

## Utilization of Ion Exchangers in Analytical Chemistry

### XIX. Separation of Aldehydes and Ketones from Organic Acids

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In a previous paper<sup>1</sup> it has been shown that aldehydes and ketones are taken up quantitatively in a column containing an anion exchanger in the bisulphite form. The adsorption occurs under the formation of  $\alpha$ -oxysulphonic acids. It was shown that in this way aldehydes can be separated from alcohols; the alcohol passes into the filtrate and may be easily washed out with water, while the aldehyde is retained in the column.

The aim of the present work is to study the separation of aldehydes and ketones from organic acids by means of anion exchangers. The anion exchanger must be in such a form that the resin retains acids but does not react with aldehydes and ketones. Investigations have been performed with anion exchangers in free base form, in chloride form, and in bicarbonate form. The compounds investigated were formaldehyde, acetaldehyde, furfural, benzaldehyde, salicylaldehyde, vanillin, crotonic aldehyde, glyoxal, acetone, and methyl-ethyl-ketone.

#### A. ANION EXCHANGERS

Experiments have been performed with anion exchangers of strongly basic type (Amberlite IRA-400 and Dowex 2, cross-linking 4 %) as well as with resins of weakly basic type (Amberlite IR-4B and Amberlite IR-45). A particle size of 0.12–0.30 mm in air dried condition has been used for all resins except for Dowex 2, where the particle size was 0.12–0.25 mm.

Anion exchangers of the strongly basic type have been used in the free base form as well as in the chloride and the bicarbonate form. The ion exchanger was transformed into the hydroxyl form by passing 400 ml 1 *M* sodium hydroxide solution through the column and subsequent washing with water (about 500 ml) until the effluent was neutral against phenolphthalein.

The anion exchangers of the weakly basic type were treated with 400 ml 1 *M* sodium carbonate solution and carefully washed with water.

In the experiments with anion exchangers (Amberlite IRA-400) in the chloride form the resin was saturated with chloride ions by percolating 400 ml 1 *M* sodium chloride solution followed by 200 ml 0.1 *M* hydrochloric acid through the resin bed. Subsequently the resin was washed with water until chloride could not be detected in the effluent.

The transformation into the bicarbonate form was performed by passing 400 ml 1 *M* sodium bicarbonate solution through the column (Amberlite IRA-400) and subsequent rinsing with water.

## B. EXPERIMENTAL METHOD

Most experiments have been performed with aldehydes and ketones without the presence of acids in order to study the behaviour of the carbonyl compounds. Ordinary column operation has been used in these experiments. The diameter and height of the column was 9.8 and 140 mm respectively.

50 ml of a solution containing 4.1 meg aldehyde or ketone were allowed to pass through the filter layer. (When benzaldehyde and salicylaldehyde were used in water solution the amounts of these aldehydes were smaller because of the low solubility of these aldehydes.) After the passage of the solution, the ion exchanger was washed with water to give a total effluent volume of 100 ml. The amount of aldehyde resp. ketone in this solution was determined. The resin was then washed with further 300 ml of water and the aldehyde resp. ketone in this filtrate was determined. The flow-rate was about 2 ml/min. In the experiments with the anion exchanger in the bicarbonate form with aldehydes in the presence of acids a modified method was used, which is described in Section F.

## C. ANALYTICAL METHODS

The determinations of aldehydes and ketones were in most cases made spectrophotometrically in ultra-violet light with Beckman spectrophotometer. The method cannot be adopted for glyoxal and formaldehyde, which do not show any absorption in ultra-violet. Glyoxal was determined colorimetrically according to Ariyama<sup>2</sup> and formaldehyde according to the chromotropic acid method<sup>3,4</sup>. As a control, colorimetric determinations were also used for furfural<sup>5</sup>, crotonic aldehyde<sup>6</sup>, and acetaldehyde<sup>7</sup>.

## D. EXPERIMENTS WITH ANION EXCHANGERS IN THE FREE BASE FORM

The simplest method would be to perform the separation by means of an anion exchanger in free base form. In this case the acids would be adsorbed and the aldehydes and ketones obtained in water solution free from ions, which could interfere with their determination. The results from adsorption experiments with aldehydes and ketones on an anion exchanger of strongly basic type (Amberlite IRA-400) are given in Table 1.

As the table shows the ketones have been recovered quantitatively in the filtrate. Of formaldehyde, furfural, and benzaldehyde 10–20 per cent have not been found in the effluent, probably due to a polymerization at the passage

Table 1.

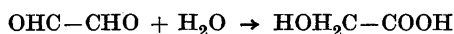
	A d d e d		Per cent of added aldehyde or ketone in the effluent	
	g	meg.	at 100 ml effluent	at 400 ml effluent
Formaldehyde	0.123	4.1	50.0	79.4
Acetaldehyde	0.181	4.1	See below.	
Furfural	0.394	4.1	74.0	85.5
Benzaldehyde in water	0.13	1.2	62.4	88.4
Benzaldehyde in 25 % alcohol	0.435	4.1	66.2	88.8
Salicylaldehyde in water	0.234	1.9	0.02	0.025
Salicylaldehyde in 25 % alcohol	0.50	4.1	0.015	0.02
Vanillin	0.62	4.1	0.010	0.015
Crotonic aldehyde	0.29	4.1	26.9	37.7
Glyoxal	0.12	4.1	<0.05	<0.20
Acetone	0.238	4.1	97.2	100.8
Methyl-ethyl-ketone	0.295	4.1	96.1	100.3

through the ion exchanger, which in hydroxyl form behaves as a strongly alkaline solution.

On passing solutions of crotonic aldehyde and acetaldehyde through the resin bed a considerable polymerization of the aldehydes seems to occur. In both cases the ion exchanger was strongly darkened after passage of the aldehyde solutions. Only 37 per cent of the ingoing amount of crotonic aldehyde was found in the effluent. For acetaldehyde an examination of the effluent in an ultra-violet spectrophotometer showed that the absorption of the filtrate was ten times stronger than that of the original solution. This may be explained by the known tendency of acetaldehyde to form cyclic compounds; such compounds have generally considerably stronger absorption in ultra-violet than the aliphatic compounds.

Salicylaldehyde and vanillin are taken up quantitatively by the resin in free base form. These two aldehydes contain a phenolic group, which may explain the quantitative retention, as this resin type is known to adsorb phenols<sup>8</sup>.

Also glyoxal is retained quantitatively by the ion exchanger. It is known that in alkaline medium glyoxal undergoes Cannizzaro's reaction even at room temperature, under formation of glycollic acid, according to the formula<sup>9</sup>:



If this reaction occurs when glyoxal comes in contact with the resin the glycollic acid should be adsorbed in the column. The following experiment shows that this explanation holds true.

1 g glyoxal in water solution was percolated through a layer of Amberlite IRA-400 (diam. 20 mm, height 180 mm), saturated with hydroxyl ions. After washing with water 200 ml 1 M NaHCO<sub>3</sub> solution was percolated through the resin layer; in the filtrate glyoxal could not be detected. The sodium ions were removed by passing the solution through a cation exchanger (Amberlite IR-120) saturated with hydrogen ions; during the filtration, part of the carbonic acid was removed; the rest of the carbonic acid was driven off by boiling the solution under reflux cooling. Afterwards the solution was percolated through a carboxylic cation exchanger (Amberlite IRC-50), saturated with barium ions, in order to transform the acid to the barium salt. After rinsing with water the filtrate was evaporated to a small volume and the barium salt precipitated in 95 per cent ethanol. The yield was 96 per cent of the calculated value. The salt was analysed and the following values were obtained.

	Found	Calculated for barium glycolate
C:	16.85	16.71
H:	2.24	2.12
Ba:	47.95	47.79

As seen from the above various complications occur if aldehydes are percolated through a strongly basic anion exchanger, saturated with hydroxyl ions. Such ion exchangers are therefore unsuitable to separate aldehydes from organic acids. On the other hand they can be used for separation of ketones from organic acids.

The complications with the aldehydes may be ascribed to the strongly basic groups of Amberlite IRA-400. It was therefore of interest to study the possibility of obtaining better results if anion exchangers of a weakly basic type were used. Therefore experiments were performed with the weakly basic ion exchangers Amberlite IR-4B and Amberlite IR-45. 4.1 meg. of furfural in water solution were percolated through these anion exchangers as before. In the filtrate from IR-B only 60 per cent of the added amount furfural was recovered. In the filtrate from IR-45 only traces of furfural could be detected. This ion exchanger, which before the experiments was light yellow in colour, darkened after the passage of the furfural solution.

While the anion exchangers of strongly basic type contain quaternary ammonium groups those of weakly basic type contain amino groups, *e. g.* —NH<sub>2</sub> and —NHR. It may be concluded that furfural reacts with amino groups of the latter type of resin under the formation of condensation products of the same type as the Schiff's bases.

## E. EXPERIMENTS WITH ANION EXCHANGERS IN THE CHLORIDE FORM

The behaviour of solutions containing aldehydes and ketones on passing through a column containing an anion exchanger (strongly basic type) in the chloride form has also been investigated. The experimental method was the same as described above. The results are presented in Table 2.

Table 2.

	A d d e d		Per cent of added aldehyde or ketone in the effluent	
	g	meg	at 100 ml effluent	at 400 ml effluent
Formaldehyde	0.123	4.1	73.0	99.2
Acetaldehyde	0.181	4.1	90.0	100.9
Furfural	0.394	4.1	80.4	101.0
Benzaldehyde in water	0.13	1.2	19.3	95.7
Benzaldehyde in 25 % alcohol	0.435	4.1	23.0	96.0
Salicylaldehyde in water	0.234	1.9	25.6	89.9
Salicylaldehyde in 25 % alcohol	0.50	4.1	24.2	90.0
Vanillin	0.62	4.1	21.8	70.3
Crotonic aldehyde	0.29	4.1	98.2	98.5
Glyoxal	0.12	4.1	79.6	82.5
Acetone	0.238	4.1	97.0	99.2
Methyl-ethyl-ketone	0.295	4.1	96.7	100.4

As seen from the table formaldehyde, acetaldehyde, furfural, crotonic aldehyde, and the ketones have been recovered quantitatively or almost quantitatively in the filtrate whereas glyoxal and the aldehydes of higher molecular weight — salicylaldehyde, benzaldehyde, and vanillin — are much more difficult to wash out. It may be pointed out that in the experiments with benzaldehyde, salicylaldehyde, and vanillin the aldehyde concentration in the effluent reaches a maximum at an effluent volume of about 150 ml.

Most aldehydes and the ketones are thus only slightly adsorbed on an anion exchanger in the chloride form. An ion exchanger in this form therefore can be used to separate organic acids from most aldehydes and ketones. A disadvantage is, however, that the aldehyde and ketone solution as well as the solution which after regeneration contains the acids also contains chloride ions.

F. EXPERIMENTS WITH ANION EXCHANGERS IN THE  
BICARBONATE FORM

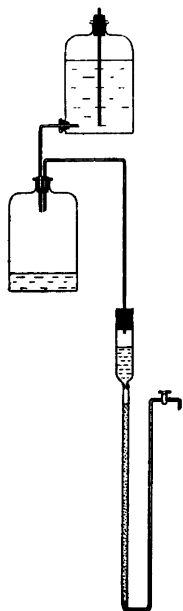


Fig. 1.

In preliminary experiments furfural solutions were percolated through layers of anion exchange resins (strongly basic type), saturated with carbonate or bicarbonate ions. It was shown that no adsorption occurred in the resin layers. In the following experiments an ion exchanger in bicarbonate form has been chosen as the pH is lower in the resin phase and therefore less risk of decomposition of the aldehydes would be at hand. The experimental method was the same as before. Only the flow-rate was increased to 8 ml/min. The results are given in Table 3. The apparatus presented in Fig. 1 was used in these experiments.

Table 3.

	Added		Per cent of added aldehyde or ketone in the effluent	
	g	meg	at 100 ml effluent	at 200 ml effluent
Formaldehyde	0.123	4.1	91.0	100.2
Acetaldehyde	0.181	4.1	100.0	100.0
Furfural	0.394	4.1	99.5	100.1
Benzaldehyde	0.13	1.2	60	100.6
Salicylaldehyde	0.234	1.9	<0.05	<0.1
Vanillin	0.62	4.1	<0.05	<0.1
Crotonic aldehyde	0.29	4.1	98.0	98.7
Glyoxal	0.12	4.1	99.0	99.4
Acetone	0.238	4.1	98.6	99.0
Methyl-ethyl-ketone	0.295	4.1	99.0	99.2

From the table it is seen that all aldehydes and ketones, with the exception of salicylaldehyde and vanillin, are quantitatively or almost quantitatively recovered in a filtrate volume of 200 ml. In the experiments with salicylaldehyde and vanillin carbon dioxide was evolved when the solutions were brought into contact with the resin. This means, that a reaction occurs between the bicarbonate ions and the phenolic group of these aldehydes. The aldehydes

are adsorbed due to their acidic character. If an acid was present in the aldehyde solution, it could be expected that part of the aldehyde should pass into the filtrate. This proved to be the case. On addition of 0.4 g acetic acid to the solution of the salicylaldehyde, 30 per cent of the aldehyde was recovered in 400 ml filtrate.

The experiments presented in Table 3 have been performed with Amberlite IRA-400. Other experiments showed that Dowex 2 (4 % cross-linking) behaved in the same manner.

From these experiments it may be concluded that a separation of aldehydes and ketones can be conveniently performed by using anion exchangers in the bicarbonate form. The aldehydes and ketones are determined in the effluent and the acids may be eluted with sodium carbonate solution. Experiments have been performed with solutions of formic acid and acetic acid containing formaldehyde and furfural.

It may be pointed out that it is not appropriate to percolate the acid solution directly through the column as the carbon dioxide evolved causes channeling in the resin bed and may even prevent the passage of the solution. Therefore the solution containing the carbonyl compound and the acid is first shaken in a beaker for  $\frac{1}{2}$ —1 minute with an anion exchanger in the bicarbonate form. The solution should not be shaken longer time than 1—2 minutes as for prolonged time of contact the aldehyde is difficult to wash out. From the beaker the solution and the resin are poured into an ion exchange column, containing a short layer, about 3 cm in height, of the anion exchanger. This resin layer takes up the last traces of the acid. In order to increase the flow-rate, the same method as before may be used (Fig. 1). The resin layer is subsequently washed with water to an effluent volume of 200 ml. In this filtrate the aldehydes are determined.

The acids, adsorbed on the ion exchanger, may afterwards be eluted by 100 ml 0.1 *M* sodium carbonate solution and subsequent washing with water. The eluate was shaken in a beaker with the cation exchanger Amberlite IR-120 in the hydrogen form in order to liberate the acids. To complete the reaction the solution and the resin were poured into a column in which there was a shallow layer of the same resin. After rinsing the column with water the effluent was boiled for ten minutes under reflux cooling in order to remove carbon dioxide. Afterwards the solution was titrated with 0.1 *N* NaOH against phenolphthalein.

The results presented in Table 4 show that the aldehydes can be quantitatively separated from the acids by means of an anion exchanger in the bicarbonate form. The acids may be eluted with carbonate solution and determined quantitatively.

Table 4.

A d d e d		F o u n d	
g acid	g aldehyde	g acid	g aldehyde
<i>Formic acid</i>	<i>Formaldehyde</i>		
0.138	0.280	0.138	0.277
0.173	0.277	0.172	0.277
0.173	0.197	0.174	0.197
<i>Acetic acid</i>	<i>Formaldehyde</i>		
0.388	0.200	0.384	0.199
<i>Acetic acid</i>	<i>Furfural</i>		
0.310	0.400	0.310	0.398
0.312	0.400	0.311	0.401

In some preliminary experiments an attempt was made to elute the acids with 0.1 *M* and 0.2 *M* sodium hydroxide solution and sodium bicarbonate solution. However, it was found that it was easier to obtain a quantitative elution by means of carbonate solution especially for formic acid.

#### SUMMARY

Experiments have been performed in order to investigate the possibility of separating aldehydes and ketones from organic acids by adsorbing the latter on anion exchangers. The experiments show that in many cases a quantitative separation cannot be obtained by means of anion exchangers in the free base form (strongly as well as weakly basic type) as the aldehydes react with the exchanger.

A quantitative separation can be performed with anion exchangers (strongly basic type) in the bicarbonate form, the acids being retained by the resin whereas the aldehydes and ketones remain in solution. The adsorbed acids are eluted with sodium carbonate solution. The acids are liberated by treating the solution with a cation exchanger (sulphonic acid type) in the hydrogen form.

The method cannot be used for solutions containing salicylaldehyde and vanillin which are adsorbed due to their phenolic hydroxyl groups.



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