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# I Extraction of metal ions with isooctyl thioglycolate II Separation of aromatic sulfonic acids with a liquid anion exchanger

Robert Kent Gillette  
*Iowa State University*

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**I. EXTRACTION OF METAL IONS WITH**  
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**OF AROMATIC SULFONIC ACIDS WITH A LIQUID**  
**ANION EXCHANGER.**

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I. EXTRACTION OF METAL IONS WITH ISOCTYL THIOGLYCOLATE  
II. SEPARATION OF AROMATIC SULFONIC ACIDS WITH A LIQUID  
ANION EXCHANGER

by

Robert Kent Gillette

A Dissertation Submitted to the  
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Head of Major Department

Signature was redacted for privacy.

Dean of Graduate College

Iowa State University  
Ames, Iowa

1968

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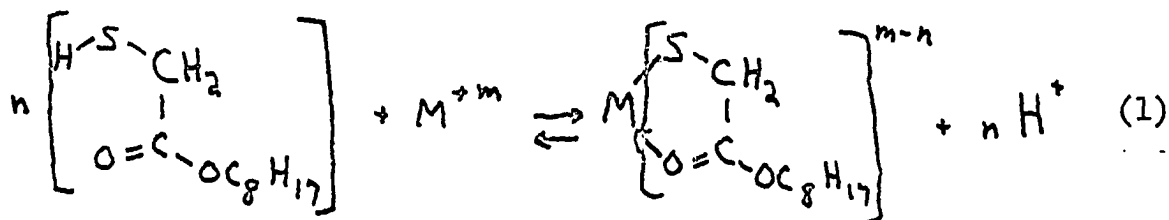
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PART I. EXTRACTION OF METAL IONS WITH  
ISOCTYL THIOLYCOLATE

## INTRODUCTION

A number of sulfur-containing analytical reagents have been used for the separation of metal ions that form insoluble sulfides when reacted with hydrogen sulfide by precipitation or solvent extraction. Some of these reagents, such as dithizone (1) and sodium diethyldithiocarbamate (1), are not very stable, which is a serious drawback to their usefulness. It would be advantageous to have a reagent that would complex some of the same metal ions, exhibit selectivity, and have greater stability.

Isooctyl thioglycolate (IOTG),  $\text{HSCH}_2\text{COOC}_8\text{H}_{17}$ , is a commercially available liquid that is immiscible, and only slightly soluble in water. The structure of this compound is such that it can form five-membered ring chelates with metal ions and thus is useful as a solvent extractant.



Isooctyl thioglycolate is available as a relatively pure liquid and it does not have an objectionable odor. It has a fairly high boiling point ( $125^\circ\text{C}$ . at 17 mm.) and is not

highly viscous. All of these properties make it possible to use pure isooctyl thioglycolate for solvent extraction, or it can be diluted with an organic solvent such as cyclohexane, chloroform, or ethyl acetate if desired. It is one of the few complexing organic compounds that can be used in solvent extraction without a diluent.

On no occasion has the behavior of isooctyl thioglycolate been systematically and extensively studied as an analytical reagent. The purpose of the present study is to investigate and describe the extraction behavior of metal ions with isooctyl thioglycolate in various acids and acid concentrations, and to evaluate its usefulness as an analytical reagent.



## SURVEY OF THE LITERATURE

Undoubtedly as an outgrowth of the classical sulfide precipitation of metal ions in qualitative analysis schemes, several sulfur-containing reagents have been studied with the aim of applying them to quantitative separations. Several of these compounds have proven useful for analytical separations and two of them, dithizone and sodium diethyldithiocarbamate, have become the bases of standard separation methods. Dithizone (1) quantitatively extracts bismuth(III), cadmium(II), cobalt(II), copper(I) and (II), gold(III), indium(III), iron(II), lead(II), manganese(II), mercury(I) and (II), nickel(II), palladium(II), platinum(II), silver(I), thallium(I) and (III), tin(II), and zinc(II), and can be made selective with pH regulation and masking agents such as cyanide, thiocyanate, and thiosulfate. However, dithizone is quite sensitive to oxidation. Another compound, sodium diethyldithiocarbamate (1), is also used in the extraction of antimony(III), arsenic(III), bismuth(III), cadmium(II), chromium(VI), cobalt(II), copper(II), gallium(III), indium(III), iron(II) and (III), lead(II), manganese(II), mercury(II), molybdenum(VI), nickel(II), niobium(V), selenium(IV), silver(I), tellurium(IV), thallium(I), tin(IV), tungsten(VI),

uranium(VI), vanadium(V), and zinc(II). The usefulness of this reagent is limited however since it decomposes rapidly in solutions of low pH.

Another group of sulfur-containing compounds that can be used as analytical reagents are the organophosphorous compounds. Handley (2) has reviewed the trialkyl thiophosphates,  $(RO)_3P=S$ ; trialkylphosphine sulfides,  $R_3P=S$ ; trialkylphosphorothioic triamides,  $(RHN)_3P=S$ ; hexaalkylphosphorothioic triamides,  $(R_2N)_3P=S$ ; dialkyl phosphorodithioates,  $(RO)_2P(S)SH$ ; and dialkyl phosphorothionates,  $(RO)_2P(O)SH$  as separatory and analytical reagents. Triisooctyl thiophosphate was found to be highly selective for silver(I) and mercury(II) from  $6M$  nitric acid, and trioctylphosphine sulfide selective for silver(I), mercury(II), and palladium(II) from aqueous nitric acid. Dibutyl phosphorodithioic acid was found to extract 22 elements significantly from aqueous hydrochloric and sulfuric acid solutions. In general, those metals that form insoluble sulfides were extracted. Dibutyl phosphorothioic acid was somewhat more selective than the dithioic derivative.

Přibil and Veselý (3) studied thioglycolic acid as a masking agent for such metals as copper(II), cadmium(II),

lead(II), zinc(II), silver(I), iron(III), and aluminum(III) in the EDTA determination of nickel(II) and manganese(II) in alkaline solution. The use of thioglycolic acid as a complexometric titrant was studied by Cabrera and West (4) for silver(I), lead(II), zinc(II), mercury(II), and cadmium(II). Thioglycolic acid has also been used for the spectrophotometric determination of iron(III), nickel(II), chromium(VI), molybdenum(VI), uranium(VI), and tungsten(VI) (5-8).

Isooctyl thioglycolate is an ester of thioglycolic acid. This ester, as well as other esters of thioglycolic acid, has not been extensively studied as an analytical reagent for complex formation and solvent extraction. It would seem that isooctyl thioglycolate should form complexes with some of the same metal ions that are complexed with thioglycolic acid. Although it has been little studied as an extractant, isooctyl thioglycolate has been used as a stabilizer in the preparation of poly-vinyl chloride (9,10) and cyclopentadienylmanganese tricarbonyls (11). This reagent has also been tested as a pesticide (12).

Mishmash (13) has shown in preliminary studies with isooctyl thioglycolate that this reagent can be used for quantitative separations of metal ions by solvent extraction

from acidic solutions. He was able to make quantitative separations of bismuth(III) from lead(II) and uranium(VI), of silver(I) from lead(II) and cadmium(II), of mercury(II) from zinc(II), and of tin(IV) from zinc(II). His studies of the effect of pH on the extraction of lead(II) and zinc(II) into isooctyl thioglycolate-ethyl acetate showed that a batch separation of these metals was not possible. However, a quantitative separation of lead(II) and zinc(II) was obtained with a column of Teflon-6 impregnated with isooctyl thioglycolate. His studies show that some elements that did not extract from 0.1M acid, such as lead(II), zinc(II), nickel (II), and cobalt(II), could be extracted at a higher pH.

It is clear that additional work must be done before the characteristics of isooctyl thioglycolate are well identified. The results of the present study should help to meet this need.

## THEORY

The techniques of liquid-liquid extraction are based on the preferential extraction of a solute into one of two immiscible liquid phases. At equilibrium the extent of partitioning between the two phases is expressed by a quantity,  $D$ , the extraction coefficient or distribution ratio where  $D$ ,

$$D = \frac{[\text{solute}]_{\text{organic phase}}}{[\text{solute}]_{\text{aqueous phase}}} \quad (2)$$

is defined as the molar concentration of the solute in the organic phase divided by the molar concentration of the solute in the aqueous phase.

Two components of a mixture can be separated by a single extraction with less than one percent cross-contamination if the  $D$  for one component is greater than 100 and the  $D$  for the other component is less than 0.01. If one component is only partially extracted and the other is essentially not extracted, the mixture can still be separated by several consecutive separations. If, however, both components are extracted, even though one is extracted to a much greater extent than the second, the mixture cannot be separated by repeated batch extraction. Each extraction performed to remove another fraction of one component is always contaminated by the

second.

A convenient means of effecting many consecutive extractions is to place one of the phases on an inert support in a column and pass the second phase through the column. If there is a significant difference in the distribution ratios of two components, even though they are both extracted to some extent, a separation can be obtained. The two components will move down the column at a rate that is dependent on their distribution ratios.

A general treatment of the theory of solvent extraction is given in Berg (14) and in the "Treatise on Analytical Chemistry" (15). Morrison and Freiser (1) have presented applications of solvent extraction for the separation of inorganic compounds.

## EXPERIMENTAL

## Apparatus

pH meter: All pH measurements were made on a Beckman Model H-2 pH meter equipped with a Beckman #41263 glass electrode and a Beckman #39170 fiber-type calomel electrode.

Spectrophotometer: A Beckman Model B spectrophotometer was used for photometric titrations. The modification of the instrument was similar to the attachment used by Fritz and Pietrzyk (16) except that a water-driven magnetic stirrer (G. F. Smith Chemical Co.) was used. Two holes were drilled near the bottom of the front side of the titration compartment to accommodate the tubing used for water to run the stirrer. A Bausch and Lomb Spectronic 600 spectrophotometer with a VOM-8 recorder was used for obtaining ultraviolet and visible spectra and for all other spectrophotometric measurements. All spectrophotometric titrations were performed in 180-ml. pyrex tall-form beakers and matched pyrex cuvettes with a one centimeter path length were used for all other spectrophotometric determinations.

Radiochemical apparatus: A Nuclear-Chicago scintillation well counter with a 3x3 inch NaI(Tl) scintillation type crystal from the Harshaw Chemical Company was used as the

detector for experiments involving radioactive tracers. A Nuclear-Chicago spectrometer, Model 1820, isolated the gamma emission from the tracers used. A decade scaler counted the pulses received from the spectrometer.

Laboratory ware: Kimble "Kimax" 125-ml. Squibb separatory funnels with Teflon stopcocks were used in extraction studies. Kimble "Kimax" burettes and Corning "Pyrex" pipettes were used throughout this work. Columns were prepared from the lower portion of "Kimax" 50-ml. burettes with Teflon stopcocks so that their dimensions were 1.1 x 28.5 cm. The top part of each column was 12 cm. long with an inside diameter of 2.2 cm.

Shaker: A Burrell shaker was used in the distribution studies of samples that required long equilibration times.

Chromatographic chamber: A large round pyrex jar, 16 in. o.d. x 12 in., with a glass cover, was used as the chromatographic chamber for all paper chromatographic studies.

#### Reagents

Isooctyl thioglycolate: Commercial isooctyl thioglycolate (b.p. 125°C. at 17 mm., sp. gr. 0.9736 at 25°C.) obtained from Evans Chemetics, Inc., was used without further purification.



Organic solvents: J. T. Baker analytical reagent grade chloroform and ethyl acetate and Eastman Chemical Company white label cyclohexane were used throughout this work.

Metal ions investigated: Reagent grade nitrate salts of silver(I), mercury(II), copper(II), and bismuth(III) were used for this investigation. Tin(IV) and antimony(III) chlorides as well as chloroauric acid were also used.

Radioactive tracers: Radioactive antimony(III) chloride ( $\text{Sb}^{124}$ ), gold(III) chloride ( $\text{Au}^{198}$ ), and silver(I) nitrate ( $\text{Ag}^{110\text{m}-110}$ ) were obtained from Oak Ridge National Laboratory.

Indicator solutions: Xylenol Orange (3,3'-bis(N,N'-di-(carboxymethyl)-aminomethyl)-o-cresol sulphonaphthalein), obtained from the LaMont Laboratories was used as a 0.5% aqueous solution. Thiomichler's Ketone (4,4'-bis(dimethylamine)thiobenzophenone) obtained from the Eastman Chemical Company was used as a 0.5% solution in acetone. Naphthyl Azoxine S (NAS, 8-hydroxy-7-(6-sulfo-2-naphthylazo)-5-quinolinesulfonic acid disodium salt) was obtained from the Eastman Chemical Company and was used as a 0.5% aqueous solution.

EDTA [disodium dihydrogen(ethylenedinitrilo)tetraacetate dihydrate]: The EDTA was white label grade obtained from the Eastman Chemical Company.

Thioglycerol: Thiovanol (thioglycerol) was obtained from Evans Chemetics Inc., and was used without further purification.

Column support and chromatographic paper: Chromosorb W (non-acid washed, 80-100 mesh) used for a column support was obtained from Johns-Manville Products Corp. and was used without any further treatment. Whatman No. 1 and No. 3 MM chromatography papers were used for paper chromatography experiments.

Paper chromatography test solutions: Test solutions of each metal ion were 0.05 M solutions of the nitrate salt containing enough nitric acid to prevent hydrolysis when possible. Tin(IV), antimony(III), and arsenic(III) chlorides were used as their aqueous solutions which were two molar in hydrochloric acid. Cerium(III), lanthanum(III), yttrium(III), scandium(III), and erbium(III) oxides were dissolved in nitric acid. Titanium(IV) chloride was dissolved in hydrochloric acid and converted to the sulfate with sulfuric acid. A saturated solution of vanadium(V) oxide in 0.01 M sulfuric acid was used for vanadium. Chloroauric acid and potassium hexachloroplatinate(IV) were dissolved in water.

Paper chromatography detection tests: A 20% (w/v) aque-

ous solution of dark ammonium sulfide was used as received from Baker and Adamson. Aluminon reagent was prepared by dissolving one gram of aluminon and one gram of ammonium acetate in 100 ml. of water.

Sea water solution: A sample of synthetic sea water (17) was prepared by dissolving 26.94 g. sodium(I) chloride, 0.87 g. potassium(I) sulfate, 1.47 g. calcium(II) chloride dihydrate, 5.67 g. magnesium(II) sulfate heptahydrate, and 6.20 g. magnesium(II) chloride hexahydrate in a liter of water. To this was added  $5 \times 10^{-5}$  mg. of  $\text{Ag}^{110\text{m}-110}$  tracer.

All other chemical were common reagent grade chemicals. Distilled water was used exclusively throughout this work.

## Analytical Procedures

### Titration methods

EDTA: Solutions of EDTA were standardized against standard zinc(II) using Naphthyl Azoxine S (NAS) indicator as described by Fritz, Abbink, and Payne (18). Standard zinc (II) solution was prepared by weighing out an appropriate amount of pure zinc metal, dissolving it in nitric acid, and diluting with water.

Bismuth(III): One to five milliliters each of nitric and perchloric acids were added to solutions containing

bismuth and these were evaporated to dense white fumes of perchloric acid to remove all traces of chloride. After dilution with water the pH of the resulting solutions was adjusted to 2.2 with ammonium acetate, and the bismuth was titrated with EDTA using Xylenol Orange indicator.

**Tin(IV):** Tin was analyzed by boiling the samples for 5 minutes after the addition of 5 ml. of concentrated hydrochloric acid, 1 ml. of concentrated sulfuric acid (to prevent volatilization of tin(IV) chloride), and an excess of EDTA. The solutions were cooled and the excess EDTA back-titrated with standard copper(II) using NAS indicator. Ammonium acetate was used as a buffer (19).

**Mercury(II):** The analysis of mercury was made without evaporating the strong solutions of hydrochloric acid because of the volatility of mercury(II) chloride. The pH of the solutions was adjusted to 2 with concentrated ammonium hydroxide, then to 6 with pyridine, and the solutions were then titrated with thioglycerol using a freshly prepared solution of Thiomichler's Ketone as the indicator (20).

**Thioglycerol:** Aqueous solutions of thioglycerol were standardized against standard mercury(II) nitrate using Thiomichler's Ketone indicator (20).

Gravimetric method

Silver(I): Silver was precipitated from homogeneous solution by slowly evaporating off excess hydrochloric acid and then determined gravimetrically as silver chloride.

Radiochemical methods

Gold(III): Gold<sup>198</sup> (64.8-hour half-life) was used as a tracer in the solvent extraction studies. Equal aliquots of the aqueous and organic phases were taken and the 0.674 Mev. gamma radiation was counted.

Antimony(III): Antimony<sup>124</sup> (60.2-day half-life) was used as a tracer in the solvent extraction investigations. Equal aliquots of the aqueous and organic phases were taken and the 0.600 Mev. gamma radiation was counted.

Silver(I): Silver<sup>110m-110</sup> (260-day half-life) was used in a column study to demonstrate its quantitative extraction from sea water. An aliquot of the recovered silver was determined by counting both the 0.68 Mev. and the 0.88 Mev. gamma radiation and comparing these to the counts given by a standard solution.

Spectrophotometric methods

Bismuth(III): Bismuth was determined spectrophotometrically in 6M hydrochloric acid as its chloro complex at

327 m $\mu$  (21).

Iron(III): Hydroxylamine hydrochloride was added to reduce all of the iron to iron(II) and the pH of the solutions was raised to 5.2 with sodium acetate. Four milliliters of a 0.25% aqueous solution of 1,10-phenanthroline were added and the absorbance of the iron-phenanthroline complex was read at 510 m $\mu$  (22).

#### Photometric titrations

Bismuth(III)-copper(II) mixture: One to five milliliters each of nitric and perchloric acids were added to the solutions were evaporated to fumes of perchloric acid to remove any organic material. Chloroacetic acid was added and the pH of the solutions was adjusted to 2 with 1:1 (v/v) ammonia. The bismuth and copper were then determined by differentiating photometric titration with EDTA at 740 m $\mu$  (23). A red-sensitive phototube was used in the detection.

Copper(II): Copper was determined with a photometric titration in the same manner as it was in the bismuth-copper(II) mixture (23).

#### Paper chromatography

The chromatographic chamber was lined with Whatman

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Iron(III): Hydroxylamine hydrochloride was added to reduce all of the iron to iron(II) and the pH of the solutions was raised to 5.2 with sodium acetate. Four milliliters of a 0.25% aqueous solution of 1,10-phenanthroline were added and the absorbance of the iron-phenanthroline complex was read at 510 m $\mu$  (22).

#### Photometric titrations

Bismuth(III)-copper(II) mixture: One to five milliliters each of nitric and perchloric acids were added and the solutions were evaporated to fumes of perchloric acid to remove any organic material. Chloroacetic acid was added and the pH of the solutions was adjusted to 2 with 1:1 (v/v) ammonia. The bismuth and copper were then determined by a differentiating photometric titration with EDTA at 745 m $\mu$  (23). A red-sensitive phototube was used in the determination.

Copper(II): Copper was determined with a photometric titration in the same manner as it was in the bismuth(III)-copper(II) mixture (23).

#### Paper chromatography

The chromatographic chamber was lined with Whatman No. 3

MM paper that had been soaked in the developing solution.

At least one hour was allowed for the chamber to become saturated after two liters of the developing solution were added.

At the end of this period, there was a layer of liquid approximately 0.25 in. deep in the bottom of the chamber.

Whatman No. 1 chromatography paper was impregnated with a 5% solution of isooctyl thioglycolate in cyclohexane. After the paper had dried, test solutions were applied with wooden applicator sticks. The dried chromatograms were developed to within one inch of the end of the paper. The zones were identified with a suitable spray reagent when the chromatograms were completely dry.

#### Extraction Procedure

Exactly ten milliliters of 0.05M metal ion solutions in 0.1M or 1.0M nitric acid were added to a 125-ml. separatory funnel. One milliliter of pure isooctyl thioglycolate was added and the phases were equilibrated for two minutes. The extraction was made with pure isooctyl thioglycolate rather than with a solution of isooctyl thioglycolate in an organic diluent because faster equilibrium could be obtained with the pure reagent. Ten milliliters of chloroform, cyclohexane, or ethyl acetate were added and the phases were equilibrated



for one minute. After the final shaking the phases were allowed to separate. The extracted elements were recovered with a back-extraction of the organic phase with an equal volume of aqueous hydrochloric acid. At least  $4\text{M}$  hydrochloric was used for the back-extraction of bismuth and copper, at least  $8\text{ M}$  hydrochloric acid for the back-extraction of mercury, and at least  $10\text{ M}$  hydrochloric acid was used to back-extract silver.

Cyclohexane was used when a solvent lighter than water was desirable. This solvent was especially good when a back-extraction was also carried out since the aqueous phase could be removed and replaced with the aqueous solution for back-extraction without any transfers. Ethyl acetate was good for extractions at low acid concentrations, but its solubility in the aqueous phase increased greatly when the concentration of hydrochloric acid was greater than  $5\text{M}$ . Cyclohexane could be used for extractions from all concentrations of hydrochloric acid with no solubility problem. Cyclohexane was satisfactory for the extraction of all metals except copper whose complex with isooctyl thioglycolate was insoluble in this solvent.

## Column Separation Procedures

Separation of traces of bismuth(III) from zinc(II):

Chromosorb W (non-acid washed, 80-100 mesh) was impregnated with pure isooctyl thioglycolate and the excess reagent was removed by repeated blotting with absorbent paper. The impregnated support was rinsed frequently with water and the organic material that floated to the top was removed. The support was slurried with water and added to a glass column so that the column was 1.1 x 4 cm. A glass wool plug was used to contain the support in the column. About 20 ml. of 1M nitric acid were then passed through the column at a moderate flow rate to insure the attainment of equilibrium and also to help settle the support. A glass wool plug was placed at the top of the column to help stabilize the support when samples and eluents were added. A 5-ml. aliquot of samples containing minor amounts of bismuth and major amounts of zinc in 1M nitric acid was added to the column and sorbed on with a flow rate of 0.5 ml./min. Twenty milliliters of 1M nitric acid were passed through the column at 2 ml./min. to remove the last traces of zinc and the column was then rinsed with water to remove the nitric acid, since nitrate interferes with the ultraviolet spectrophotometric determina-

tion of bismuth at 327 m $\mu$ . The effluent was monitored with a spectrophotometer at 327 m $\mu$  until no absorbance was observed. The bismuth was eluted with 6M hydrochloric acid and determined spectrophotometrically at 327 m $\mu$ . The column was regenerated by rinsing with water and 1M nitric acid.

Separation of traces of silver(I) from sea water: A column (1.1 x 9 cm.) of isooctyl thioglycolate impregnated Chromosorb W was prepared in the same manner as was the column for the separation of traces of bismuth(III) from zinc(II). A liter of synthetic sea water containing  $5 \times 10^{-5}$  mg. of silver<sup>110m-110</sup> was passed through the column at a rate of 4.0 ml./min. When the entire sample of sea water had passed through the column, the eluent was changed to concentrated hydrochloric acid and the silver was eluted into a volumetric flask and determined radiochemically.

## RESULTS AND DISCUSSION

The extraction of bismuth(III) from different concentrations of hydrochloric, nitric, and perchloric acids into isooctyl thioglycolate-cyclohexane is shown in Figure 1. There was approximately 0.10 mmole. of bismuth present for each extraction. The results of the extraction are based on EDTA titrations of the aqueous phase and are given in Table 1.

Table 1. Effect of acidity on extraction of bismuth(III) with isooctyl thioglycolate-cyclohexane

Molarity of acid	% Bi(III) extracted from HCl	% Bi(III) extracted from HNO <sub>3</sub>	% Bi(III) extracted from HClO <sub>4</sub>
0.1	99.5	99.5	100.0
1.0	67.7	99.0	99.5
2.0	3.7	--	--
3.0	1.7	99.0	99.0
4.0	---	96.1	--
5.0	2.2	86.8	99.0
7.0	2.2	43.7	97.0
9.0	---	24.2	96.6
11.0	---	0.7	--

The extraction is essentially quantitative in 0.1 to 3M nitric or perchloric acid. Formation of water-soluble bismuth chloride complexes in hydrochloric acid and bismuth nitrate complexes in nitric acid apparently compete with isooctyl thioglycolate complexing. Oxidation of the organic

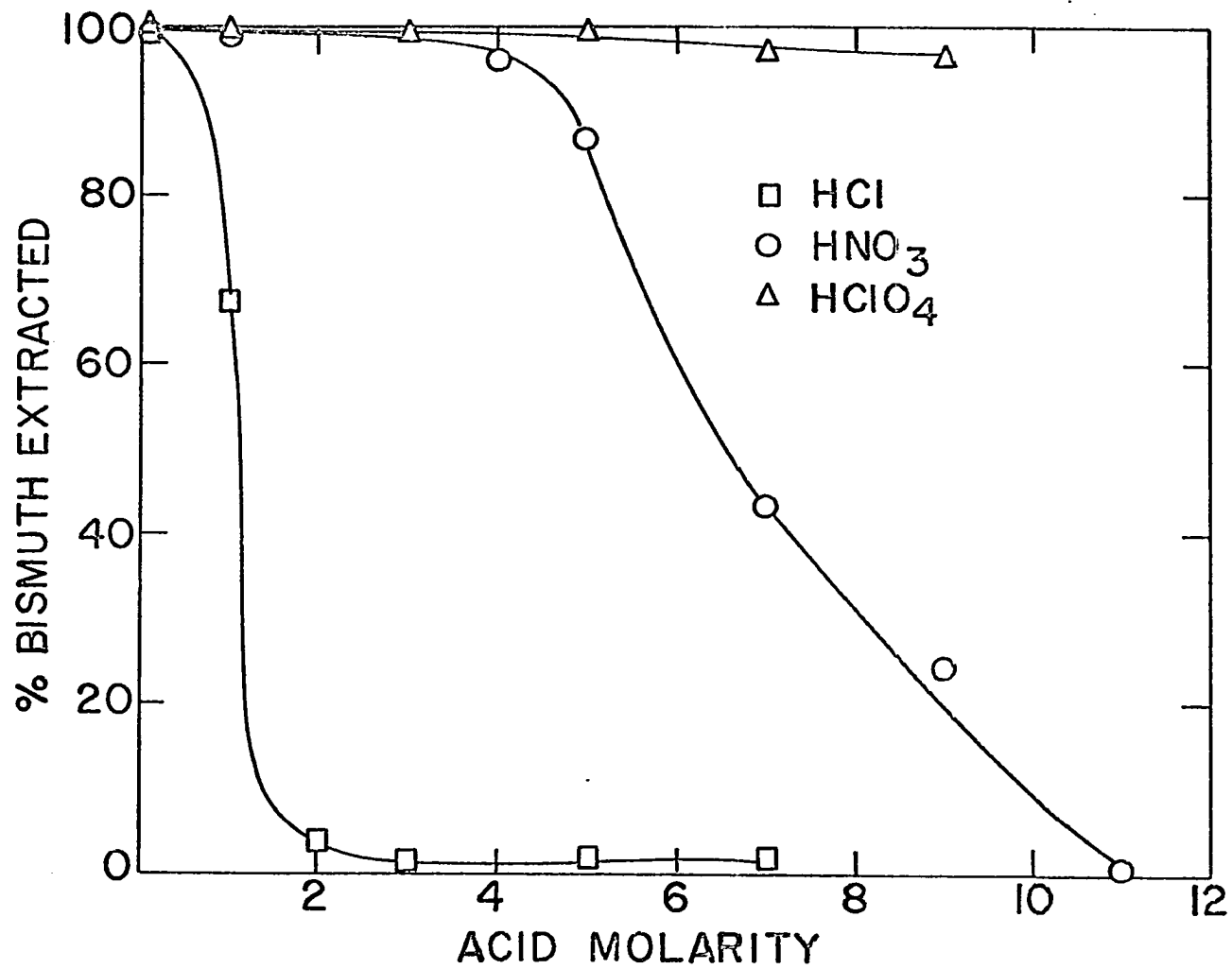


Figure 1. Effect of acidity on extraction of bismuth with IOTG

phase was noticed at the higher concentrations of nitric acid. The effect of competing complexes makes 4 to 12M solutions of hydrochloric acid quite useful for stripping extracted bismuth from the organic layer.

Silver(I) is quantitatively extracted into isooctyl thioglycolate-cyclohexane from 0.1 to 7M aqueous nitric acid using only a single extraction. Approximately 1.25 mmole. of silver was present for the extraction and the results, shown in Table 2, are based on a gravimetric determination after a back-extraction with concentrated hydrochloric acid. With this much silver present a two-fold volume excess of concentrated hydrochloric acid was necessary to form the soluble anionic chloro complex.

Table 2. Effect of nitric acid on the extraction of silver (I) with isooctyl thioglycolate-cyclohexane

Molarity of HNO <sub>3</sub>	% Ag(I) extracted
0.1	99.0
3.0	98.2
5.0	97.9
7.0	98.0

The extraction of gold(III) into isooctyl thioglycolate-ethyl acetate was studied from acid solutions that varied from 10<sup>-3</sup>M to 6M in hydrochloric acid. The extractions were

complete over the entire range even though the gold complex is not very soluble in ethyl acetate.

Copper(II) is best extracted by isooctyl thioglycolate in chloroform because the copper complex is very sparingly soluble in ethyl acetate and cyclohexane. The extraction of copper(II) from 0.1M nitric acid into isooctyl thioglycolate-chloroform was 99% complete in a single extraction. From 0.1M, 1.0M, and probably from somewhat higher nitric acid concentrations, quantitative separation of copper is obtained using two extractions with isooctyl thioglycolate in chloroform.

The results of studies of the extraction of tin(IV) and antimony(III) from hydrochloric acid are shown in Figure 2. The extraction of tin, as shown by the results in Table 3,

Table 3. Effect of hydrochloric acid on the extraction of tin(IV) with isooctyl thioglycolate

Molarity of HCl	% Sn(IV) extracted with cyclohexane diluent	% Sn(IV) extracted with ethyl acetate diluent
0.25	78.8	96.6
0.50	87.0	89.0
0.75	87.4	64.2
1.0	75.5	47.0
2.0	5.5	--
3.0	0.1	--

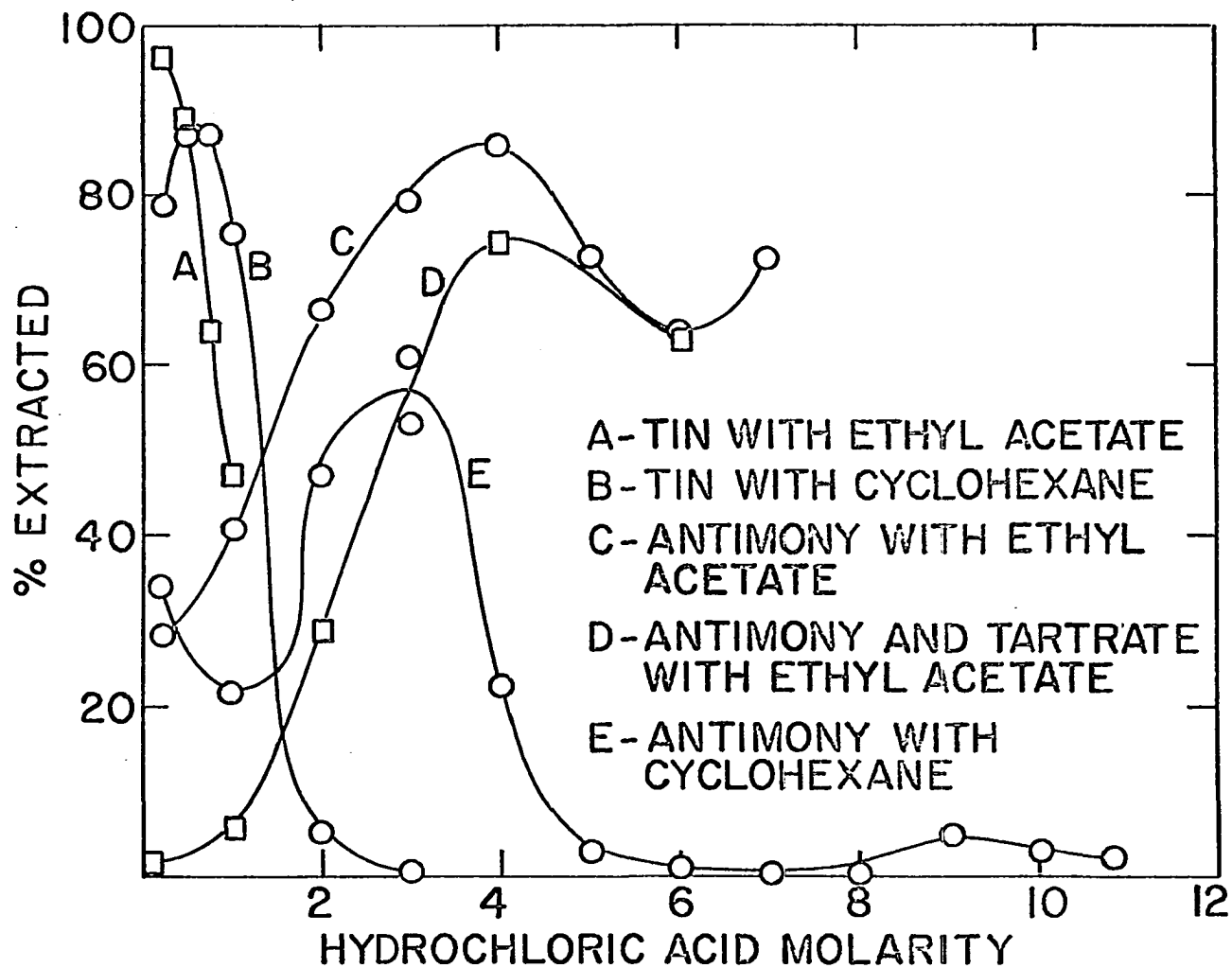


Figure 2. Effect of acid concentration on extraction of tin(IV) and antimony(III) with IOTG



is nearly complete from dilute hydrochloric acid into isooctyl thioglycolate-ethyl acetate, but falls off rapidly with increasing hydrochloric acid concentrations. The results of the extractions are based on EDTA titrations of the aqueous phases.

Results for antimony(III), given in Table 4, were determined radiochemically and were difficult to reproduce; they show significant but not quantitative extraction. When ethyl acetate was used as the organic diluent, it had previously been equilibrated with the corresponding concentration of hydrochloric acid. In the extraction of antimony(III) from 0.2M hydrochloric acid into isooctyl thioglycolate-cyclohexane, the sample was partially hydrolyzed before the extraction. Thus tin and antimony appear to interfere in the batch extraction of bismuth, copper, gold, mercury, and silver from other metal ions. However, data obtained using paper impregnated with isooctyl thioglycolate (see below) indicate that tin and antimony are tightly held in the isooctyl thioglycolate phase in paper chromatographic separations.

Table 4. Effect of hydrochloric acid on the extraction of 0.005M antimony(III) chloride with isooctyl thioglycolate

Molarity of HCl	% Sb(III) extracted cyclohexane diluent	% Sb(III) extracted ethyl acetate <sup>b</sup> diluent	% Sb(III) extracted <sup>a</sup> ethyl acetate <sup>b</sup> diluent
0.1	--	--	1.9
0.2	34.2 <sup>c</sup>	28.7	--
1.0	21.8	40.8	5.5
2.0	47.1	66.8	28.9
3.0	57.2	79.2	--
4.0	22.1	86.0	74.7
5.0	3.1	72.8	--
6.0	1.2	63.7	63.2
7.0	0.5	72.3	--
8.0	0.8	--	--
9.0	5.0	--	--
10.0	3.2	--	--
10.8	2.1	--	--

<sup>a</sup>Aqueous phase was also 0.02M in tartaric acid.

<sup>b</sup>Equilibrated with the corresponding concentration of HCl.

<sup>c</sup>Sample partially hydrolyzed before the extraction.

Back-extraction with aqueous solutions of hydrochloric acid permits easy recovery of extracted elements from the organic isooctyl thioglycolate phase. The results in Table 5 and Figure 3 show that bismuth(III) and copper(II) are quantitatively back-extracted by 4M or greater solutions of hydrochloric acid, and mercury(II) is back-extracted by 8 to

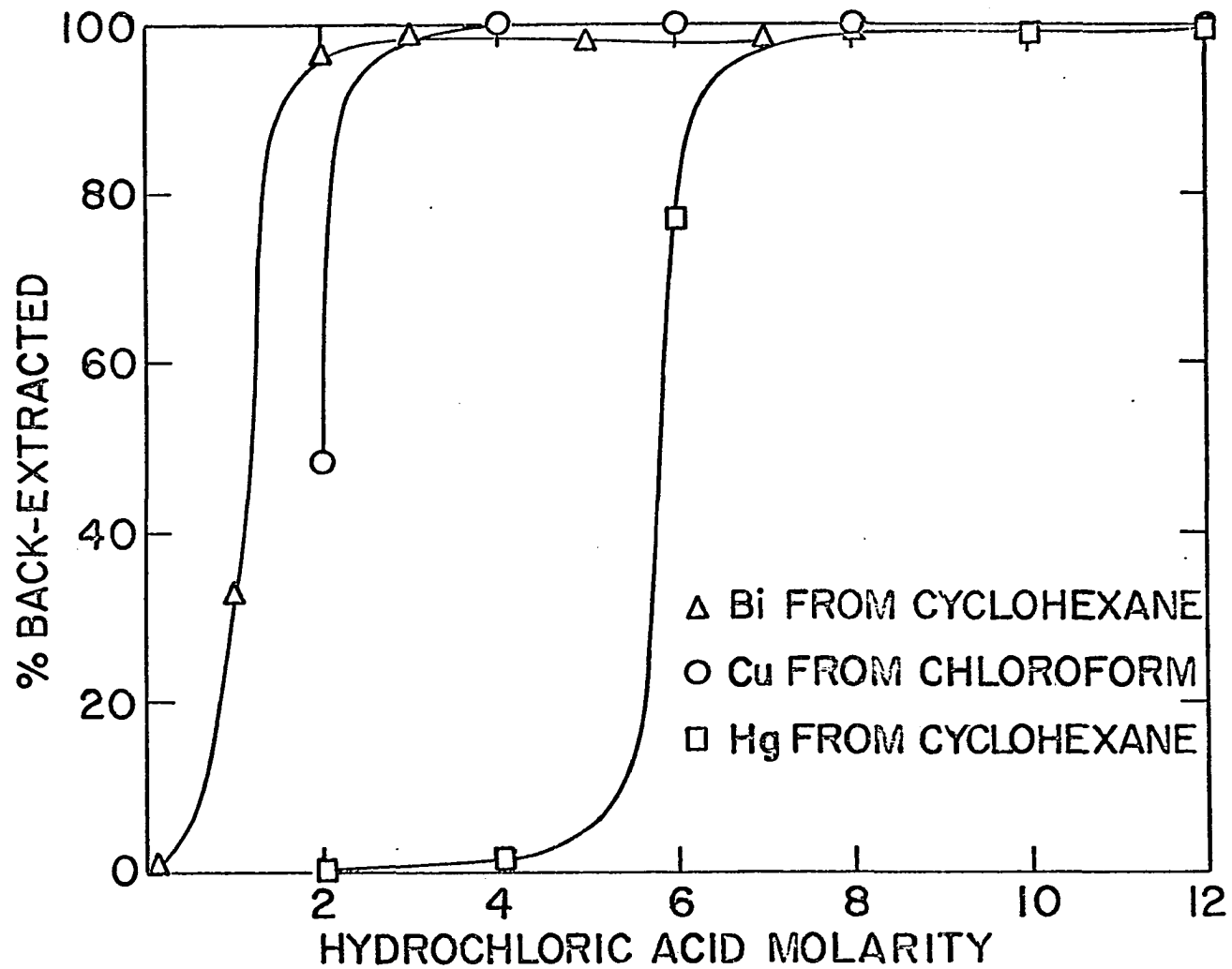


Figure 3. Effect of HCl concentration on back-extraction of bismuth, copper, and mercury

12M hydrochloric acid. Silver(I) may be back-extracted from the organic phase with 10 to 12M hydrochloric acid. At this high acid concentration, silver forms a water-soluble anionic chloro complex. Evaporation of most of the acid after the back-extraction results in the formation of beautiful crystals of silver chloride.

Table 5. Effect of hydrochloric acid concentration on back-extraction of bismuth(III), copper(II) and mercury(II)

Molarity of HCl	% Bi(III) back-extracted	% Cu(II) back-extracted	% Hg(II) back-extracted
0.1	0.5	--	--
1.0	32.3	--	--
2.0	96.3	48.2	0.0
3.0	98.3	--	--
4.0	--	100.6	1.6
5.0	97.8	--	--
6.0	--	100.6	76.5
7.0	97.8	--	--
8.0	--	100.7	98.7
10.0	--	97.2	98.8
12.0	--	99.9	99.2

An equimolar mixture of bismuth(III) and copper(II) was taken to show the quantitative nature of the extraction with isooctyl thioglycolate. Both metals were extracted with isooctyl thioglycolate and chloroform and then back-extracted with aqueous 4M hydrochloric acid. Bismuth and copper were determined by a differentiating photometric titration (23).

The results given in Table 6 are the average of three trials.

Table 6. Quantitative analysis of a mixture of bismuth(III) and copper(II) by solvent extraction

Metal	mmole. Taken	mmole. Found	% Recovery
Bi(III)	0.2520	0.2535	100.6
Cu(II)	0.2469	0.2448	99.1

Columns containing a support impregnated with isooctyl thioglycolate are useful for the isolation and concentration of traces of extractable elements. A column of Chromosorb W (non-acid washed, 80-100 mesh) impregnated with isooctyl thioglycolate effected a quantitative separation of small amounts of bismuth(III) from large amounts of zinc(II). The metal ions retained by the column were readily eluted with aqueous hydrochloric acid. Results for several separations using these columns are given in Table 7. The columns could be used several times before they had to be prepared freshly.

Table 7. Quantitative separations on a Chromosorb W-isooctyl thioglycolate column

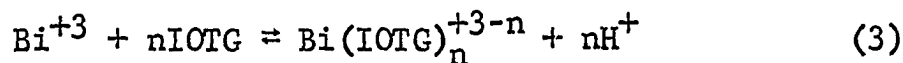
Bi(III) taken mmoles.	Zn(II) taken mmoles.	Bi(III) found mmoles.	% Recovery
0.00494	5	0.00497	100.6
0.1482	15	0.1486	100.3
0.1976	20	0.1970	99.7

Another isooctyl thioglycolate impregnated Chromosorb W column was used to show the usefulness of isolating traces of extractable elements. A sample of synthetic sea water (17) containing  $5.0 \times 10^{-5}$  mg. of silver(I) was passed through the column to concentrate the silver which was then eluted with concentrated hydrochloric acid. The recovered sample contained  $5.2 \times 10^{-5}$  mg. of silver.

Paper chromatography with Whatman No. 1 chromatographic paper impregnated with a 5% solution of isooctyl thioglycolate in cyclohexane was used to check for interfering elements. When the developing solution was 0.1M nitric acid, Hg(II), Au(III), As(III), Sb(III), Ag(I), Cu(II), Sn(IV), and Bi(III) remained at the origin, indicating complete extraction into the isooctyl thioglycolate. Thorium(IV), U(VI), Ti(IV), Al(III), Zn(II), Ce(III), Pb(II), Ni(II), Fe(III), Y(III), Sc(III), Er(III), V(V), and Cd(II) traveled with the solvent front, indicating no extraction into the isooctyl thioglycolate, and Pt(IV), La(III), and Co(II) formed streaks. When the developing solution was 0.1M hydrochloric acid, Ag(I), Cu(II), Sn(IV), and Bi(III) remained at the origin, Th(IV), U(VI), Ti(IV), Al(III), Zn(II), V(V), Pt(IV), Cd(II), Y(III), Sc(III), Er(III), Ni(II), and Fe(III) traveled with the

solvent front, and Sb(III), Pb(II), and Co(II) formed streaks.

Quantitative results were obtained for the extraction of bismuth(III) with a 2.5% (v/v) solution of isooctyl thioglycolate in cyclohexane instead of first extracting with pure isooctyl thioglycolate. However, longer shaking was required with the diluted reagent. Experiments were undertaken to find the relationship between the distribution coefficient and the concentration of the extracting reagent. The concentration of bismuth(III) nitrate ( $5.0 \times 10^{-4} \text{M}$ ) and the hydrogen ion concentration ( $1 \text{M}$ ) were kept constant and the reagent concentration was varied from  $2.9 \times 10^{-3} \text{M}$  to  $4.8 \times 10^{-2} \text{M}$  in cyclohexane. Equal volumes of the aqueous and organic phases were shaken for two hours on a Burrell shaker to insure equilibrium. The organic phase was then back-extracted with  $6 \text{M}$  hydrochloric acid and the aqueous phase analyzed spectrophotometrically (21). The equilibrium that is being considered is



and the equilibrium constant,  $K_{\text{eq}}$ , would be

$$K_{\text{eq}} = \frac{[\text{Bi}(\text{IOTG})_n^{3-n}][\text{H}^+]^n}{[\text{Bi}^{+3}][\text{IOTG}]^n} \quad (4)$$

The distribution coefficient,  $D$ , is defined as the concentra-

tion of bismuth(III) in the organic phase divided by the concentration of bismuth in the aqueous phase, or

$$D = \frac{[\text{Bi}(\text{IOTG})_n]}{[\text{Bi}^{+3}]} \quad (5)$$

and is given in Table 8. If the distribution coefficient is substituted into the equilibrium constant expression and the equation then solved for the distribution coefficient, the following mathematical relationships are obtained:

$$K_{\text{eq}} = \frac{D[\text{H}^+]^n}{[\text{IOTG}]^n} \quad (6)$$

$$D = \frac{K_{\text{eq}}[\text{IOTG}]^n}{[\text{H}^+]^n} \quad (7)$$

$$\log D = n \log[\text{IOTG}] + \log K_{\text{eq}} - n \log[\text{H}^+] \quad (8)$$

If the logarithm of the distribution coefficient is plotted against the logarithm of the molar concentration of isooctyl thioglycolate, the slope will give the number of isooctyl thioglycolate molecules complexed with each bismuth ion. A least means square slope of 2.07 was obtained for Figure 4. This indicates that the extracted complex consists of two moles of isooctyl thioglycolate to one of bismuth. The equilibrium constant for Equation 3 is  $1.3 \times 10^4$ . This was calculated from Equation 8 using the values of the logarithm of



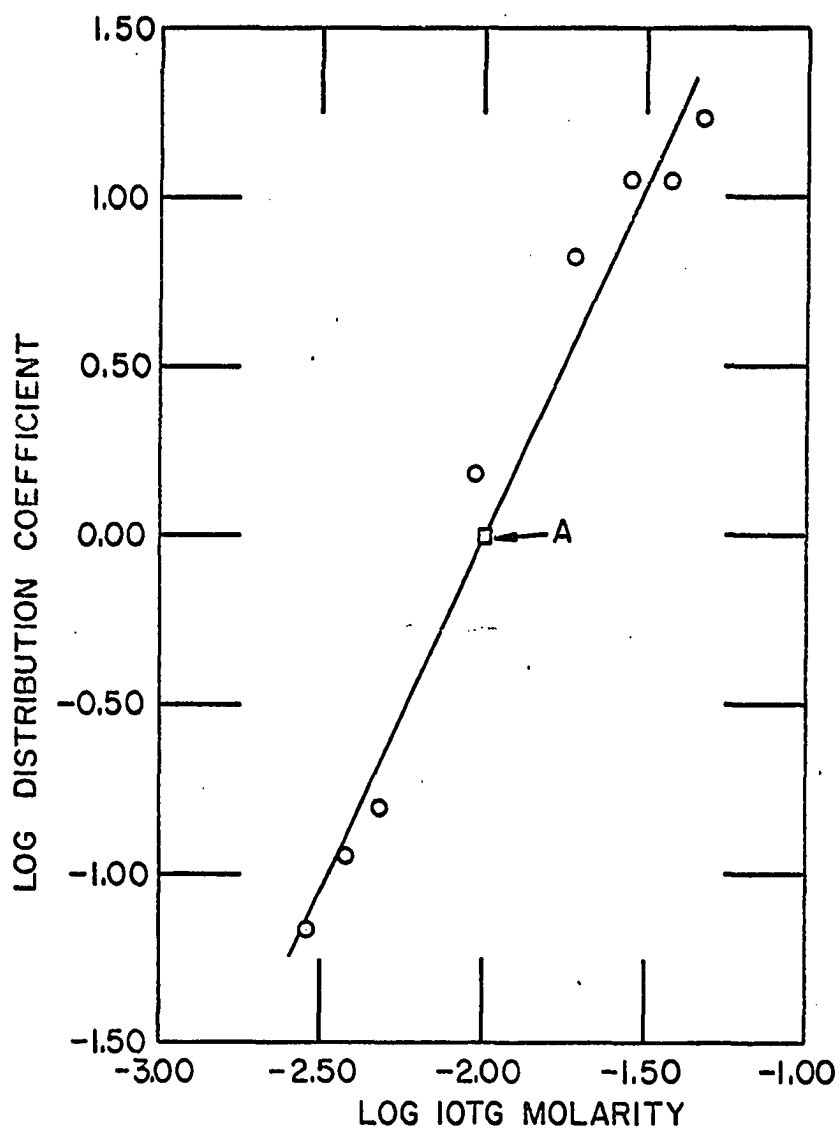


Figure 4. Distribution coefficients of bismuth(III) nitrate as a function of the isooctyl thioglycolate (IOTG) molarity in cyclohexane

the distribution coefficient and isooctyl thioglycolate molarity at point A on Figure 4.

Table 8. Effect of the isooctyl thioglycolate molar concentration on the distribution coefficient of bismuth (III)

Molarity of IOTG	log [IOTG]	Distribution coefficient	Log D
$0.286 \times 10^{-2}$	-2.544	0.068	-1.167
$0.381 \times 10^{-2}$	-2.419	0.113	-0.947
$0.476 \times 10^{-2}$	-2.322	0.157	-0.804
$0.952 \times 10^{-2}$	-2.021	1.52	0.182
$1.90 \times 10^{-2}$	-1.721	6.66	0.823
$2.86 \times 10^{-2}$	-1.544	11.3	1.053
$3.81 \times 10^{-2}$	-1.419	11.3	1.053
$4.76 \times 10^{-2}$	-1.322	17.5	1.243

The combining ratio of isooctyl thioglycolate to mercury (II) was determined by dissolving samples of pure isooctyl thioglycolate in acetone and titrating with standard mercury (II) nitrate using a pyridine buffer and Thiomichler's Ketone indicator (24). The results of this determination, shown in Table 9, indicate that the complex consists of two moles of isooctyl thioglycolate to one of mercury.

Table 9. Combining ratio of isooctyl thioglycolate to mercury(II)

mmole. IOTG	0.7478	0.7615	0.7747
mmole. Hg(II)	0.3749	0.3800	0.3846
<u>mmole. IOTG</u> <u>mmole. Hg(II)</u>	1.99	2.00	2.01

## SUMMARY

Isooctyl thioglycolate is a water-immiscible organic complexing agent that quantitatively extracts bismuth(III), copper(II), gold(III), mercury(II), and silver(I) from aqueous nitric acid solutions. Antimony(III) and tin(IV) are partially extracted and thus cannot be isolated with a single extraction. Paper chromatographic results with paper impregnated with isooctyl thioglycolate show that other metal ions studied are not extracted from 0.1M acid. The extraction of bismuth(III) and silver(I) from 3M and 7M nitric acid, respectively, was accomplished. Bismuth, copper, mercury, and silver are easily back-extracted into aqueous hydrochloric acid and can be determined by standard analytical methods.

Columns packed with a solid support impregnated with isooctyl thioglycolate were used to isolate and concentrate trace amounts of extractable elements from large amounts of nonextracted substances. A trace of silver(I) was quantitatively recovered from a sample of synthetic sea water.

With the ability to quantitatively extract large amounts of bismuth(III), copper(II), gold(III), mercury(II), and silver(I) from aqueous nitric acid solutions in a single

extraction and to isolate and concentrate trace amounts of these elements, isooctyl thioglycolate is very useful as an analytical reagent. This reagent compares favorably with other sulfur-containing analytical reagents since the extraction kinetics are very rapid, selectivity is achieved with adjustments in the acid concentration, and it is not sensitive to oxidation.

PART II. SEPARATION OF AROMATIC SULFONIC ACIDS WITH A  
LIQUID ANION EXCHANGER

## INTRODUCTION

The analysis of a mixture of aromatic sulfonic acids and sulfuric acid has been a problem to the analytical chemist for some time. Since both sulfuric acid and sulfonic acids are strong acids, it is difficult to do a differential analysis of a mixture with a simple acid-base titration. Sulfate may be determined by precipitation as barium sulfate and total sulfonic acid determined by difference following an acid-base titration for total acid. This scheme would be satisfactory if it were not for the fact that many sulfonic acids form insoluble barium salts and would precipitate with the sulfate. In addition, the problem of coprecipitation and adsorption of the soluble barium sulfonates with the barium sulfate precipitate is difficult to overcome. A convenient means of resolving mixtures of sulfate and sulfonates would be very useful.

Aromatic sulfonic acids are essential to the dye industry for use as dye intermediates. To be used in dye-forming reactions it is important that isomers of the desired sulfonic acid as well as other closely-related compounds be absent to avoid possible side reactions. Thus the resolution of isomers of aromatic sulfonic acids is an important task for the analytical chemist.

Although consideration has been given to these problems for many years, the solutions thus far found involve cumbersome methods and lengthy procedures and in many cases have been applied to only a limited number of sulfonic acids. One approach to the separation of sulfate from sulfonic acids and to the resolution of sulfonic acids which has not been explored involves the use of liquid anion exchangers. These exchangers function in a manner analogous to conventional solid ion exchange resins but have several distinct advantages over the solid resins. Liquid ion exchangers are more versatile than solid ion exchange resins in that the kinetics are more rapid, a higher selectivity is obtained, and a greater capacity is realized. One liquid ion exchanger is the long-chain aliphatic tertiary amine that is marketed under the trade name Alamine 336.

It was the purpose of this research to determine the effect of variables such as organic diluent and competing anions on the partition of halides with Alamine 336 and to apply this knowledge to the separation of aromatic sulfonic acids. Sulfonic acids were readily separated from sulfate with a single batch extraction while isomeric sulfonic acids were selectively eluted from Teflon columns coated with the liquid anion exchanger.



## SURVEY OF THE LITERATURE

## Separation of Sulfonic Acids and Their Derivatives

Aromatic sulfonic acids are used extensively in the dye industry, primarily for the preparation of dye intermediates. Generally the procedure for preparing the aromatic sulfonic acids involves the reaction of the un-sulfonated aromatic compounds with a large excess of sulfuric acid. Following the reaction, the products usually include isomeric sulfonates of the original substituted aromatic compound as well as the unreacted sulfate. For use in the preparation of dyes it is important that the desired sulfonic acids be free of isomers or closely related compounds since these would also enter into the dye-forming reaction. Thus it is important to be able to separate the aromatic sulfonic acids from any sulfate remaining in their mixture, as well as to resolve the various isomers of the sulfonic acid prepared so that relatively pure compounds are used in the dye-forming reactions.

In 1917 Dennis (25) received a patent on his method of separating aromatic sulfonic acids from excess sulfuric acid. By equilibrating mixtures of benzene sulfonic acids and sulfuric acid with benzene he found that the sulfonic acid was extracted into the benzene and the sulfuric acid remained in

the aqueous phase. Much later, in 1957, Houff et al. (26) developed a different separation procedure which is applicable when the sulfonic acid forms a soluble barium salt. Barium is added to the reaction mixture and barium sulfate precipitated. The soluble barium sulfonate is passed through a cation exchange column in the hydrogen form and the free sulfonic acid is collected in the eluate. This procedure involves many steps, and the initial precipitation of barium sulfate is likely to lead to serious coprecipitation and adsorption of the soluble barium sulfonates.

A somewhat less complicated method was developed by Glogau et al. (27) for the separation of sulfonic acids and sulfuric acid in mixtures of the two. The separation is based on the difference in molecular size of the two species and is carried out taking advantage of the screening effect of a highly cross-linked ion exchange resin, Dowex 1x16. Sulfuric acid is taken up by the resin from an aqueous mixture and the other component passes through the column.

The actual resolution of mixtures of aromatic sulfonic acids can be very laborious. An example of this is the separation of the reaction products in the sulfonation of 2-naphthol which is based on the varying solubilities of their alkali

salts (28). The mixture of reaction products consists mainly of 2-naphthol-6-sulfonic acid, 2-naphthol-3,6-disulfonic acid, and 2-naphthol-6,8-disulfonic acid. The sodium salt of 2-naphthol-6-sulfonic acid is quite insoluble in cold water and precipitates out leaving an aqueous solution of the sodium salts of the other two components. If a small amount of salt is then added to the aqueous solution, the sodium salt of 2-naphthol-3,6-disulfonic acid precipitates leaving the third acid in solution. Finally the 2-naphthol-6,8-disulfonic acid may be precipitated as its potassium salt which is insoluble in cold water to which a small amount of potassium chloride has been added.

Newer separation methods have been applied to the resolution of mixtures of sulfonic acids. Paper chromatography is very useful for a survey of compounds to see if separations are possible. Latinák (29-35) and Latinák and Skalický (36, 37) have determined  $R_f$  values on paper for a large number of substituted naphthalene sulfonic acids used as dye intermediates. Ordinary filter paper was used in most of these studies, while a few of the investigations were carried out with filter paper impregnated with an aqueous sodium bicarbonate solution. Various solvent systems were studied for the developing solu-

tion. The  $R_f$  values were found to be influenced by the number of sulfonic acid functional groups as well as by the relative positions of the sulfonic acid groups and other functional groups present on the naphthalene ring. Other paper chromatography systems have been investigated for the separation of sulfonic acids as well as other organic acids (38-42).

Thin-layer chromatography is generally faster than paper chromatography but has not been studied as extensively for sulfonic acid separations. Roseira (43) has used thin-layer chromatography to separate 1-aminonaphthalene-8-sulfonic acid from 1-aminonaphthalene-5-sulfonic acid while de Deyne (44) determined  $R_f$  values for the isomeric  $\alpha$ -naphthol monosulfonic acids. In the former study unactivated silica gel was used while activated silica gel was used in the latter.

Funasaka and co-workers (45-50) have published a series of papers concerning the separation and determination of aromatic sulfonic acids by salting-out chromatography with cation exchange resins. Sodium chloride solutions were used to elute monosulfonic acids while calcium chloride solutions were used to elute the disulfonic acids. The separations were carried out at 40°C. to speed up the otherwise slow kinetics. Flow rates of 0.2-0.3 ml./min. were used and 300-600

ml. of eluent were required to complete the elution from columns that were 20-50 cm. long. Steuerle (51) used Sephadex G 25 columns to separate mixtures of aromatic sulfonic acids. A neutral potassium bromide solution was used to elute the sulfonic acids from columns that were 1-5 meters long. The separations required 6-24 hours to complete.

Although sulfonic acids themselves are not volatile, several attempts have been made to separate certain of their volatile derivatives by gas chromatography. Kirkland (52) prepared the methyl esters of several sulfonic acids with diazomethane and these were resolved in a reduced pressure column. In the same study he prepared the sulfonyl chloride derivatives using either thionyl chloride or phosgene with a dimethylformamide catalyst. The sulfonyl chloride derivatives were separated on a column of Chromosorb coated with silicon grease while Apiezon L grease on Chromosorb was used to separate the methyl esters. Funasaka et al. (53) used diazomethane to prepare the methyl esters of  $\alpha$ - and  $\beta$ -naphthalene sulfonic acids after first converting the sulfonates to the un-ionized acids on a cation exchange column in the hydrogen form. The methyl esters were then separated on a gas chromatographic column. Parsons (54) prepared the fluoride derivatives of

naphthalene mono-, di-, and tri-sulfonic acids and of benzene trisulfonic acid and separated them on a column of diatomaceous silica coated with SE-30. The fluoride derivatives were prepared by reacting the sulfonic acids first with phosphorus pentachloride and then with potassium fluoride.

### Liquid Ion Exchangers

Smith and Page (55) first examined the use of long-chain aliphatic amines as a means of separating strong acids from weak acids. It was found that long-chain aliphatic amine salts of mineral acids were almost insoluble in water but were readily soluble in some organic solvents. Tertiary aliphatic amines had the greatest extracting power, which improved with an increase in the length of the chain. The amine was easily recovered with an equilibration of excess alkali and could then be used for further extractions.

Moore (56) and Coleman and co-workers (57) have made comparisons of the extraction behavior of liquid and solid ion exchangers. The order of preference of anions for both liquid and solid ion exchangers was typically found to be  $\text{ClO}_4^- > \text{NO}_3^- > \text{Cl}^- > \text{HSO}_4^- > \text{F}^-$ . The liquid-liquid system is, however, considerably easier to operate than is the solid-liquid

system, and in addition, the extent of extraction as well as the selectivity are easily controlled by choice of amine structure and diluent, where such variables are not easily altered in solid-liquid systems.

The basic technology of liquid ion exchangers, primarily amines and alkyl phosphoric acids, has been described by Kunin and Winger (58). In addition to a quite comprehensive discussion of the basic principles of their functioning, consideration is given to the relationship of their structure to their selectivity, and to the details of their use. Finally, comparisons are made between the characteristics of liquid and solid ion exchangers in which advantages of the liquid exchangers, such as their more rapid kinetics, higher selectivity, and greater capacity, are pointed out.

Coleman et al. (59) lists many of the liquid anion and cation exchangers that are available and points out their usefulness in inorganic separations. Inert supports impregnated with liquid ion exchangers for separations have been reported by Cerrai (60). Green (61) has reviewed the uses of liquid ion exchangers for use in inorganic analyses. Since then, liquid anion exchangers have been used in inorganic analyses by Brinkman and co-workers (62,63), by Pierce and

Henry (64), and by Watanabe and Akatsuka (65).

Long-chain aliphatic amines have been used in the solvent extraction-infrared analysis of sulfonic acids (66), but, to date the advantages of liquid ion exchangers have not been used for the separation of mixtures of substituted sulfonic acids. It is hoped that the work to be described will help to correct this situation.



## EXPERIMENTAL

## Apparatus

pH meter: All pH measurements were made on a Corning Model 7 pH meter equipped with a Corning #476022 glass electrode and a Corning #476002 fiber-type calomel electrode. A Corning Model 12 pH meter equipped with a Corning #476022 glass electrode and a Corning #476002 fiber-type calomel electrode with saturated potassium chloride in methyl alcohol was used for nonaqueous potentiometric titrations.

Spectrophotometer: A Bausch and Lomb Spectronic 600 spectrophotometer with a VOM-8 recorder was used for all spectrophotometric measurements. Matched pyrex cuvettes with a one centimeter path length were used for all spectrophotometric determinations. A Bausch and Lomb flow-through cell with a one centimeter path length was used for monitoring column effluents. The flow-through cell had separable inlet and outlet tubes fitting ground, tapered openings at the top. A Perkin Elmer Model 21 infrared spectrophotometer was used to obtain infrared spectra.

Laboratory ware: Kimble "Kimax" 125-ml. Squibb separatory funnels with Teflon stopcocks were used in extraction studies. Kimble "Kimax" burettes and Corning "Pyrex" pipettes

were used throughout this work. A 2-ml. micrometer burette obtained from Cole-Parmer Instrument and Equipment Co. was used to add small volumes of samples to the columns. The columns used were 29.5 cm. in length. The lower portion of the column, 15 cm. long with an inside diameter of 1.3 cm., held the support by means of a plug of glass wool. The top part of the column was 7 cm. long with an inside diameter of 3 cm. The liquid flow through the column was controlled with a Teflon stopcock in the middle of a 7 cm. pyrex tube with a 2 mm. bore.

#### Reagents

Alamine 336: Commercial Alamine 336 (tricaprylyl tertiary amine), obtained from General Mills, Inc., was used without further purification.

Organic solvents: Analytical reagent grade chloroform, ethyl acetate, nitrobenzene, carbon tetrachloride, and methyl alcohol were obtained from J. T. Baker Chemical Co. White label cyclohexane, tert-butyl alcohol, and iso-propyl alcohol from Eastman Chemical Company were used. In addition to these, toluene from Baker and Adamson, and ethylene glycol from Matheson Coleman and Bell were used.

Tetrabutylammonium hydroxide: Practical grade tetrabutylammonium hydroxide, 10% in methyl alcohol, was obtained from Eastman Chemical Company.

Column support: Chromosorb W (non-acid washed, 80-100 mesh) used for a column support was obtained from Johns-Manville Products Corp. This was washed with 6M hydrochloric acid until there was no evidence of iron present and then 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.

Indicator solutions: Thorin [2(2-hydroxy-3,6-disulfo-1-naphthylazo)benzenearsonic acid] obtained from Hach Chemical Co. (Ames, Iowa) was used as a 0.2% aqueous solution. Alcohol solutions that were 0.1% in 2',7'-dichlorofluorescein (Eastman Chemical Company) and 2',4',5',7'-tetrabromofluorescein sodium salt or Eosin Y (Hartman-Leddon Co., Philadelphia, Pa.) were used.

Sulfonic acids investigated: Reagent grade o-aminobenzene sulfonic acid, 2-aminotoluene-4-sulfonic acid, 2-aminotoluene-5-sulfonic acid, 4-aminotoluene-2-sulfonic acid, 4,5-dihydroxy-m-benzenedisulfonic acid (disodium salt), 2,4-dinitrobenzene sulfonic acid, 2,4-dinitro-1-naphthol-7-

sulfonic acid, 2-naphthol-6,8-disulfonic acid (dipotassium salt), o-sulfobenzoic acid (monoammonium salt), 6-thymol sulfonic acid, and p-toluene sulfonic acid were obtained from Eastman Chemical Company. Technical grade 8-amino-1-naphthol-3,6-disulfonic acid (monosodium salt), 2-amino-5-nitrobenzene sulfonic acid (sodium salt), 1-naphthol-4-sulfonic acid (sodium salt), 1-naphthol-5-sulfonic acid (sodium salt), and 2-naphthol-8-sulfonic acid (sodium salt, recrystallized) were obtained from Eastman Chemical Company. Reagent grade sulfanilic acid and sulfosalicylic acid were obtained from Mallinckrodt, reagent grade 2-naphthalene sulfonic acid and 2-naphthol-3,6-disulfonic acid (disodium salt) from Matheson Coleman and Bell, practical 4,5-dihydroxy-2,7-naphthalene disulfonic acid (disodium salt) and 6,7-dihydroxynaphthalene-2-sulfonic acid (sodium salt) from Eastman Chemical Company, and purified 2-naphthol-6-sulfonic acid (sodium salt) from Gallard-Schlesinger Chemical Mfg. Corp.

Alamine 336 hydrogen nitrate solutions: In the preliminary studies with the halides, the tertiary ammonium nitrate in an organic diluent was used as the extracting medium. Two methods of preparing the tertiary ammonium nitrate were employed. The first method involved equilibrating the Alamine

336 for five minutes with an equal volume of 1M nitric acid. Three phases resulted at the end of this equilibration, two of which were clearly organic. When the aqueous phase was replaced with a fresh batch of 1M nitric acid and the mixture shaken for five minutes, three phases still resulted, but the proportions of the two organic phases had changed. The amount of the more viscous organic phase increased while the amount of the other organic phase decreased. When fresh portions of 1M nitric acid were used several more times, the third phase disappeared. Infrared spectra of the prepared organic phase and of Alamine 336 show that the tertiary ammonium nitrate had been prepared. Nonaqueous acid-base titrations of the Alamine 336 and of the tertiary ammonium nitrate show that the salt was quantitatively prepared. The second method of preparing the amine salt was done by shaking a solution of Alamine 336 in the desired diluent with an equal volume of 1M nitric acid for five minutes. A 5% (v/v) solution of the Alamine 336 in an organic diluent was usually used and this required only one five-minute shaking period. The amine salt was almost exclusively prepared in this manner since the preparation was simpler and the product less viscous and therefore easier to use.

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

All other chemicals were common reagent grade chemicals. Distilled water was used exclusively throughout this work.

### Analytical Procedures

#### Spectrophotometric methods

Sulfonic acids: All sulfonic acids were determined spectrophotometrically in aqueous solutions using a distilled water blank. The sulfonic acids studied along with the wavelengths used for analysis and molar absorptivities are given in Table 10.

Iodide: A dilute solution of sodium hydroxide was added dropwise to the solutions containing iodide until they were about neutral, and they were diluted to 15.0 ml. Then 0.5 ml. of a 0.67% alcoholic solution of o-tolidine (Matheson Coleman and Bell) and 5 ml. of 3% hydrogen peroxide were added and mixed thoroughly. The absorbance of the resulting solution was measured at 633 m $\mu$  after 5 minutes (67).

#### Titration methods

Chloride, bromide, and iodide: The halides were titrated

Table 10. Sulfonic acids investigated

Sulfonic acid	Wavelength (m $\mu$ )	Molar absorptivity
<u>o</u> -Aminobenzene sulfonic acid	271	270
8-Amino-1-naphthol-3,6-disulfonic acid (monosodium salt)	340	5,120
2-Amino-5-nitrobenzene sulfonic acid (sodium salt)	367	7,830
2-Aminotoluene-4-sulfonic acid	271	130
2-Aminotoluene-5-sulfonic acid	273	750
4-Aminotoluene-2-sulfonic acid	275	745
4,5-Dihydroxy- <u>m</u> -benzene disulfonic acid (disodium salt)	290	3,460
4,5-Dihydroxy-2,7-naphthalene disulfonic acid (disodium salt)	348	11,200
6,7-Dihydroxynaphthalene-2-sulfonic acid (sodium salt)	282	4,780
2,4-Dinitrobenzene sulfonic acid	256	9,200
2,4-Dinitro-1-naphthol-7-sulfonic acid	284	10,700
2-Naphthalene sulfonic acid	275	4,630
2-Naphthol-3,6-disulfonic acid (disodium salt)	282	4,390
2-Naphthol-6,8-disulfonic acid (dipotassium salt)	289	5,700
1-Naphthol-4-sulfonic acid (sodium salt)	298	4,330
1-Naphthol-5-sulfonic acid (sodium salt)	302	4,060
2-Naphthol-6-sulfonic acid (sodium salt)	282	4,860
2-Naphthol-8-sulfonic acid (sodium salt)	281	2,390
Sulfanilic acid	271	200
<u>o</u> -Sulfobenzoic acid (monoammonium salt)	272	760
Sulfosalicylic acid	301	2,940
6-Thymol sulfonic acid	273	1,080
<u>p</u> -Toluene sulfonic acid	267	248

with aqueous silver(I) nitrate using adsorption indicators. Dichlorofluorescein was used for chloride at pH 4 and Eosin Y was used for bromide and iodide at pH 3.

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 (68).

Alamine 336: The tertiary amine was titrated potentiometrically in 1:1 ethylene glycol-iso-propyl alcohol with hydrochloric acid in the same solvent mixture (69). The acid was standardized with a potentiometric titration against tris(hydroxymethyl)-aminomethane (THAM) (Fisher Scientific Company).

Alamine 336 hydrochloride and hydrogen nitrate: The tertiary ammonium salts were titrated potentiometrically in tert-butyl alcohol with tetrabutylammonium hydroxide. The titrant was in 30% methyl alcohol-70% tert-butyl alcohol and standardized with a potentiometric titration against benzoic acid (Mallinckrodt).



## Measurement of Partition Coefficients

A study of the behavior of sulfonic acids with a liquid anion exchanger under given conditions can be approached from one of two directions. It is possible to determine batch partition coefficients of the sulfonic acids and relate these values to column behavior, or the partition coefficients can be calculated from observed elution curves. The use of the batch method is the more efficient for it permits a more rapid and systematic study of variables such as acid concentration and solvent choice.

Partition coefficients are a convenient means of describing the extent to which a sulfonic acid is taken up from a solution by a solution of liquid anion exchanger. The batch partition coefficient,  $K$ , is defined as the molar concentration of the sulfonic acid in the organic phase divided by the molar concentration of the sulfonic acid in the aqueous phase.

$$K = \frac{[\text{sulfonic acid}]_{\text{organic phase}}}{[\text{sulfonic acid}]_{\text{aqueous phase}}} \quad (9)$$

The batch partition coefficient obtained from equilibration studies, along with known column parameters, can be used to determine the volume of eluent required to elute a given constituent to its maximum concentration on the Gaussian

elution curve. This can be computed from Equation 10:

$$V = KV_S + V_m \quad (10)$$

where  $V$  is the volume of eluent in ml. required to elute a component to its maximum concentration,  $V_S$  is the volume of the stationary phase, and  $V_m$  is the volume of the mobile phase.

Partition coefficients were determined in the following manner: twenty milliliters of a solution containing 0.20 mmole. of the sulfonic acid of concern under the given conditions were pipetted into a 125-ml. separatory funnel. Twenty milliliters of a 5% (v/v) solution of Alamine 336 hydrochloride in toluene were 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 partition coefficients were then determined from the amount of sulfonic acid found 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 2M 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 6M 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 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% (v/v) solution of Alamine 336 hydrochloride in toluene and allowed to stand for about sixteen hours. This was then added to a glass column with a glass wool plug used to contain the sup-

port. The interstitial Alamine 336 hydrochloride in toluene was displaced by passing 2M 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.

## RESULTS AND DISCUSSION

## Preliminary Studies with Halides

The initial investigations carried out with Alamine 336 involved the extraction behavior of the halides. Batch distribution studies were performed with an aqueous solution of the anion being investigated and a solution of the tertiary ammonium salt in an organic diluent just as in solvent extraction. Various organic diluents for the tertiary ammonium nitrate were investigated to see what their effect would be on the partition coefficient of bromide. This study was carried out by dissolving a known amount of the viscous amine salt in the desired organic solvent. An equal volume of 0.01M sodium bromide and 5% (v/v) tertiary ammonium nitrate in the organic diluent were used. The organic solvents investigated were chloroform, ethyl acetate, nitrobenzene, toluene, and cyclohexane. A comparison of the partition coefficients of bromide in the different solvents indicates that the organic diluent has a marked effect on the extraction behavior of bromide. As can be seen from Table 11 this effect does not apparently relate to changes in the dielectric constant of the organic diluent being considered.

Table 11. Effect of organic diluent on the partition coefficient of bromide

Solvent	Dielectric constant	Partition coefficient
Chloroform	4.81	5.11
Ethyl acetate	6.02	2.47
Nitrobenzene	34.82	2.05
Toluene	2.38	1.88
Cyclohexane	2.02	0.95

The time required for the system to reach equilibrium is an important consideration since it is essential that partition coefficients be analyzed only after sufficient equilibration time is allowed so that a true equilibrium state is reached. The effect of the equilibration time on partition coefficients was studied for bromide. Equal volumes of 5% (v/v) tertiary ammonium nitrate in chloroform and 0.01M sodium bromide were used. The results, shown in Table 12, indicate that equilibrium is reached very rapidly with this liquid anion exchanger.

Table 12. Effect of equilibration time on the partition coefficient of bromide

Equilibration time (min.)	Partition coefficient
1.0	4.88
2.0	4.99
3.0	4.96

Distribution studies were carried out for chloride, bromide, and iodide, using chloroform and toluene as the organic diluent. These solvents were chosen because of their limited solubility in aqueous acidic solutions and because the partition coefficients for bromide using the tertiary ammonium nitrate in chloroform and in toluene were significantly different (see Table 11). Equal volumes of 5% (v/v) tertiary ammonium nitrate in the organic solvent and 0.01M solutions of the sodium halide were used. The results of these distribution studies, shown in Table 13, show that iodide is extracted to a greater extent than bromide, which is extracted to a greater extent than chloride.

Table 13. Partition coefficients of chloride, bromide, and iodide

Halide	Organic solvent	Partition coefficient	Separation factor
Chloride	chloroform	1.74	3.9
Bromide	chloroform	6.80	13.5
Iodide	chloroform	91.6	
Chloride	toluene	0.434	5.3
Bromide	toluene	2.32	23.5
Iodide	toluene	54.5	

The separation factor,  $\alpha_B^A$ , shows the preference of the liquid anion exchanger under a particular set of conditions for one anion (A) over a second anion (B), and is defined by Equa-

tion 11.

$$\alpha_B^A = \frac{K_A}{K_B} \quad (11)$$

As a general rule the separation factor should be greater than ten for optimum separations. The partition coefficients were lower in toluene, but the separation factor was higher.

Toluene was used in all further partition coefficient investigations. When solutions of the tertiary ammonium nitrate in toluene were shaken with an aqueous phase there was a good phase separation along with better separation factors for the halides.

A study was performed with the halides to find the effect of increasing the concentration of a competing anion in the aqueous phase. The nitrate ion was chosen for this study since the nitrate salt of the amine was being used. The results of this investigation are given in Table 14 and are shown in Figure 5. The partition coefficient for iodide was determined only at 0.40M sodium nitrate, and this was found to be 1.56. Equal volumes of 5% (v/v) tertiary ammonium nitrate in toluene and 0.01M sodium halide were used. The results of this study indicate that the partition coefficients of the halides can be lowered by increasing the concentration of a competing anion. The separation factor improves slightly



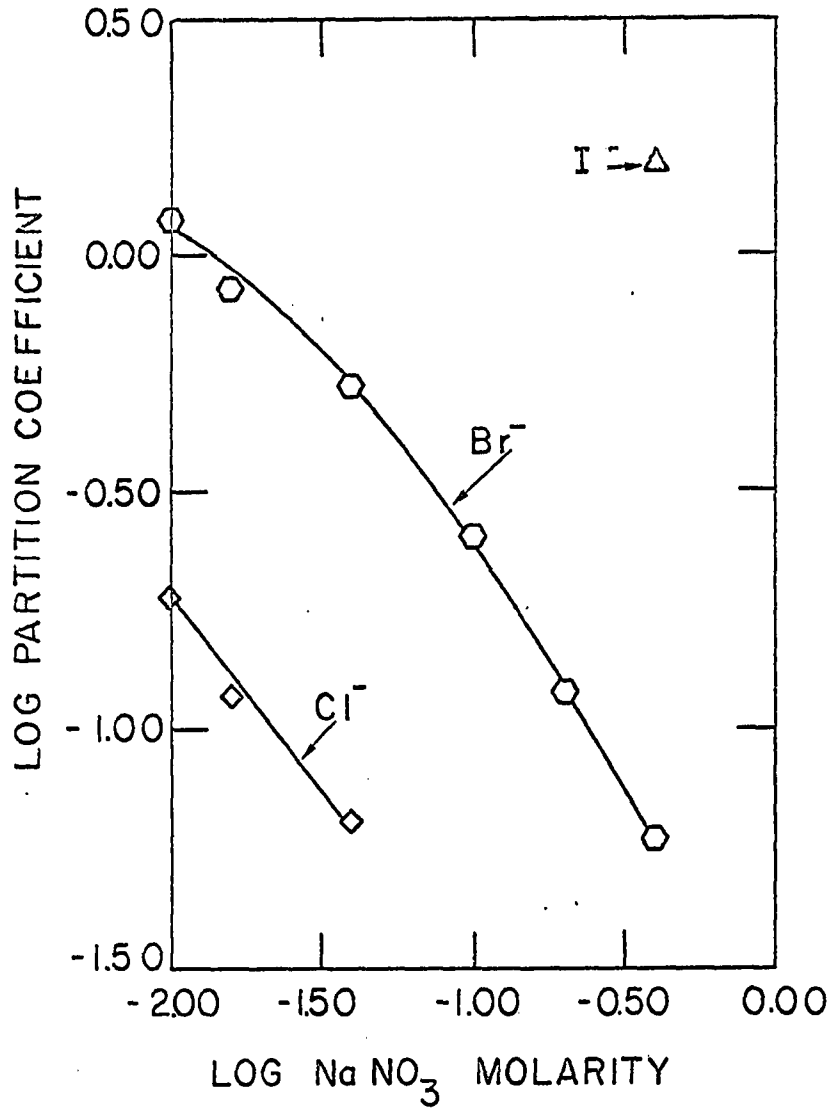


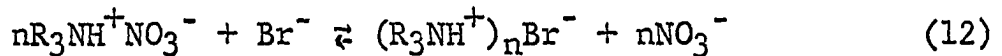
Figure 5. Effect of sodium nitrate concentration on the partition coefficient of chloride, bromide, and iodide

however with increasing sodium nitrate concentration, and the partition coefficients begin to get too small for possible separations.

Table 14. Effect of sodium nitrate concentration on the partition coefficient of chloride and bromide

[NaNO <sub>3</sub> ]	K <sub>Cl<sup>-</sup></sub>	K <sub>Br<sup>-</sup></sub>	Separation factor
0.00	0.364	2.04	5.6
0.01	0.194	1.22	6.3
0.02	0.119	0.862	7.2
0.04	0.0641	0.527	8.2
0.10		0.256	
0.20		0.123	
0.40		0.0592	

The equilibrium for the exchange of bromide is given in Equation 12 below,



and the equilibrium constant expression is shown in Equation 13

$$K_{eq.} = \frac{[(R_3NH^+)_nBr^-][NO_3^-]^n}{[R_3NH^+NO_3^-][Br^-]} \quad (13)$$

The batch partition coefficient, analogous to that in Equation 9, can be substituted into Equation 13 to give

$$K_{eq.} = \frac{K[NO_3^-]^n}{[R_3NH^+NO_3^-]^n} \quad (14)$$

Solving for the partition coefficient, K, gives

$$K = \frac{K_{eq.} [R_3NH^+NO_3^-]^n}{[NO_3^-]^n} \quad (15)$$

If the logarithm of each side of Equation 15 is taken, Equation 16 results.

$$\log K = \log K_{eq.} + n \log [R_3NH^+NO_3^-] - n \log [NO_3^-] \quad (16)$$

When the logarithm of the partition coefficient of bromide is plotted against the logarithm of the nitrate molarity, the resulting slope is equal to negative n, the number of tertiary ammonium ions combined with each bromide ion. The slope in Figure 5 for both chloride and bromide is approximately -1, indicating that there is a 1:1 combining ratio.

An increase in the concentration of sodium nitrate gradually lowered the partition coefficients of chloride and bromide. When the partition coefficient is much larger, as in the case of iodide, an anion that is more strongly taken up by the exchanger than is the iodide ion should bring the partition coefficient of iodide down faster. The perchlorate ion is very strongly taken up by anion exchangers, and partition coefficients for iodide were determined as a function of sodium perchlorate concentration and are given in Table 15. Equal volumes of 5% (v/v) tertiary ammonium nitrate in

toluene and 0.01M sodium iodide were used. From this study it is clear that the perchlorate ion lowers the partition coefficient of iodide considerably.

Table 15. Effect of sodium perchlorate concentration on the partition coefficient of iodide

[NaClO <sub>4</sub> ]	Partition coefficient
0.00	54.5
0.01	17.5
0.02	10.7
0.04	4.23
0.10	0.686
0.20	0.225
0.40	0.088

A qualitative separation of the halides was performed with Alamine 336 hydrogen nitrate on a Chromosorb W column, with no organic diluent present. The sample added to the column consisted of approximately 0.05 mmole. each of sodium chloride, sodium bromide, and sodium iodide and the chloride was eluted with 0.03M sodium nitrate. The eluent was changed to 0.40M sodium nitrate to elute the bromide and to 0.10M sodium hydroxide to strip off the iodide. The sodium hydroxide neutralized the tertiary ammonium nitrate to free the iodide and left the tertiary amine on the support. A sodium hydroxide solution was used to elute the iodide when a one

molar perchlorate solution produced tailing. The elution curve is given in Figure 6.

#### Studies with Sulfate and Sulfonic Acids

The preliminary studies with the halides have shown that a 5% (v/v) solution of the tertiary ammonium nitrate in toluene resulted in good separation factors as well as in good phase separations; thus this system was chosen for studies of sulfate and sulfonic acid behavior. The sulfonic acids studies were analyzed spectrophotometrically and nitrate interfered with these determinations. Since the presence of chloride did not interfere with any of the spectrophotometric determinations, the chloride form of Alamine 336 was used for the studies. All partition coefficients were determined using a 5% (v/v) solution of Alamine 336 hydrochloride in toluene.

The partition coefficient for sulfate was determined as a function of the hydrochloric acid concentration in the aqueous phase. An equal volume of 5% (v/v) Alamine 336 hydrochloride in toluene and 0.013M sodium sulfate were used. The partition coefficients were very low, as shown in Table 16 and Figure 7.

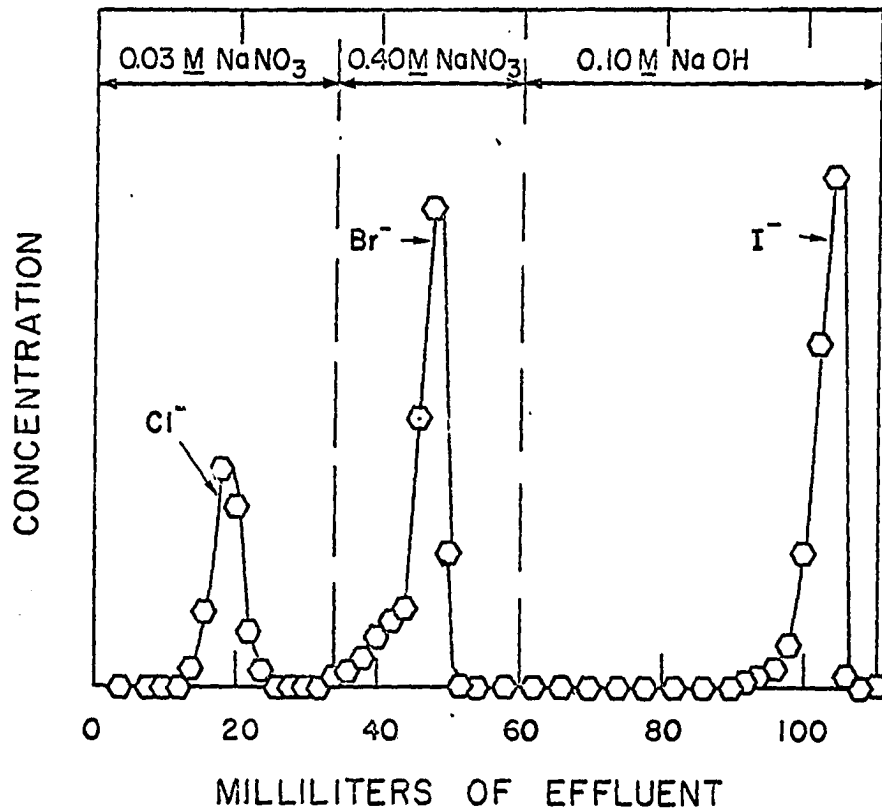


Figure 6. Elution curve for qualitative chloride-bromide-iodide separation (column: Chromosorb W, Alamine 336 hydrogen nitrate, 1.3 x 12 cm.; flow rate: 1.2 ml./min.; 0.05 mmole. each of sodium chloride, sodium bromide, and sodium iodide)

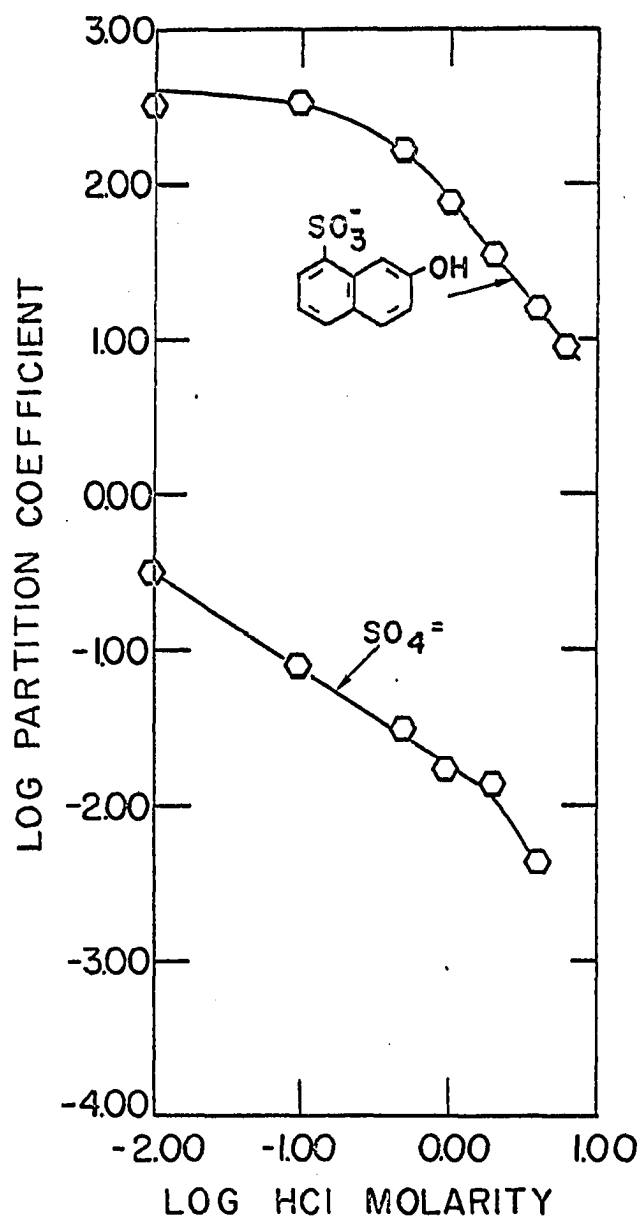


Figure 7. Effect of hydrochloric acid concentration on the partition coefficient of sulfate and 2-naphthol-8-sulfonate

Table 16. Effect of hydrochloric acid concentration on the partition coefficient of sulfate and 2-naphthol-8-sulfonate

[HCl]	$K(SO_4^{=})$	$K(2\text{-naphthol-8-sulfonate})$
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

Essentially the same study that was carried out for sulfate was also done for 2-naphthol-8-sulfonic acid (sodium salt). The partition coefficients were determined with a spectrophotometric analysis of the aqueous phase after equilibration. The partition coefficients were much higher than for sulfate, but they also decreased with increasing hydrochloric acid concentration. These results are given in Table 16 and Figure 7.

In the studies with the halides the tertiary ammonium nitrate was used. It was shown that the slope obtained when the logarithm of the partition coefficient of bromide was plotted against the logarithm of the nitrate molarity indicated the combining ratio of tertiary ammonium ions to bromide ions. A similar relationship was worked out for Alamine 336



hydrochloride and sulfonic acids using equations analogous to Equations 12-16. In this case the logarithm of the partition coefficient of the sulfonic acid was plotted against the logarithm of the chloride molarity. This was done with several sulfonic acids and the results are shown in Table 17 and Figure 8. The concentration of sodium chloride was varied in each sample while the concentration of hydrochloric acid was held constant at one molar. There appears from the slope to be one Alamine 336-hydrochloride for the monosulfonic acids and two for the disulfonic acid.

Table 17. Effect of total chloride concentration on the partition coefficient of several sulfonic acids

Total [Cl <sup>-</sup> ]	2-Naphthol-8-sulfonic acid sodium salt	2-Naphthalene sulfonic acid	2-Naphthol-3,6-disulfonic acid disodium salt
1.0	80.0	124	18.9
1.1	72.3	115	15.3
1.3	59.1	99.0	11.4
1.6	48.1	84.8	7.33
2.0	39.6	68.7	5.12

An increase in the perchlorate concentration, as shown in Table 15, resulted in a rapid decrease in the partition coefficient of iodide. The effect of perchloric acid concentration as well as of sodium bromide concentration on the partition coefficient of several sulfonic acids was investi-

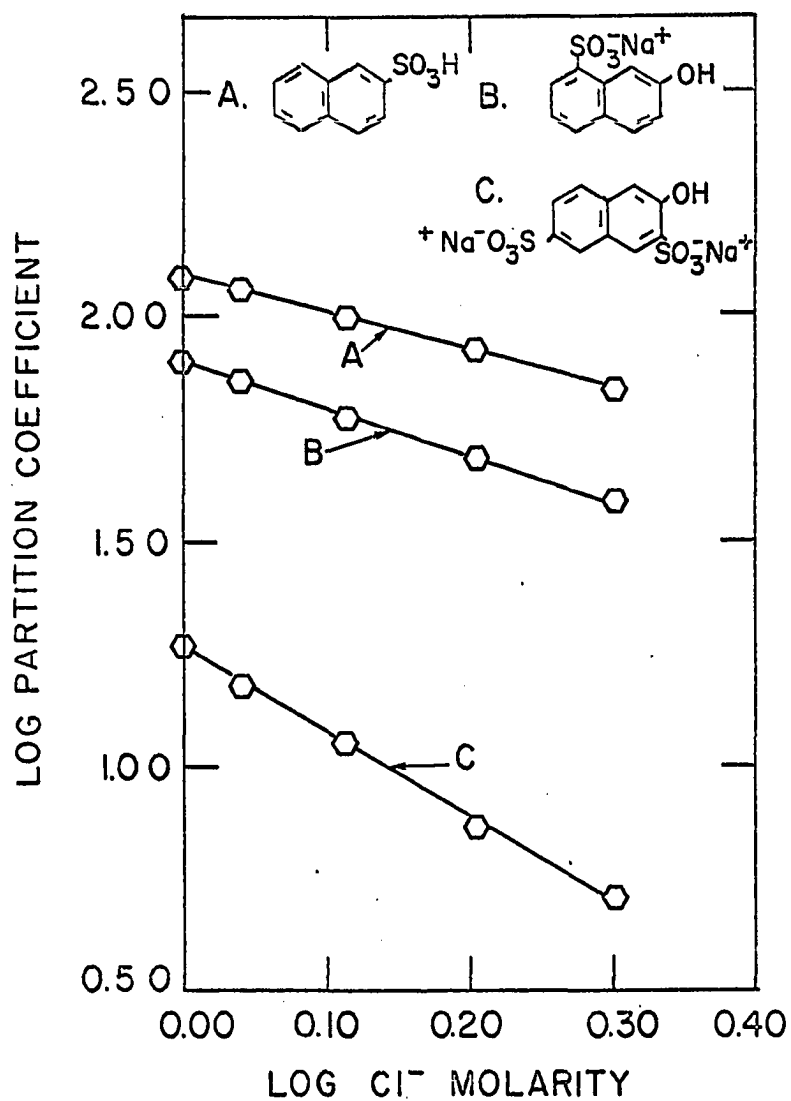


Figure 8. Effect of chloride concentration on the partition coefficients of several sulfonic acids

gated. The perchlorate anion is more highly extracted by Alamine 336 than the bromide anion. The partition coefficients of sulfonic acids will be lower in a perchlorate medium since the perchlorate will displace the sulfonic acid to a greater extent. The samples used in determining the partition coefficients shown in Table 18 (Figures 9 and 10) were each 1.0 molar in hydrochloric acid. The partition coefficients listed in Table 19 (Figure 11) were determined for solutions containing no added hydrochloric acid.

The organic phase in the partition coefficient studies with perchloric acid shown in Figure 11 was approximately 0.1M Alamine 336 hydrochloride in toluene. At perchloric acid concentrations greater or equal to 0.10M partition coefficients for all the sulfonic acids appeared to approach zero. When the concentration of the perchloric acid in the aqueous phase becomes equal to the concentration of the amine hydrochloride in the organic phase all of the sulfonic acids are displaced into the aqueous phase. This is probably due to the quantitative formation of the tertiary ammonium perchlorate.

The effect of increased sulfonic acid concentration on the partition coefficient was studied for 2-naphthalene

Table 18. Effect of sodium bromide and perchloric acid concentration on the partition coefficients of several sulfonic acids

Sulfonic acid	[NaBr]				[HClO <sub>4</sub> ]			
	0.1	0.3	0.6	1.0	0.1	0.3	0.6	1.0
2-Naphthol-8-sulfonic acid sodium salt	37.2	13.3	7.10	4.36	1.22	0.195	0.0949	0.0526
2-Naphthol-6-sulfonic acid sodium salt	7.82	4.00	2.06	1.31	0.395	0.111	0.0714	0.0526
2-Naphthalene sulfonic acid	72.3	35.2	21.6	14.5	10.8	2.37	1.04	0.563
2-Naphthol-3,6-disulfonic acid disodium salt	5.67	1.68	0.531	0.220	0.0564	~0	~0	~0
p-toluene sulfonic acid	5.58	2.88	1.60	1.14	1.07	0.288	0.0909	0.0638

Table 19. Effect of perchloric acid concentration on the partition coefficient of several sulfonic acids

[HClO <sub>4</sub> ]	Compound <sup>a</sup>	Compound <sup>b</sup>	Compound <sup>c</sup>	Compound <sup>d</sup>	Compound <sup>e</sup>
0.01	132	499	999	713	163
0.05	2.89	12.1	89.5	10.7	24.4
0.08	0.149	0.389	2.26	0.432	2.54

<sup>a</sup>4,5-Dihydroxy-m-benzene disulfonic acid disodium salt.

<sup>b</sup>4,5-Dihydroxy-2,7-naphthalene disulfonic acid disodium salt.

<sup>c</sup>2-Naphthol-3,6-disulfonic acid disodium salt.

<sup>d</sup>2-Naphthol-6,8-disulfonic acid dipotassium salt.

<sup>e</sup>2-Naphthol-6-sulfonic acid sodium salt.

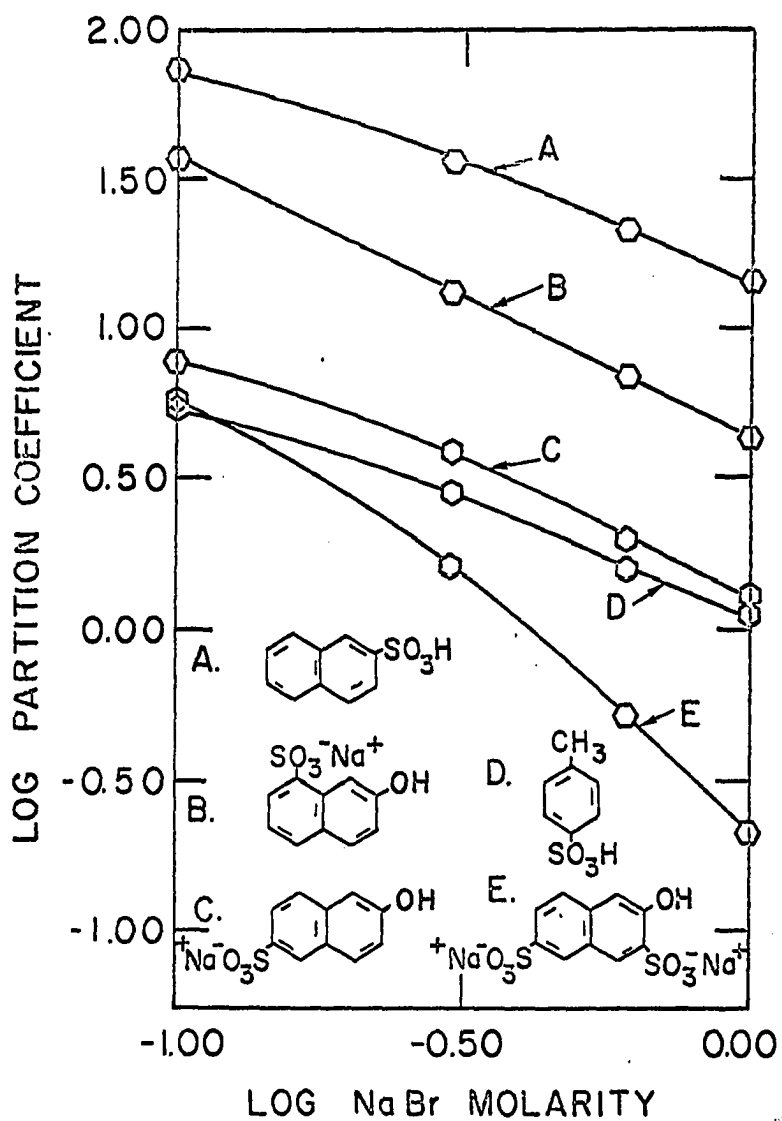


Figure 9. Effect of sodium bromide concentration on the partition coefficient of several sulfonic acids

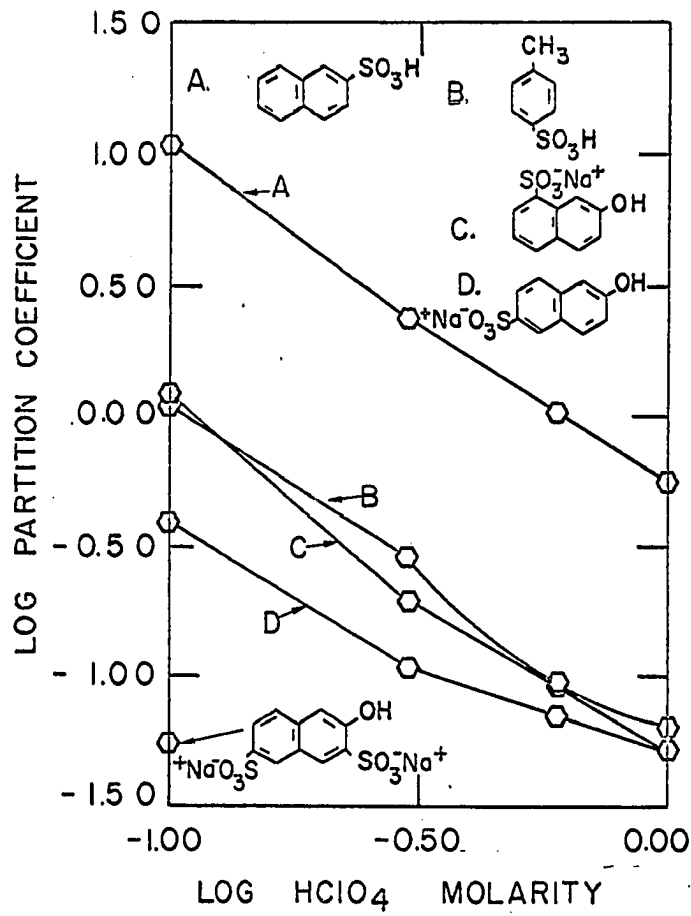


Figure 10. Effect of perchloric acid concentration on the partition coefficient of several sulfonic acids

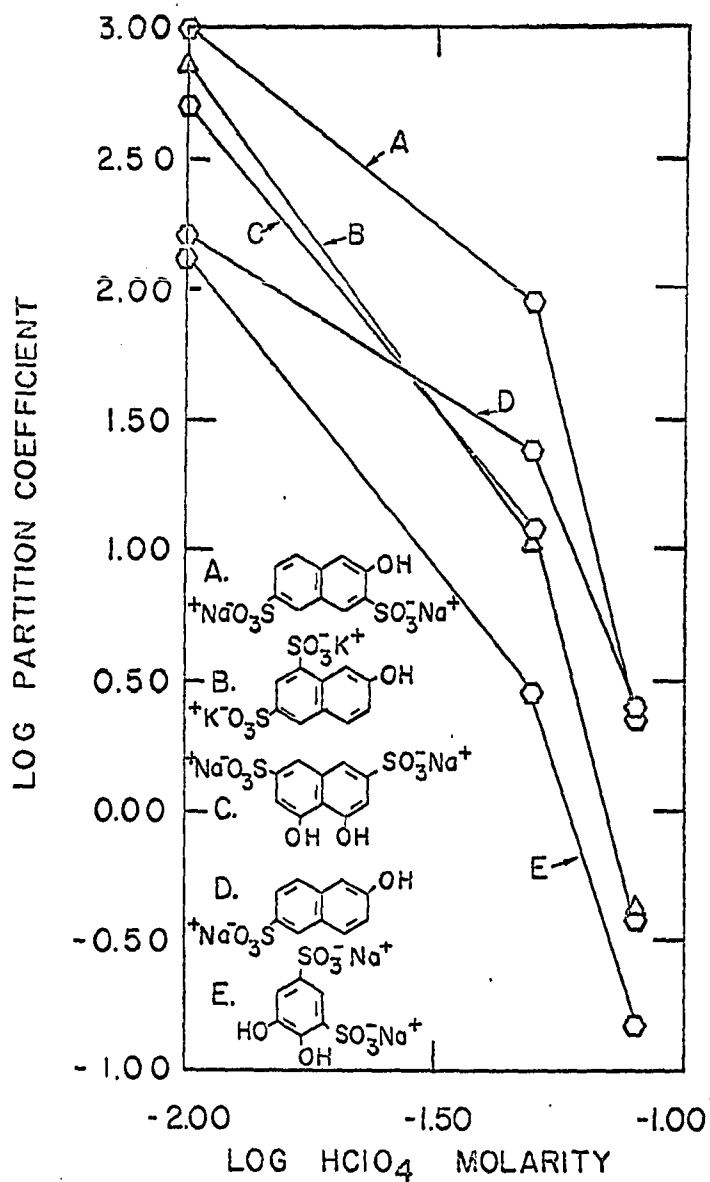


Figure 11. Effect of perchloric acid concentration on the partition coefficient of several sulfonic acids



sulfonic acid. The concentration of Alamine 336 hydrochloride in toluene was kept constant at 0.1 molar and the aqueous phase was kept 0.3M sodium chloride-1.0M hydrochloric acid while the concentration of 2-naphthalene sulfonic acid was increased. The results of this loading study are given in Table 20 (Figure 12). Since the partition coefficient 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.

Table 20. Effect of loading of 2-naphthalene sulfonic acid on the partition coefficient

% Loading	[2-Naphthalene sulfonic acid]	Partition coefficient
1.0	0.0010	59.6
2.5	0.0025	61.5
5.0	0.0050	52.5
10.0	0.0100	42.5
50.0	0.0500	33.9
62.5	0.0625	29.7
75.0	0.0750	24.6
87.5	0.0875	13.5
100.0	0.1000	9.71
125.0	0.1250	3.87
150.0	0.1500	2.17

The effect of the Alamine 336 hydrochloride concentration in toluene on the partition coefficient was studied for 2-naphthol-6-sulfonic acid (sodium salt) and 2-naphthol-3,

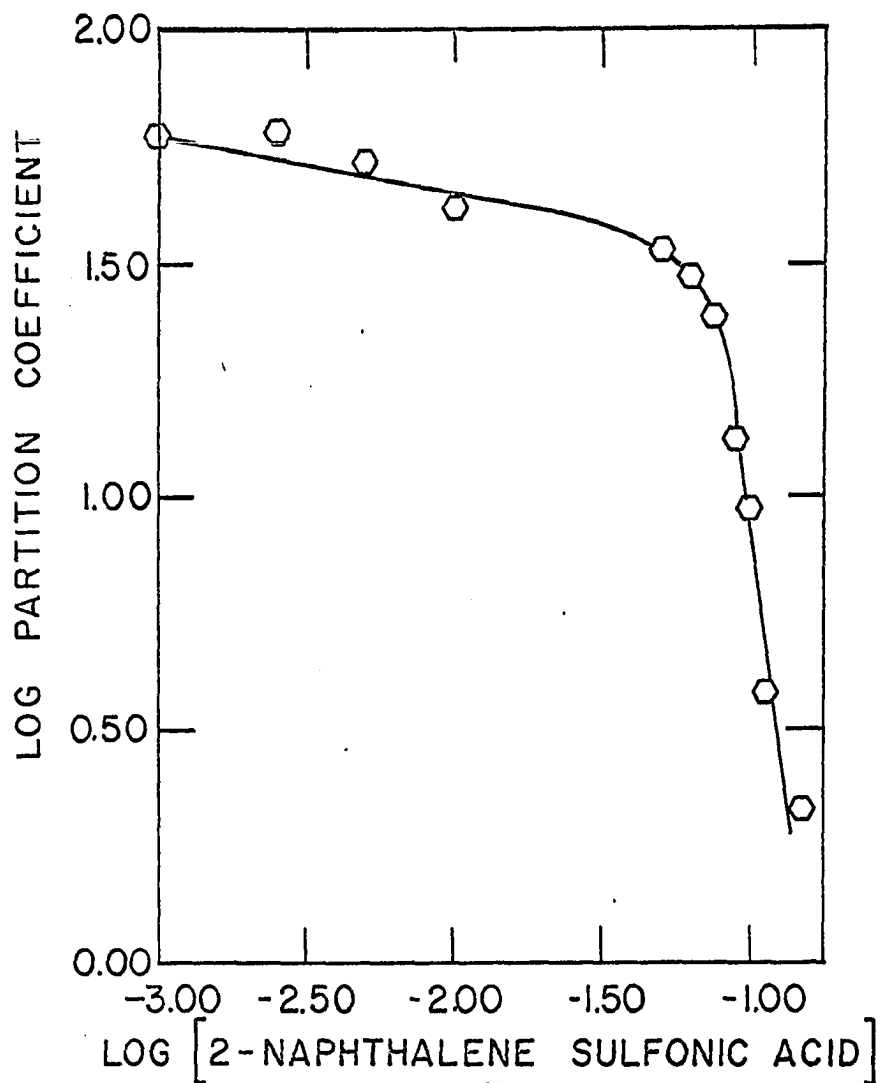


Figure 12. Effect of loading on the partition coefficient of 2-naphthalene sulfonic acid

6-disulfonic acid (disodium salt). The results of this study are given in Table 21 and Figure 13.

Table 21. Effect of Alamine 336 hydrochloride concentration on the partition coefficient of two sulfonic acids

$[R_3NH^+Cl^-]$	$K^a$	$K^b$
0.0212	0.827	0.562
0.0416	2.98	2.14
0.0604	6.16	5.38
0.1016	16.1	17.8
0.1516	32.4	41.5
0.1997	53.3	72.5

<sup>a</sup>2-Naphthol-6-sulfonic acid sodium salt.

<sup>b</sup>2-Naphthol-3,6-disulfonic acid disodium salt.

A relationship like that in Equation 16 was derived for Alamine 336 hydrochloride and sulfonic acids. When the logarithm of the partition coefficient of the sulfonic acid is plotted against the logarithm of the Alamine 336 hydrochloride molarity, the resulting slope is equal to  $n$ , the number of tertiary ammonium ions combined with each sulfonic acid anion. The slope of the lines in Figure 13 indicates that there are approximately two tertiary ammonium ions for every sulfonic acid.

A survey of the extraction behavior of twenty-two sulfonic acids was carried out under fixed conditions. The sulfonic acid solutions were 0.01M in sulfonic acid and 0.5M in hydro-

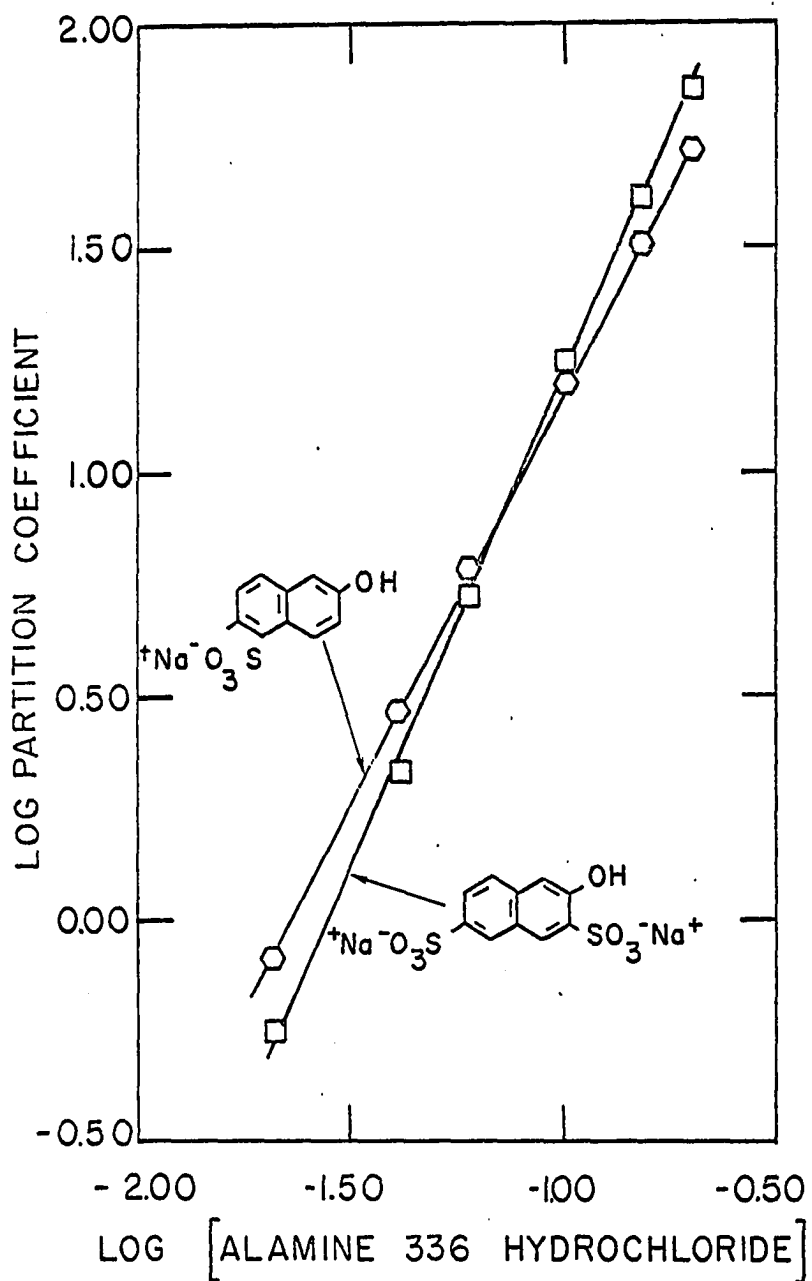


Figure 13. Effect of Alamine 336 hydrochloride concentration on the partition coefficient of two sulfonic acids

chloric 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 22.

#### Separations of Sulfonic Acids

The partition coefficient for sulfate in 1.0M hydrochloric acid, given in Table 16, and for 2-naphthalene sulfonic acid in 1.0M hydrochloric acid, given in Table 17 indicate that it should be possible to separate these components by batch extraction. A mixture was prepared that was 0.05M 2-naphthalene sulfonic acid, 0.10M sulfuric acid, and 1.0M 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 1.0M 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 23. A batch separation such as this would be very useful for

Table 22. Survey of sulfonic acids and their partition coefficients

Sulfonic acid	K
Sulfanilic acid	~0
2-Aminotoluene-5-sulfonic acid	~0
2-Aminotoluene-4-sulfonic acid	~0
4-Aminotoluene-2-sulfonic acid	0.0067
8-Amino-1-naphthol-3,6-disulfonic acid (monosodium salt)	0.0345
<u>o</u> -Aminobenzene sulfonic acid	0.0380
4,5-Dihydroxy- <u>m</u> -benzene disulfonic acid (disodium salt)	3.29
Sulfosalicylic acid	7.45
<u>p</u> -Toluene sulfonic acid	13.3
6,7-Dihydroxynaphthalene-2-sulfonic acid (sodium salt)	13.3
<u>o</u> -Sulfobenzoic acid (monoammonium salt)	14.4
1-Naphthol-5-sulfonic acid (sodium salt)	15.9
2-Naphthol-6,8-disulfonic acid (dipotassium salt)	16.1
4,5-Dihydroxy-2,7-naphthalene disulfonic acid	20.4
2-Naphthol-8-sulfonic acid (sodium salt)	35.6
6-Thymol sulfonic acid	39.0
1-Naphthol-4-sulfonic acid (sodium salt)	43.7
2-Naphthol-3,6-disulfonic acid (disodium salt)	62.9
2-Amino-5-nitrobenzene sulfonic acid (sodium salt)	119
2-Naphthalene sulfonic acid	176
2,4-Dinitro-1-naphthol-7-sulfonic acid	298
2,4-Dinitrobenzene sulfonic acid	740

removing a large amount of sulfonic acid from sulfonation mixtures.

Table 23. Batch separation of 2-naphthalene sulfonic acid from sulfate<sup>a</sup>

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

<sup>a</sup>2.00 mmole. Alamine 336 hydrochloride.

The relationship of partition coefficients and column behavior for several sulfonic acids was studied using a 1.3 x 11 cm. column of Chromosorb W coated with Alamine 336 hydrochloride without any organic diluent. It was found that sulfonic acids having partition coefficients of less than 0.04 (see Table 22) could be eluted quantitatively from the column with 60 ml. of 0.5M hydrochloric acid, while sulfonic acids having partition coefficients 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 0.1M perchloric acid-1.0M hydrochloric acid, those sulfonic acids with partition coefficients 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 partition coefficients from other sulfonic acids. Flow rates of 1.0 ml./min. were used with a 1.3 x 11 cm. column to Chromosorb W containing 1.00 ml. of Alamine 336. The amino-sulfonic acids with low partition coefficients were eluted with 0.5M hydrochloric acid and the second component was then stripped off the column with 1.0M perchloric acid-1.0M hydrochloric acid. The results of these separations are given in Table 24.

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. Elution curves were prepared by monitoring the effluent spectrophotometrically using a flow-through cell. The column was connected to the flow-through cell with a short piced of 2 mm. i.d. polyethylene tubing, which allowed no mixing. Using this means of detection it was found experimentally that 22.5 ml. of 2M hydrochloric acid were required to elute 2-naphthol-3,6-disulfonic acid disodium salt to



Table 24. Quantitative separations of sulfonic acids

Separation	mmole. Added	mmole. Found	% Recovery
I. a) Sulfanilic acid	0.0500	0.0518	103.6
b) <u>p</u> -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- <u>m</u> -benzene disulfonic acid (disodium salt)	0.0500	0.0499	99.8
IV. a) <u>o</u> -Aminobenzene sulfonic acid	0.0500	0.0524	104.8
b) 2-Amino-5-nitrobenzene sulfonic acid (sodium salt)	0.0500	0.0497	99.4
V. a) <u>o</u> -Aminobenzene sulfonic acid	0.0500	0.0512	102.4
b) 6,7-Dihydroxynaphthalene-2-sulfonic acid (sodium salt)	0.0500	0.0502	100.4

its maximum concentration. This compared favorably with a maximum elution volume of 18.7 ml. calculated using Equation 10 where  $V_S = 2.6$  ml.,  $V_m = 5.4$  ml., and  $K = 5.12$ . A similar elution of 2-naphthol-6-sulfonic acid sodium salt was performed and the experimentally determined maximum elution volume was 28.5 ml. compared to a calculated volume of 34.0 ml. ( $V_S = 2.6$  ml.,  $V_m = 5.4$  ml.,  $K = 11$ ). It can be seen that the actual column behavior can be quite reliably predicted from a knowledge of column parameters and the use of an expression which was originally designed to describe solvent extraction column behavior. It is notable that the concentration of Alamine 336 hydrochloride on the support, as determined by a nonaqueous acid-base titration, was the same as the concentration of the amine salt in the solution that the Teflon was placed in. From this it appears that the Teflon exhibits little, if any, preference for Alamine 336 hydrochloride or toluene.

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 behavior of the sulfonic acids was predictable from the column parameters and Equation

10. The partition coefficients 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 2M 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 x 7.6 cm. Teflon column using a flow rate of 0.5 ml./min. The first component was eluted with 2M hydrochloric acid, and the second component was stripped off with 0.1M perchloric acid. The results of these separations are given in Table 25.

Table 25. Quantitative separations of sulfonic acids

Separation		$\mu$ mole. Added	$\mu$ mole. Found	% 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

## SUMMARY

A liquid anion exchanger, Alamine 336, was investigated to find its potential use for the separation of aromatic sulfonic acids. Preliminary studies of variables such as organic diluent and competing anions on the partition of the halides produced a qualitative separation of chloride, bromide, and iodide. Kinetic studies showed that equilibrium was reached after several minutes of equilibration exhibiting a distinct advantage over solid ion exchange resins. The halide investigations were useful not only in producing a halide separation, but also for suggesting conditions for the separation of aromatic sulfonic acids.

Partition coefficients were determined for twenty-two aromatic sulfonic acids, and several quantitative separations were carried out on Chromosorb W columns impregnated with Alamine 336. The behavior of aromatic sulfonic acid isomers on a Teflon column coated with Alamine 336 hydrochloride in toluene was predicted from the partition coefficients and the column parameters, and quantitative separations were performed. Sulfate-free 2-naphthalene sulfonic acid was obtained from a mixture of the sulfonic acid and sulfuric acid with a single equilibration with Alamine 336 hydrochloride in

toluene.

Rapid kinetics, high selectivity, and high capacity make liquid anion exchangers very attractive for the separation of aromatic sulfonic acids. No special equipment is required and the operating procedures are simple.

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