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Utilization of Ion Exchangers in Analytical Chemistry

XXIX. Sorption and Elution of Some Low-Molecular-Weight Organic Acids

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The sorption and elution of glycolic, oxalic, pyruvic, gluconic, maleic, and *p*-toluenesulfonic acids using the strongly basic resin Dowex 2 (acetate form) and the weakly basic resin Dowex 3 (free-base form) have been studied. All acids except gluconic acid can be taken up quantitatively by the resins.

Glycolic, oxalic, gluconic, and maleic acids can be quantitatively displaced from both types of resins by means of sulfuric acid or ammonium carbonate. From the strongly basic resin, pyruvic acid can be displaced quantitatively only by means of acid elutriants. The elution of this acid from the weakly basic resin is in no case quantitative. Hydrochloric acid is the most effective elutriant for *p*-toluenesulfonic acid when the strongly basic resin is concerned, whereas the weakly basic resin is most easily regenerated with sodium hydroxide.

Several authors have used anion exchange resins for the isolation of organic acids. The results are summarized in Samuelson's monograph [1]. This topic has also been studied in some more recent papers [2-6]. The uptake of the acids does not seem to have caused any troubles whereas in some cases it has been reported that the recovery in the elution step is incomplete. Most authors have been interested in the chromatographic separation of different acids from each other. Very little attention has been given to the question of whether the recovery in the regeneration step can, from an analytical point of view, be considered as quantitative. For this reason it seemed to be appropriate to study in greater detail the uptake and especially the elution of different types of organic acids.

EXPERIMENTAL TECHNIQUE

Ion Exchange Column. The ion exchange column was of common construction (Ref.[1], Fig. 23). The diameter and length of the resin bed were 9 mm and 170 mm. The resin had the particle size 0.20—0.30 mm in an air-dry condition. The acetate form of the resin was prepared by passing 400 ml *M* sodium acetate solution through the column and sub-

sequent washing with water. In order to transform the resin into the free-base form it was instead treated with the same amount of *M* sodium hydroxide solution, precautions being taken to exclude carbon dioxide. Dowex 2 was regenerated according to the ordinary column technique whereas the regeneration of Dowex 3 was achieved by a combined batch and column operation to avoid channeling due to the swelling of the resin. Fifty ml of the elutriant was placed in the funnel attached to the column. After placing a stopper in the upper end of the funnel the column was shaken in order to transfer the resin into the funnel. The resin was then allowed to settle in the column and the elutriant passed through.

The resins are not quite stable in water and interference occurred because of dissolution of resin material. In order to eliminate as far as possible this source of error the resin was conditioned with 500 ml *M* sodium hydroxide solution and afterwards with 500 ml of the elutriant. The conditioning was repeated several times.

In all experiments the added amount of acid was about 2 meq and the flow rate about 2 ml/min. All figures given in the tables are expressed in per cent of the added amount.

Determination of the Acids. Glycolic, gluconic, and maleic acids were determined by oxidation with dichromate in sulfuric acid solution according to the following scheme.

$$\begin{aligned} C_2H_4O_3 + 3\ O &\longrightarrow 2\ CO_2 + 2\ H_2O \\ C_6H_{12}O_7 + 11\ O &\longrightarrow 6\ CO_2 + 6\ H_2O \\ C_4H_4O_4 + 6\ O &\longrightarrow 4\ CO_2 + 2\ H_2O \end{aligned}$$

The equivalent weights of glycolic, gluconic, and maleic acids are 1/6, 1/22 and 1/12 of the molecular weights, respectively.

The acid was introduced into a 1-liter flask and 0.5 *N* $K_2Cr_2O_7$-solution, to an excess of at least 1 meq, was added from a micro-buret. After addition of water to 60 ml volume, 100 ml conc. sulfuric acid was added under shaking. The flask was allowed to stand for 30 min and then cooled. After adding 500 ml distilled water, the flask was again cooled to room temperature. The excess potassium dichromate was determined in the usual manner by adding potassium iodide and titrating with sodium thiosulfate. In control experiments with the pure acids, the error was in all cases less than 0.5 %.

Oxalic acid was determined by oxidation with permanganate. Pyruvic acid was analyzed according to a colorimetric method [7]. *p*-Toluenesulfonic acid was determined spectrophotometrically in ultraviolet at 260 mμ. The spectrophotometric readings were made with a Beckman spectrophotometer model DU.

Blank experiments were run in order to obtain a correction for the dissolution of organic matters from the resin. The correction was in no case greater than 2 %.

RESULTS

The experiments with glycolic, oxalic, pyruvic, maleic, and *p*-toluenesulfonic acids show that all these acids can be taken up quantitatively by the acetate form of a strongly basic resin and by the free-base form of a weakly basic resin. The uptake of gluconic acid is incomplete with both types of resin. The amount of acid which passes through the column is indicated under the Tables 1 and 2. The fact that gluconic acid is not retained quantitatively is explained by the presence of lactones.

The results presented in Tables 1 and 2 show that glycolic, oxalic, gluconic, and maleic acids can be easily displaced from both types of resins by means of 0.5 *M* sulfuric acid or 0.5 *M* ammonium carbonate solutions. As can be seen from Table 3, oxalic acid is eluted with 150 ml of *M* HCl, 0.5 *M* H_2SO_4, 0.5 *M* $(NH_4)_2SO_4$, 0.5 *M* $(NH_4)_2CO_3$, or *M* NaOH.

The behavior of pyruvic and *p*-toluenesulfonic acids is much more complicated. Table 4 shows that pyruvic acid is recovered quantitatively from the strongly basic resin with hydrochloric acid or sulfuric acid, whereas unsatis-

Table 1. Elution of acids from the strongly basic resin Dowex 2 (acetate form).

Acid	Elution with 150 ml 0.5 *M* H_2SO_4 %		Elution with 150 ml 0.5 *M* $(NH_4)_2CO_3$ %	
Glycolic acid	99.0;	99.8	99.1;	99.5
Oxalic acid	99.2;	99.3	99.8;	100.2
Pyruvic acid	99.3;	99.9	55.9;	58.9
Gluconic acid *	76.8;	77.0	78.8;	76.6
Maleic acid	99.5;	100.1	99.7;	99.9
p-Toluenesulfonic acid	1.2;	2.0	0.0;	0.0

* The amount of gluconic acid in the effluent from the sorption step was 22.8, 23.0, 23.1, and 23.1 % respectively.

Table 2. Elution of acids from the weakly basic resin Dowex 3 (free-base form).

Acid	Elution with 150 ml 0.5 *M* H_2SO_4 %		Elution with 150 ml 0.5 *M* $(NH_4)_2CO_3$ %	
Glycolic acid	99.0;	99.4	99.1;	99.7
Oxalic acid	99.4;	100.2	99.3;	99.7
Pyruvic acid	24.2;	30.9	27.6;	28.9
Gluconic acid *	79.4;	78.6	79.6;	78.5
Maleic acid	100.0;	100.1	100.1;	100.1
p-Toluenesulfonic acid	25.6;	27.8	65.3;	68.9

* The amount of gluconic acid in the effluent from the sorption step was 20.1, 20.7, 20.1, and 20.6 % respectively.

Table 3. Elution of oxalic acid from the strongly basic resin Dowex 2 (acetate form) and the weakly basic resin Dowex 3 (free-base form) with 150 ml of different elutriants.

Elutriant	Elution from Dowex 2 %		Elution from Dowex 3 %	
M HCl	99.4;	100.0	99.7;	100.3
0.5 *M* H_2SO_4	99.4;	99.3	99.4;	100.2
0.5 *M* $(NH_4)_2SO_4$	99.7;	99.9	100.0;	100.1
0.5 *M* $(NH_4)_2CO_3$	99.8;	100.2	99.6;	99.7
M NaOH	100.1;	100.1	99.8;	100.1

factory results are obtained with the other elutriants. From the free-base form of the weakly basic resin, pyruvic acid can be removed only to a limited extent even when large quantities and high concentrations of the elutriants are used.

Table 4. Elution of pyruvic acid from the strongly basic resin Dowex 2 (acetate form) and the weakly basic resin Dowex 3 (free-base form).

Elutriant	Elution from Dowex 2 %		Elution from Dowex 3 %	
150 ml *M* HCl	99.6;	99.8	29.1;	34.3
300 ml *M* HCl	—		20.7;	29.5
500 ml *M* HCl	—		35.0;	36.8
150 ml 3 *M* HCl	—		24.6;	26.4
150 ml 0.5 *M* H_2SO_4	99.3;	99.9	24.4;	30.9
300 ml 0.5 *M* H_2SO_4	—		21.7;	24.6
500 ml 0.5 *M* H_2SO_4	—		32.9;	35.0
150 ml 1.5 *M* H_2SO_4	—		26.4;	26.4
150 ml 0.5 *M* $(NH_4)_2SO_4$	91.0;	94.8	23.6;	26.0
300 ml 0.5 *M* $(NH_4)_2SO_4$	88.9;	89.7	23.8;	24.6
500 ml 0.5 *M* $(NH_4)_2SO_4$	89.0;	89.9	30.5;	32.3
150 ml 1.5 *M* $(NH_4)_2SO_4$	86.4;	90.6	9.4;	12.4
150 ml 0.5 *M* $(NH_4)_2CO_3$	55.9;	58.9	27.6;	28.9
300 ml 0.5 *M* $(NH_4)_2CO_3$	63.0;	64.6	17.7;	24.6
500 ml 0.5 *M* $(NH_4)_2CO_3$	68.3;	70.9	33.7;	36.4
150 ml 1.5 *M* $(NH_4)_2CO_3$	32.7;	35.4	16.5;	19.7
150 ml *M* NaOH	82.7;	84.6	21.1;	30.9
300 ml *M* NaOH	84.6;	86.6	27.0;	27.0
500 ml *M* NaOH	85.0;	86.4	39.4;	40.6
150 ml 3 *M* NaOH	63.0;	66.9	14.8;	20.7

In separate experiments it was observed that the strongly basic resin, used for the uptake of pyruvic acid and subsequently treated with ammonium sulfate, could not be regenerated with hydrochloric acid. No traces of pyruvic

Table 5. Elution of p-toluenesulfonic acid from the strongly basic resin Dowex 2 (acetate form) and the weakly basic resin Dowex 3 (free-base form).

Elutriant	Elution from Dowex 2 %		Elution from Dowex 3 %	
150 ml *M* HCl	0.8;	2.2	21.9;	24.1
300 ml *M* HCl	32.4;	33.8	44.4;	46.8
500 ml *M* HCl	70.1;	72.8	71.3;	72.9
150 ml 0.5 *M* H_2SO_4	1.2;	2.0	25.6;	27.8
300 ml 0.5 *M* H_2SO_4	10.1;	11.4	44.0;	45.0
500 ml 0.5 *M* H_2SO_4	40.5;	41.3	62.0;	63.6
150 ml 0.5 *M* $(NH_4)_2SO_4$	0.0;	0.0	25.7;	29.1
300 ml 0.5 *M* $(NH_4)_2SO_4$	0.0;	0.0	35.8;	36.6
500 ml 0.5 *M* $(NH_4)_2SO_4$	0.0;	0.0	44.6;	45.5
150 ml 0.5 *M* $(NH_4)_2CO_3$	0.0;	0.0	65.3;	68.9
300 ml 0.5 *M* $(NH_4)_2CO_3$	0.0;	0.0	76.3;	79.4
500 ml 0.5 *M* $(NH_4)_2CO_3$	0.0;	0.0	82.9;	86.8
150 ml *M* NaOH	0.6;	1.4	94.9;	98.6
300 ml *M* NaOH	7.3;	9.2	99.9;	100.0
500 ml *M* NaOH	29.3;	30.6	—	

Table 6. Elution of p-*toluenesulfonic acid from the strongly basic resin Dowex 2 (acetate form) with 250 ml hydrochloric acid of different concentration.*

Elutriant concentration	Elution %
1 *M*	39.3
2 *M*	61.6
3 *M*	81.5
4 *M*	83.4
6 *M*	81.3

acid could be detected in the effluent from the regeneration step when the solution was investigated by the colorimetric method. Similar experiments in which the resin was treated with ammonium carbonate or sodium hydroxide instead of ammonium sulfate gave the same results. In some experiments with pyruvic acid, the determinations were made by an alkalimetric titration. The results indicate that the incomplete recovery of pyruvic acid is due to a decomposition of the acid during the ion exchange cycle.

The data given in Table 5 show that, for the elution of *p*-toluenesulfonic acid from the strongly basic resin, hydrochloric acid is more effective than sulfuric acid and sodium hydroxide. It is interesting to note that no traces of the acid have been detected in the effluent after treatment with large amounts of ammonium sulfate and ammonium carbonate solutions in the elution step. The influence of the strength of hydrochloric acid used as elutriant for *p*-toluenesulfonic acid has been studied. The results are given in Table 6. As can be seen from the table, 3 *M* hydrochloric acid is an effective elutriant. As a complement to the data presented in the tables two elutions with 500 ml 3 *M* hydrochloric acid were performed. The recovery was 100.0 % in both experiments.

From the weakly basic resin, *p*-toluenesulfonic acid is eluted quantitatively by means of sodium hydroxide solution (Table 5). The other elutriants investigated are less effective and are unsatisfactory for practical use.

Separate experiments show that *p*-toluenesulfonic acid is not fixed in an irreversible manner by any of the elutriants used in the present investigation. After the passage of 150 ml of the elutriants giving an incomplete elution from the strongly basic resin, a quantitative displacement is achieved on subsequent treatment with 500 ml 3 *M* hydrochloric acid. In similar experiments with the weakly basic resin a complete recovery is obtained by final displacement with 300 ml *M* sodium hydroxide.

As already mentioned gluconic acid is not taken up quantitatively under the conditions used in the experiments described above. A quantitative uptake of gluconic acid can be achieved by passing a solution of the sodium salt through a column filled with a strongly basic resin in the acetate form. From an acid solution, gluconic acid can be conveniently taken up by shaking the solution with an excess of the free-base form of the weakly basic resin for 24 h. The acid can then be eluted completely with 150 ml 0.5 *M* H_2SO_4 from both the strongly basic and the weakly basic resin.

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