Separation of Aromatic Sulfonic Acids with a Liquid Anion Exchanger

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Solutions of the hydrochloride of Alamine 336 in toluene strongly extract aryl sulfonic acids from aqueous solutions. Sulfuric acid is only slightly extracted and may be separated quantitatively from aromatic sulfonic acids. Several sulfonic acid mixtures were separated quantitatively on columns impregnated with Alamine 336. The behavior of aromatic sulfonic acids on a Teflon column containing Alamine in toluene may be predicted from batch distribution ratios.

THE SEPARATION of aromatic sulfonic acids from each other and from sulfuric acid constitutes an analytical problem of long standing. Separation of sulfuric acid by precipitation as barium sulfate is widely used to remove sulfate, but barium salts of sulfonic acids are likely to be coprecipitated. Separation of various sulfonic acids from each other by paper chromatography (*1–9*), thin-layer chromatography (*10, 11*), salting-out column chromatography (*12–17*), and gas chromatography (*18–20*) have been successful in some instances, but these methods have not been broadly applied.

Anion exchange resins sorb aromatic sulfonic acids so strongly that it is often difficult to elute them quantitatively from a column. We have found that high molecular weight amines, however, are well suited for the separation of aromatic sulfonic acids. One brief study (*21*) in the recent literature confirms this.

In the present work, it is shown that sulfuric acid may be separated from aromatic sulfonic acids by simple extraction with an organic solution of Alamine 336, a high-molecular weight tertiary amine. Distribution ratios for extraction of a number of sulfonic acids by Alamine 336 are given. Quantitative separation of several sulfonic acids from each other are achieved using columns filled with Alamine 336 on a solid support.

EXPERIMENTAL

Apparatus. A Bausch and Lomb Spectronic 600 spectrophotometer with a VOM-8 recorder was used for all spectrophotometric measurements. A Bausch and Lomb flow-through cell and matched borosilicate glass cuvettes with a one-centimeter path length were used.

Reagents and Solutions. Commercial Alamine 336 (tricapryl amine), obtained from General Mills, Inc., was used without further purification. All acids and organic solvents were analytical reagent grade.

A 5% solution of Alamine 336 hydrochloride was prepared by shaking a 5% (v/v) solution of Alamine 336 in toluene for 5 minutes with an equal volume of 6*M* hydrochloric acid and used with no further treatment.

Chromosorb W (nonacid washed, 80–100 mesh) was obtained from Johns-Manville Products Corp. This was washed with 6*M* hydrochloric acid until there was no evidence of iron present and then was rinsed with distilled water, acetone, and dried at 110 °C. Tee Six (Teflon), 60–100 mesh, was obtained from Analytical Engineering Laboratories, Inc., and used without further treatment.

Analytical Procedure. SULFONIC ACIDS. All sulfonic acids were determined spectrophotometrically in aqueous solutions using a distilled water blank.

SULFATE. Sulfate was titrated with barium(II) perchlorate in 80% methyl alcohol with an adsorption indicator, Thorin. The titrant was adjusted to an apparent pH of 3.5 with perchloric acid and the sample was adjusted to an apparent pH of 3.1 with perchloric acid or magnesium acetate.

Distribution Ratios. Distribution ratios were determined in the following manner: 20 ml of a solution containing 0.20 mmole of the sulfonic acid was pipetted into a 125-ml separatory funnel. Twenty milliliters of a 5% solution of Alamine 336 hydrochloride in toluene was added, and the phases were equilibrated for five minutes and allowed to separate. An aliquot from the aqueous phase was taken and diluted to be analyzed spectrophotometrically. The distribution ratios were then determined from the amount of sulfonic acid in the aqueous phase and the amount of sulfonic acid in the organic phase, found by difference.

Column Separation Procedures. The columns used for separations were prepared by two different methods. In the first method, acid washed Chromosorb W was added to a solution of Alamine 336 in ethyl ether. This solution was stirred with air passing over it until the last trace of ether had evaporated. A dry white powder resulted, which was slurried with 2*M* hydrochloric acid and added to a glass column. A glass wool plug was used to contain the support in the column. About 50 ml of 6*M* hydrochloric acid was passed through the column at a flow rate of 1 ml/min to prepare the Alamine 336 hydrochloride. Excess hydrochloric acid was removed with distilled water. A glass wool plug was placed at the top of the support to help stabilize the support when samples and eluents were added. The sulfonic acid sample mixture was prepared by adding 1 ml of each sulfonic acid (each dissolved in the first eluting solution) to the column with a micrometer burette. This was sorbed onto the support at a flow rate of 1 ml/min and the first

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Table I. Effect of HCl Concentration on Distribution Ratio of Sulfate and 2-Naphthol-8-Sulfonate

Equal volume of 5% Alamine 336 hydrochloride in toluene and 0.013*M* sodium sulfate or 0.01*M* 2-naphthol-8-sulfonic acid (sodium salt)

HCl	$D(SO_4^{2-})$	*D*(2-Naphthol-8-sulfonate)
0.01	0.333	317
0.1	0.0851	332
0.5	0.0324	170
1.0	0.0177	76.8
2.0	0.0142	36.0
4.0	0.0045	16.4
6.0	~0	8.97

Table II. Survey of Sulfonic Acids and Their Distribution Ratios

Equal volume of 5% Alamine 336 hydrochloride in toluene and 0.01*M* sulfonic acid—0.5*M* hydrochloric acid

Sulfonic acid	Wavelength mμ	Molar absorptivity	*D*
Sulfanilic acid	271	200	~0
2-Aminotoluene-5-sulfonic acid	273	750	~0
2-Aminotoluene-4-sulfonic acid	271	130	~0
4-Aminotoluene-2-sulfonic acid	275	745	0.0067
8-Amino-1-naphthol-3,6-disulfonic acid (monosodium salt)	340	5,120	0.0345
o-Aminobenzene sulfonic acid	271	270	0.0380
4,5-Dihydroxy-*m*-benzene disulfonic acid (disodium salt)	290	3,460	3.29
Sulfosalicylic acid	301	2,940	7.45
p-Toluene sulfonic acid	267	248	13.3
6,7-Dihydroxynaphthalene-2-sulfonic acid (sodium salt)	282	4,780	13.3
o-Sulfobenzoic acid (monoammonium salt)	272	760	14.4
1-Naphthol-5-sulfonic acid (sodium salt)	302	4,060	15.9
2-Naphthol-6,8-disulfonic acid (dipotassium salt)	289	5,700	16.1
4,5-Dihydroxy-2,7-naphthalene disulfonic acid	348	11,200	20.4
2-Naphthol-6-sulfonic acid (sodium salt)	282	4,860	30.7
2-Naphthol-8-sulfonic acid (sodium salt)	281	2,390	35.6
6-Thymol sulfonic acid	273	1,080	39.0
1-Naphthol-4-sulfonic acid (sodium salt)	298	4,330	43.7
2-Naphthol-3,6-disulfonic acid (disodium salt)	282	4,390	62.9
2-Amino-5-nitrobenzene sulfonic acid (sodium salt)	367	7,830	119
2-Naphthalene sulfonic acid	275	4,630	176
2,4-Dinitro-1-naphthol-7-sulfonic acid	284	10,700	298
2,4-Dinitrobenzene sulfonic acid	256	9,200	740

Table III. Batch Separation of 2-Naphthalene Sulfonic Acid from Sulfate

Equal volume of 5% Alamine 336 hydrochloride in toluene and 0.05*M* 2-naphthalene sulfonic acid–0.10*M* sulfuric acid–0.10*M* hydrochloric acid

	Taken, mmole	Found, mmole	% Recovery
2-Naphthalene sulfonic acid	1.000	0.971	97.1
Sulfate	1.975	1.987	100.6

component eluted at the same flow rate. Following the elution of the first sulfonic acid, the eluent was changed to elute the second component. The sulfonic acid recoveries were determined spectrophotometrically.

In the second method, Teflon was added to a 5% solution of Alamine 336 hydrochloride in toluene and allowed to stand for about 16 hours. This was then added to a glass column with a glass wool plug used to contain the support. The interstitial Alamine 336 hydrochloride in toluene was displaced by passing 2*M* hydrochloric acid which had been equilibrated with Alamine 336 hydrochloride through the column. The sulfonic acid sample mixture was again prepared by adding samples of each sulfonic acid (each dissolved in the first eluting solution) to the column with a micrometer burette. The remainder of the separation procedure for Teflon columns was the same as with the Chromosorb W columns.

A freshly packed column was used for each separation, although regeneration with sodium hydroxide and then 2*M* hydrochloric acid might be possible.

RESULTS

Distribution Ratios. Preliminary studies in which organic solutions of Alamine nitrate in various organic solvents were equilibrated with aqueous solutions of halide ions showed that good phase separations were obtained and reproducible distribution ratios could be obtained in toluene. Since nitrate interferes with UV spectrophotometric measurement of aryl sulfonates, a 5% solution of Alamine hydrochloride in toluene was used for all distribution ratio measurements and separations.

The distribution ratio for sulfate was determined as a function of the hydrochloric acid concentration in the aqueous phase. An equal volume of 5% Alamine 336 hydrochloride in toluene and 0.013*M* sodium sulfate was used. The distribution ratios are very low, as shown by Table I. Essentially the same study was carried out for 2-naphthol-8-sulfonic acid (sodium salt), resulting in much higher distribution ratios (see Table I).

The effect of chloride on the extraction of several aryl sulfonic acids by Alamine hydrochloride in toluene is illustrated in Figure 1. The slope of the plot for mono sulfonic acids is approximately minus one and that for disulfonic acids is minus two. These are the slopes that would be expected for exchange of mono- and di-valent anions. It thus appears that Alamine hydrochloride in toluene is functioning smoothly as a liquid anion exchanger.

Bromide is more tightly held by Alamine than chloride, hence the distribution ratios of sulfonic acids are smaller in the presence of added bromide. This effect is shown in Figure 2. Distribution ratios for sulfonic acids are still lower in the presence of perchlorate (see Figure 3 and Figure 4). In Figure 3, a constant amount of hydrochloric acid is present, while only perchloric acid is added in Figure 4. It will be seen that perchlorate lowers the distribution ratios sufficiently to permit back-extraction of aryl sulfonic acids.

The effect of increased sulfonic acid concentration on the distribution ratio was studied for 2-naphthalene sulfonic acid. The concentration of Alamine 336 hydrochloride in toluene was kept constant at 0.1 molar, and the aqueous phase was kept 0.3*M* sodium chloride–1.0*M* hydrochloric acid while the concentration of 2-naphthalene sulfonic acid was increased. The results of this loading study are given in Figure 5. Since the distribution ratio does not drop very rapidly until a 50% loading has been reached, this is an added advantage over standard solid ion exchangers. This high capacity makes Alamine 336 quite useful for large-scale separations.

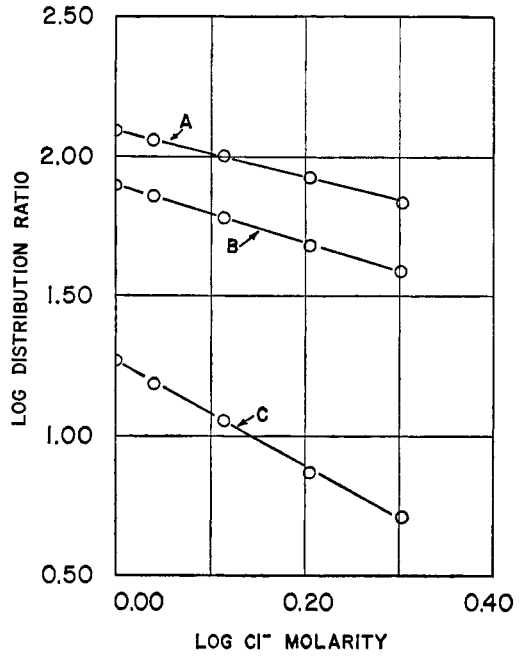

Figure 1. Effect of chloride concentration on the distribution ratio

2-Naphthalene sulfonic acid (A), 2-naphthol-8-sulfonic acid (B), and 2-naphthol-3,6-disulfonic acid (C). Equal volume of 0.01*M* sulfonic acid and 5% Alamine 336 hydrochloride in toluene.

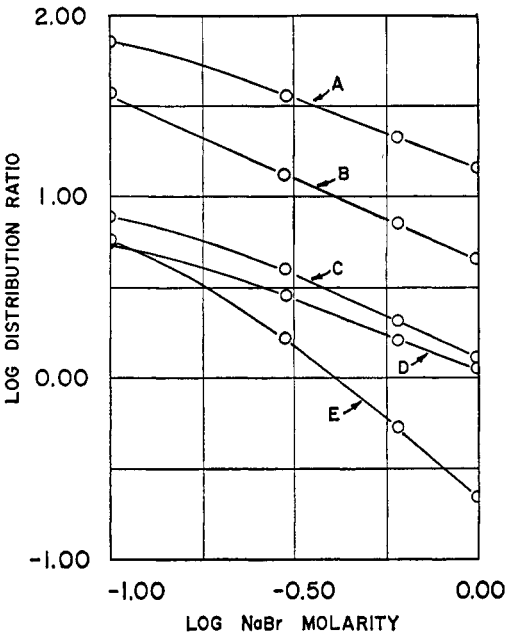

Figure 2. Effect of sodium bromide concentration on the distribution ratio

2-Naphthalene sulfonic acid (A), 2-naphthol-8-sulfonic acid (B), 2-naphthol-6-sulfonic acid (C), *p*-toluene sulfonic acid (D), and 2-naphthol-3,6-disulfonic acid (E). Equal volume of 0.01*M* sulfonic acid and 5% Alamine 336 hydrochloride in toluene. Aqueous phase was 1.0*M* HCl plus added NaBr.

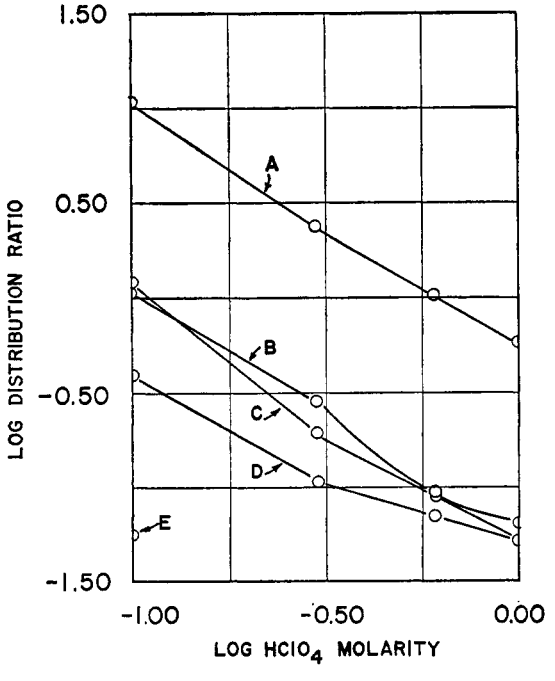

Figure 3. Effect of perchloric acid concentration on the distribution ratio

2-Naphthalene sulfonic acid (A), *p*-toluene sulfonic acid (B), 2-naphthol-8-sulfonic acid (C), 2-naphthol-6-sulfonic acid (D), and 2-naphthol-3,6-disulfonic acid (E). Equal volume of 0.01*M* sulfonic acid and 5% Alamine 336 hydrochloride in toluene. Aqueous phase was 1.0*M* HCl plus added $HClO_4$.

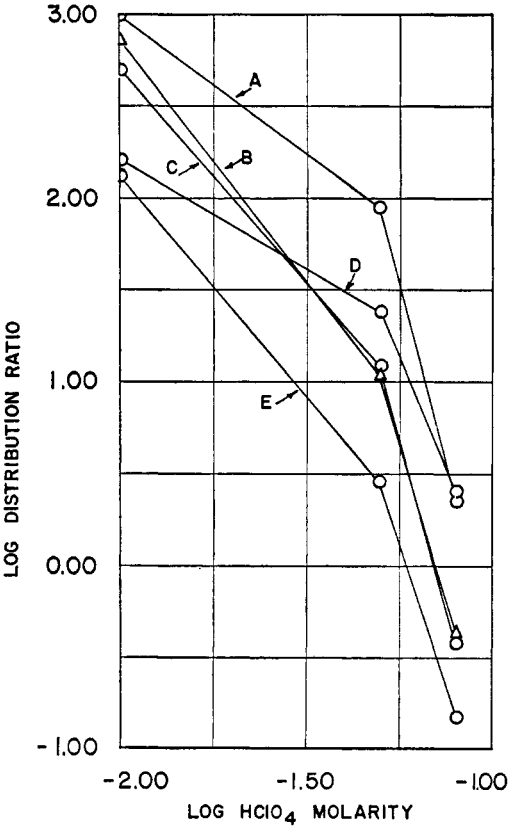

Figure 4. Effect of perchloric acid concentration on the distribution ratio

2-Naphthol-3,6-disulfonic acid (A), 2-naphthol-6, 8-disulfonic acid (B), 4,5-dihydroxy-2,7-naphthalene disulfonic acid (C), 2-naphthol-6-sulfonic acid (D), and 4,5-dihydroxy-*m*-benzene disulfonic acid (E). Equal volume of 0.01*M* sulfonic acid and 5% Alamine 336 hydrochloride in toluene. HCl absent.

A survey of the extraction behavior of 23 sulfonic acids was carried out under fixed conditions. The sulfonic acid solutions were 0.01*M* in sulfonic acid and 0.5*M* in hydrochloric acid, and an equal volume of 5% (v/v) Alamine 336 hydrochloride in toluene was used as the organic phase for the extractions. The results of this study are given in Table II.

Separation of Sulfonic Acids from Sulfate. The distribution ratios for sulfuric acid and for 2-naphthalene sulfonic acid in Table I indicate that it should be possible to separate these components by batch extraction. A mixture was prepared and was 0.05*M* 2-naphthalene sulfonic acid, 0.10*M* sulfuric acid, and 1.0*M* hydrochloric acid. A batch separation of an aqueous mixture of 2-naphthalene sulfonic acid and sulfate was accomplished with a single equilibration with an equal volume of 5% (v/v) Alamine 336 hydrochloride in toluene. The sulfate remained in the aqueous phase while the sulfonic acid was extracted by the Alamine 336 hydrochloride. The sulfonic acid was back-extracted into an aqueous 1.0*M* sodium hydroxide solution for analysis. This represented a 50% loading of 2-naphthalene sulfonic acid for the liquid anion exchanger, and an excellent recovery of sulfate-free 2-naphthalene sulfonic acid was obtained. The results of this separation are given in Table III. The distribution ratios in Table II for other sulfonic acids indicate that this separation of aryl sulfonic acid from sulfate should be broadly applicable. The separation should be useful in preparative work as well as for analysis.

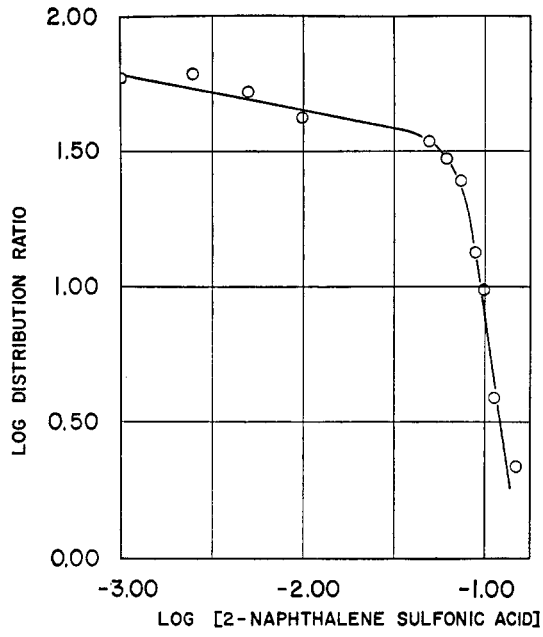

Figure 5. Effect of loading on the distribution ratio of 2-naphthalene sulfonic acid

Organic phase kept constant at 0.1*M* Alamine 336 hydrochloride in toluene and the aqueous phase was kept 0.3*M* NaCl–1.0*M* HCl while the concentration of 2-naphthalene sulfonic acid was increased.

Table IV. Quantitative Separations of Sulfonic Acids

Flow rate of 1.0 ml/min with a 1.3 × 11 cm column of Chromosorb W containing 1.00 ml of Alamine 336. Component (a) was eluted with 0.5*M* hydrochloric acid and component (b) was eluted with 1.0*M* perchloric acid–1.0*M* hydrochloric acid

Separation	Added, mmole	Found, mmole	% Recovery
I. a) Sulfonic acid	0.0500	0.0518	103.6
b) *p*-Toluene sulfonic acid	0.0500	0.0524	104.8
II. a) Sulfanilic acid	0.0500	0.0520	104.0
b) 2-Naphthol-3,6-disulfonic acid (disodium salt)	0.0500	0.0499	99.8
III. a) Sulfanilic acid	0.0500	0.0523	104.6
b) 4,5-Dihydroxy-*m*-benzene disulfonic acid (disodium salt)	0.0500	0.0499	99.8
IV. a) *o*-Aminobenzene sulfonic acid	0.0500	0.0512	102.4
b) 2-Amino-5-nitrobenzene sulfonic acid (sodium salt)	0.0500	0.0497	99.4
V. a) *o*-Aminobenzene sulfonic acid	0.0500	0.0512	102.4
b) 6,7-Dihydroxynaphthalene-2-sulfonic acid (sodium salt)	0.0500	0.0502	100.4

Table V. Quantitative Separations of Sulfonic Acids

Flow rate of 0.5 ml/min with a 1.3 × 7.6 cm column of Teflon with 5% Alamine 336 hydrochloride in toluene as stationary phase. Component (a) was eluted with 2*M* hydrochloric acid and component (b) was eluted with 0.1*M* perchloric acid

Separation	Added, μmole	Found, μmole	% Recovery
I. a) 2-Naphthol-6-sulfonic acid (sodium salt)	3.00	3.01	100.3
b) 2-Naphthol-8-sulfonic acid (sodium salt)	3.00	2.97	99.0
II. a) 2-Naphthol-3,6-disulfonic acid (disodium salt)	3.00	3.00	100.0
b) 2-Naphthol-8-sulfonic acid (sodium salt)	3.00	2.93	97.6

Column Separations of Sulfonic Acids. The rather wide variations in distribution ratios of various sulfonic acids suggest the possibility of separation by column chromatography. Therefore, column behavior for several sulfonic acids was studied using a 1.3 × 11 cm column of Chromosorb W coated with Alamine 336 hydrochloride without any organic diluent. It was found that sulfonic acids having distribution ratios of less than 0.04 (see Table II) could be eluted quantitatively from the column with 60 ml of 0.5*M* hydrochloric acid, while sulfonic acids having distribution ratios of 3.3 or greater did not break through even after 100 ml of the eluent had been passed through the column. By changing the eluent to 0.1*M* perchloric acid-1.0*M* hydrochloric acid, those sulfonic acids with distribution ratios greater than 3.3 could be rapidly and quantitatively eluted from the column.

Several quantitative column separations were obtained with a Chromosorb W column impregnated with Alamine 336 hydrochloride without an organic diluent. This column procedure was especially useful for separating the amino-sulfonic acids having low distribution ratios from other sulfonic acids. Flow rates of 1.0 ml/min were used with a 1.3 × 11 cm column of Chromosorb W containing 1.00 ml of Alamine 336. The amino-sulfonic acids with low distribution ratios were eluted with 0.5*M* hydrochloric acid, and the second component was then stripped off the column with 1.0*M* perchloric acid–1.0*M* hydrochloric acid. The results of these separations are given in Table IV.

Teflon was also tested as a solid support for the Alamine 336 hydrochloride. A 5% (v/v) solution of Alamine 336

hydrochloride in toluene on the Teflon was used as the stationary phase. It was found experimentally that 22.5 ml of 2*M* hydrochloric acid were required to elute 2-naphthol-3,6-disulfonic acid disodium salt to its maximum concentration. This compared favorably with a maximum elution volume ($\bar{v}$) of 18.7 ml calculated using the equation,

$$\bar{v} = V_m + DV_s$$

where $\bar{v}$ is the volume needed to elute to maximum solute concentration; V_s = 2.6 ml, the volume of the stationary phase; V_m = 5.4 ml, the volume of the mobile phase; D = 5.12, the distribution ratio. This and other examples showed that the actual column behavior can be reliably predicted from a knowledge of column parameters and the use of an expression which was originally designed to describe solvent extraction behavior.

Several quantitative column separations of sulfonic acids with similar functional groups present were obtained with a Teflon column with 5% (v/v) Alamine 336 hydrochloride in toluene as a stationary phase. The distribution ratios for 2-naphthol-3,6-disulfonic acid disodium salt, 2-naphthol-6-sulfonic acid sodium salt, and 2-naphthol-8-sulfonic acid sodium salt in 2*M* hydrochloric acid are 5.12, 12.3, and 39.6, respectively. Using this technique it was possible to separate two sulfonic acids whose separation factor was only 3.2 with no difficulty on a 1.3 × 7.6 cm Teflon column using a flow rate of 0.5 ml/min. The first component was eluted with 2*M* hydrochloric acid, and the second component was stripped off with 0.1*M* perchloric acid. The results of these separations are given in Table V.

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An Ion Exchange Method for the Determination of Aliphatic Amides and Esters

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An ion exchange method for the determination of amides and esters has been developed. The amide or ester is passed through a 30 × 0.8 cm (i.d.) column of Amberlite IR-120 resin in the H^+ form at a flow rate of 2 ml per minute. The column is maintained at a temperature of 80 °C. The effluent is recycled three times and is finally titrated with standard alkali. The method is simple, fast, reproducible, and suitable for water soluble aliphatic amides and esters.

DETECTION AND DETERMINATION of esters and amides have received considerable attention during recent years (*1–16*). Some novel methods for the detection of these substances are based on the use of ion exchange resins and enzymes (*14–16*). The classical method for the determination of esters and amides based on saponification is tedious and time-consuming. The limitations of the classical methods have been admirably discussed by Bednarski and Hume (*9*). Moreover, the classical method is applicable only to macrogram quantities. After saponification, either back titration is used or an ion exchange procedure is used to get rid of excess alkali (*9, 12*). As far as we are aware no attempt has been made to use ion exchange resins both for hydrolysis and for the release of an equivalent amount of the acid. The present communication describes the catalytic hydrolysis of esters and amides quantitatively by ion exchange resin in H^+ form. This method is based on our previous work on qualitative analysis (*15, 16*). The ion exchange method offers many advantages over the earlier methods: The hydrolysis of esters and amides is done using ion exchange resins as catalysts. Ion exchangers are selective and more efficient catalysts, and this can be utilized in developing more selective procedures. The ammonium salt formed in cases of amides is automatically converted into the corresponding acid by the resin in the H^+ form which also acts as an exchanger. The method therefore becomes simpler, faster, and more compact.

EXPERIMENTAL

Apparatus. ION EXCHANGE COLUMN. A 60 cm long column (borosilicate glass) provided with outer and inner tubes (i.d. 3.3 cm and 0.8 cm, respectively) is used. The upper portion of the column is fitted with a small funnel and the lower portion with a glass stopcock. The resin in H^+ form is filled in the inner tube up to a height 30 cm over a glass wool bed. There are two holes in the outer tube. The lower hole is connected with a steam bath through a rubber tube; the upper hole serves to pass out the steam. The temperature (80 °C) of the inner tube remains constant throughout the experiment.

Reagents. All chemicals used were of reagent grade. Amberlite IR-120 resin was used in H^+ form.

Amides and esters solutions were prepared in demineralized water: formamide 0.50% (v/v); acetamide 0.20% (wt/v); propionamide 0.20% (wt/v); *N-N*-dimethyl formamide 0.50% (v/v); ethyl formate 0.50% (v/v); ethyl acetate 0.40% (v/v); ethyl malonate 0.40% (v/v); ethyl cyanoacetate 0.40% (v/v); *n*-valeramide 0.40% (wt/v); *N*-methyl formamide

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