the strong acid fraction and weak acid fraction. The various fractions were analysed for the total content of acid by potentiometric titration with 0.1 N sodium hydroxide solution and for lignin content by measuring the optical density in a Beckman spectrophotometer, model DU, at 280 nm after suitable dilution. The results from the potentiometric titrations were evaluated according to the Gran method in order to determine separately the weak and strong acids. The results are given in Table 1.

In fraction c and f only strong acids should be present but when a molecule contains strong as well as weak acid groups, the latter will necessarily be found in the strong acid fraction. The potentiometric titration diagrams are given in Fig. 2 for fraction c and in Fig. 3 for fraction d. The abnormal shape of the curve in Fig. 2 between pH 7 and 10 is caused by the alkaline consumption of the originally present phenolic groups as well as those formed during the titration. The weak acid fraction, Fig. 3, does not contain any appreciable amount of strong acids and in addition the curve shows normal behaviour in the alkaline pH-range.

DISCUSSION

Although the necessary conditions to obtain a satisfactory separation by means of ion exclusion require the maintenance of rather critical experimental variables within narrow limits, the method operates very well according to the procedure described above. This method is most useful when a separation of weak and strong electrolytes is desired for purification purposes. The method also gives information as to whether the weak acid groups are attached to the same molecule as the strong acids or whether they belong to separate molecules. In the former case the weak acid groups appear in the strong acid fraction but in the latter case they are found in the weak acid fraction.

The results reported in Table 1 show that the lignin sulphonic acids are found quantitatively in the high polymer fraction and in the strong acid frac-

tions. From this it can be concluded that all the lignin sulphonic acids are of high polymer nature. Similar experiments with a waste liquor from a sulphite rayon pulp cook show that the lignin sulphonic acids in this instance are partly of a low-molecular-weight nature, i.e. they are partly retained by an Amberlite IR4B resin. Further, it can be concluded from the results in Table 1 that only about 50% of the strong acids in the liquor are of a high polymer nature and that the high polymer molecules containing strong acid groups also contain about 15% weak acid groups. The liquor contains about 15% of molecules containing only weak acid groups (calculated on an acidity basis).

REFERENCES


Received April 10, 1957.

Acta Chem. Scand. 11 (1957) No. 7