

[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, LOS ANGELES]

The Use of Thenoyltrifluoroacetone in Ion Exchange Separations<sup>1</sup>

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RECEIVED NOVEMBER 3, 1953

Conditions are established under which thenoyltrifluoroacetone can be successfully employed as an eluting agent in ion exchange separations of rare earths. Complete separation of yttrium and europium using this reagent and very short column is demonstrated. Possible applications of the method are discussed.

## Introduction

In the separation of rare earths on ion exchange columns it is customary to use a solution of complexing anion with the pH adjusted to provide the proper concentration of complexing species. Citrate ion has been most commonly used in such separations<sup>2</sup> and gives very good separations of most of the rare earth and rare earth-like elements. However, some of the elements are eluted at very nearly the same rate so that separation by this means requires long columns and is impractical for separation of short-lived radioactive nuclides. The work reported here was undertaken to test the utility of the chelating agent, thenoyltrifluoroacetone, as a complexing species in ion exchange separations. This compound, hereafter referred to as HTTA, has found great use as a selective agent for extracting various metal ions into an organic phase.<sup>3</sup> The very selective nature of HTTA in these extraction separations suggested that it might be useful in ion exchange separations of the rare earths.

In predicting the degree of separation of a given pair of ions by ion exchange it is usual<sup>4</sup> to define a separation factor,  $\alpha$ , as the ratio of the equilibrium distribution coefficients of the two ions. These considerations applied to HTTA and the ammonium form of a resin are

$$\alpha = \frac{K_d^M}{K_d^M} = \frac{K_{\text{exchange}}^{M_1}}{K_{\text{exchange}}^{M_2}} \times \frac{K_{\text{complex}}^{M_1}}{K_{\text{complex}}^{M_2}}$$

$$K_{\text{exchange}} = \frac{(\text{MR}_3)(\text{NH}_4^+)^2}{(\text{M}^{+3})(\text{NH}_4\text{R})^3}$$

$$K_{\text{complex}} = \frac{(\text{M}^{+3})(\text{TTA}^-)^3}{[\text{M}(\text{TTA})_3]}$$

If the value of  $K_{\text{complex}}$  varies widely (as it does for HTTA) for different metal ions,  $\text{M}^{+3}$ , then one would expect large values for the separation factor,  $\alpha$ .

## Experimental and Results

1. **General.**—Dow Chemical Company HTTA was used without further purification. Technical 1,4-dioxane was purified by the method of Fieser.<sup>5</sup> The ammonium hydroxide, ammonium chloride hydrochloric acid and citric acid used were all of reagent grade. Dowex 50 cation exchange resin, hydrogen form, of particle size 250-500 mesh was used. The resin was converted to the ammonium form by allowing it to stand overnight in a saturated solution of ammonium chloride.

The tracer solutions used were obtained as follows: Car-

(1) This work was supported in part by the U. S. Atomic Energy Commission.

(2) Many references are given by Jack Schubert, F. C. Nachod (Editor), "Ion Exchange," Academic Press, Inc., New York, N. Y., 1949, pp. 167-220.

(3) A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds," Prentice-Hall, Inc., New York, N. Y., 1952, pp. 451-468.

(4) E. R. Tompkins and S. W. Mayer, THIS JOURNAL, **69**, 2859 (1947).

(5) L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., New York, N. Y., 1941, pp. 368-369.

rier free Y<sup>91</sup> tracer solution was obtained from the Isotopes Division, Atomic Energy Commission. Small samples of this supply were diluted with 0.1 N HCl to provide convenient activities for column work. A mixture of Eu<sup>152</sup> and Eu<sup>154</sup> tracers was obtained from a 0.1 g. sample of Eu<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub> which had been irradiated in the Oak Ridge nuclear reactor. The solid was dissolved in dilute HCl and small samples of this stock solution were further diluted with 0.1 N HCl to provide convenient activities for column work.

2. **Solubility of HTTA.**—The solubility of HTTA in dioxane-water mixtures was measured by titration of solutions of HTTA in dioxane with water to the appearance of a second phase. The values given in Table I are the solubilities of solid HTTA in various mixtures of water and dioxane at room temperature. It can be seen that a wide range of HTTA concentrations is available provided a sufficient amount of dioxane is present.

TABLE I

SOLUBILITIES OF HTTA IN WATER-DIOXANE MIXTURES		
Weight % HTTA	Weight % H <sub>2</sub> O	Weight % C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>
1.1	76.0	22.9
2.1	65.7	32.2
3.7	59.4	36.9
6.4	49.8	43.8
10.0	41.0	49.0
11.5	38.8	49.7
15.0	33.6	51.4
17.4	29.6	53.0

3. **Equilibrium Studies.**—The following method was used in equilibrium studies to determine the values of the equilibrium distribution coefficient,  $K_d$ , at conditions close to those of column operation. Samples of Dowex 50 (NH<sub>4</sub><sup>+</sup> form) weighing 0.2-0.3 g. were weighed out into cork-stoppered glass vials. Then 7.00 ml. of the following HTTA solution was added to each vial: 50.0 ml. water: 47.0 ml. dioxane: 2.3 g. HTTA. The proportions in this solution were designed such that further addition of water and tracer solution would produce a solution closely approximating the "2%" HTTA solution (2% HTTA, 38% dioxane, 60% water) used in column operation. Then 250 microliters of diluted tracer solution (Y or Eu) was added to each vial from a micropipet along with 0.5 ml. of wash liquid. Next the vials were shaken and each vial was adjusted to the proper pH with NH<sub>4</sub>OH and/or HCl solutions. All pH's were measured on a Beckman Model G pH meter which was frequently standardized with Beckman phosphate buffer solution. A control sample was also provided for each set of runs in which tracer and HTTA solution but no resin were added to a vial. The control samples were adjusted to a pH of approximately 1.0.

All samples were shaken overnight on a mechanical shaker to ensure attainment of equilibrium. The pH of each sample was remeasured since there was usually a decrease in pH. The resin was allowed to settle, and a sample of solution was drawn from each vial, dried on a watch glass, and counted with a thin window Geiger-Müller tube.

It was assumed that the counts registered by the control sample corresponded to no adsorption of tracer by resin. Then the percentage tracer absorbed could be calculated from the relation

$$\% \text{ tracer absorbed} = \frac{(\text{counts/min. of control}) - (\text{counts/min. of sample})}{(\text{counts/min. of control})} \times 100$$

$K_d$  could then be calculated from the relation

$$K_d = \frac{\% \text{ tracer absorbed}}{100 - \% \text{ tracer absorbed}} \times \frac{\text{vol. of liquid (estimated)}}{\text{mass of resin}}$$

Values of  $K_d$  for various  $pH$ 's in the case of yttrium and of europium were determined, using 2% HTTA. Figure 1 summarizes the results. In the  $pH$  range 4.8-6.0,  $K_d$  for europium is lower than  $K_d$  for yttrium. The hydrated ionic radius of europium is less than that of yttrium so it would be expected that europium would be more strongly adsorbed than yttrium. That such is not the case implies that the TTA<sup>-</sup> chelate with europium is more stable than the TTA<sup>-</sup> chelate with yttrium.

A plot of  $\log K_d$  against  $pH$  should give a straight line provided the activities of  $NH_4R$ ,  $NH_4^+$  and HTTA are constant. In this work measurements of  $K_d$  were made at column-operating conditions, and no attempt was made to keep such factors as amount of resin and  $NH_4^+$  concentration constant. The data for yttrium correspond to carrier free tracer concentrations, while those for europium were obtained with macro quantities of europium present. It can be seen that the yttrium data are more nearly linear than the data for europium. The non-linearity of the europium curve is probably due to the relatively large amount of europium having exceeded the solubility of the  $Eu(TTA)_3$  salt at the higher  $pH$ 's.

From the plots of  $\log K_d$  vs.  $pH$  it is possible to calculate values of the separation factor  $\alpha$ . The values of  $\alpha$  calculated from smooth curves drawn through the experimental points in Fig. 1 indicate that maximum separation should be achieved at an elutriant  $pH$  of about 5.4. However, other factors must also be considered in selecting a starting  $pH$  for column operation. If  $K_d$  is too large, then passage of rare earth down the column is very slow, so that a rapid separation is not possible.

Another complicating factor with HTTA solutions is the slow but measurable decrease of  $pH$  with time after an HTTA solution is adjusted to a  $pH$  of 4.5-6.5 with  $NH_4OH$ . It was found that separate "2%" HTTA solutions made from separate lots of HTTA varied markedly in their rates of  $pH$  decrease. This suggests that careful purification of HTTA would be necessary before definitive rates of  $pH$  decrease for different HTTA concentrations could be measured.

A tentative explanation for this decrease in  $pH$  can be obtained from the work of Cook and Taft.<sup>6</sup> They state that in aqueous solution or in 50% (vol.) aqueous dioxane the principal species present is the hydrate of HTTA which undergoes an extremely rapid base-catalyzed cleavage forming trifluoroacetic acid. It is possible that this reaction could occur slowly even at a  $pH$  of 5; the production of trifluoroacetic acid would account for the observed decrease in  $pH$ .

**4. Column Studies.**—Small columns with an inner bore of 1-2 mm. were used in all studies. The columns had a resin bed 10 cm. in length supported at the bottom by a small glass wool plug. The Dowex 50 (ammonium form) used in the columns was graded by allowing it to settle in approximately 8 cm. of water and discarding all resin which settled in less than two minutes or greater than seven minutes.

It was found necessary to condition the column by allowing 50% aqueous dioxane solution to flow through the column for several hours prior to addition of tracer and subsequent elution. After the column had been conditioned, tracer was added. A small quantity of resin (never more than 1/20 of that already in the column) was shaken for about 15 minutes with separate or mixed tracer solution. The resin was filtered by suction, air-dried for about 5 minutes and added directly to the top of the resin bed.

After tracer was adsorbed on the column, two concentrations of HTTA solutions were used as elutriants. "5%" HTTA consisted of the proportions: 5.0 g. HTTA, 45.0 ml. of dioxane; 50.0 ml. of water. "2%" HTTA consisted of the proportions: 2.0 g. of HTTA; 38.0 ml. of dioxane; 60.0 ml. of water. These percentages are close to the true percentages by weight. The  $pH$  of the elutriant solution was adjusted by dropwise addition of ammonium hydroxide.

After the tracer was on the column, the conditioning liquid was removed from the upper portion; elutriant solu-

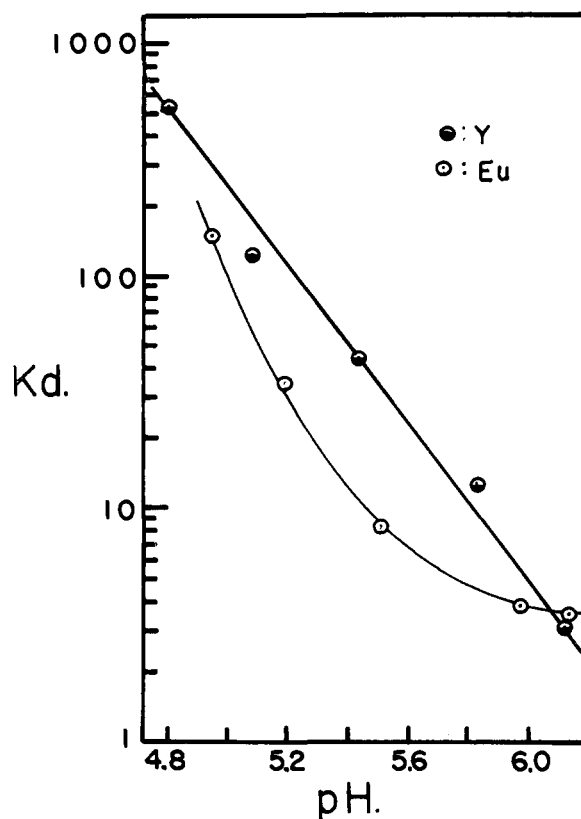


Fig. 1.—Dependence of the distribution coefficient on  $pH$ .

tion at the proper  $pH$  was added from the reservoir (rubber tubing but not "Tygon" may be used) and column operation was started. Successive samples of effluent were collected during 20-minute periods on one inch watch glasses by means of an automatic fraction collector. The flow rate obtained with a reasonable height of the reservoir was 0.1 ml. per sq. cm. per minute. The samples were then dried and counted as previously described.

The identities of the yttrium and europium peaks were easily established by aluminum absorption curves since the europium tracer has a much higher percentage of  $\gamma$ -radiation.

The first column runs were made using yttrium tracer and "5%" HTTA. The best results were obtained at  $pH$  4.97 and showed a sharp yttrium peak followed by three much smaller peaks, undoubtedly due to long-lived radioactive impurities in the yttrium tracer solution. Such curves obtained from a column only 10 cm. in length illustrate that HTTA is indeed useful in rare earth separations.

Many column runs were made using "5%" HTTA and starting  $pH$ 's in the region 4.8-5.2. Some mechanical difficulties were encountered due to crystal formation and subsequent stoppage in the column. Even in the absence of these difficulties the elution curves were not reproducible although at times they were very good. Substitution of ammonium acetate for ammonium hydroxide as a reagent for adjusting the  $pH$  gave a slower change in  $pH$  with time but did not improve the reproducibility of the results. When "2%" HTTA was used the crystal formation was avoided and the elution curves were reproducible.

A number of separations of mixtures of yttrium and europium were made using "2%" HTTA at  $pH$ 's in the region 5.8-6.0. Aluminum absorption curves of peak activities confirmed the conclusion drawn from  $K_d$  measurements that europium was eluted before yttrium. Typical elution curves are obtained with a narrow europium peak and, well separated from it, a broader yttrium peak. The ratio of the volumes of elutriant solution at the two peaks is approximately 1.7.

For comparison purposes an elution was also performed on a mixture of yttrium and europium using 0.17 *M* citric acid adjusted to  $pH$  3.06 with  $NH_4OH$  and a 10-cm. column of

(6) E. H. Cook and R. W. Taft, THIS JOURNAL, **74**, 6163 (1952).

Dowex 50). Under these conditions there was essentially no separation of yttrium and europium. The single peak in the citrate elution curve was shown to contain both yttrium and europium by comparison of an absorption curve with that obtained on the original tracer mixture. With slightly different conditions and longer columns, europium and yttrium have been separated using citrate.<sup>7</sup> These workers found yttrium between dysprosium and holmium in the order expected from crystal ionic radii. Others have reported<sup>8</sup> that, under conditions slightly different from those of Ketelle and Boyd and also different from those employed here, europium, gadolinium and yttrium are eluted at very nearly the same rate.

### Discussion

The fact that successful separations by ion ex-

(7) B. H. Ketelle and G. E. Boyd, *THIS JOURNAL*, **69**, 2800 (1947).

(8) Geoffrey Wilkinson and Harry G. Hicks, *Phys. Rev.*, **75**, 1370 (1949).

change using mixed solvents can be achieved suggests that many new complexing agents which are insoluble in water can be used if a suitable mixed solvent can be found which is sufficiently polar in nature to permit ion exchange to occur reversibly. The fact that the reaction by which the metal chelate is formed is not rapid does not rule out the use of the chelating agent, since HTTA is known to be slow in forming these complexes.

The method may be useful for more rapid and efficient separation of those rare earth elements which are commonly separated by citrate elution. It may also be applicable to the separation of certain transuranium elements.

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## Studies on Ion Exchange Resins. IX. Capacity and Specific Volumes of Quaternary Base Anion Exchange Resins<sup>1</sup>

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RECEIVED NOVEMBER 27, 1953

The exchange capacities, wet weights and volumes of a quaternary ammonium anion exchange resin in a number of univalent anionic states including the halide, strong mineral acid anion, hydroxide, chloro-substituted acetate and benzene and naphthalene sulfonate states, were measured. The exchange capacity was the same for all anions, and showed the absence of appreciable adsorption effects. The swelled volume of the resin phase was correlated with the partial molal volumes of the exchange anions. Swelling appears to be determined, to a considerable extent, by ion-pair formation.

This paper describes the exchange capacity of a quaternary base anion exchange resin for various univalent inorganic and organic anions. The specific wet weight and the specific volume of the resin phase when these ions occupy the exchange positions are also given. A subsequent paper in this series will present selectivity coefficient data on these same systems.

### Experimental Methods

A series of Dowex 1 and Dowex 2 resins (Dow Chemical Co., Midland, Michigan) were used for these studies.<sup>3</sup> These resins are prepared from a polystyrene-divinylbenzene (DVB) copolymer having varying degrees of cross-linking. The designation DVB 8 refers to the 8% cross-linked material, which is the standard commercial product. DVB resins 1, 2, 4, 6 and 16 were also used. The exchange groups in the Dowex 1 resins are largely of the benzyltrimethylammonium type. In Dowex 2 resins they are of the benzyloethanol-dimethylammonium type. Similar resins have been prepared by chloromethylation of the styrene-divinylbenzene copolymer, followed by treatment with the corresponding amine.<sup>4,5</sup> Since the chloromethylation step itself introduces a small amount of cross-linking, the actual degree of cross-linking is higher than that corresponding to the DVB content.

In this paper most of the data are for the Dowex 2 type of resin, which is referred to simply by its percentage cross-linking. Data for the Dowex 1 type of resin are so specified. Both types of resins were conditioned by treatment with 1

*m* (molal) sodium hydroxide and 1 *m* hydrochloric acid solutions alternately, using a twofold excess in terms of exchange capacity each time, at a flow rate of approximately 0.1 ml./min./inl. bed of resin. Three cycles of this treatment were followed by passing a 10-fold excess of 1 *m* sodium chloride through the bed at the same, slow flow rate. The resins were then rinsed with carbon dioxide free distilled water until the conductance of the effluent dropped to less than  $2 \times 10^{-6}$  mho. They were then air-dried to a free-flowing state and dry screened to -18 + 30 mesh and -30 + 60 mesh sizes for the DVB 8 and to -60 + 100 mesh for the DVB 1, 2, 4, 6 and 16 resins. This chloride state of the resins was taken as the "standard" state upon which all subsequent calculations of specific capacity, etc., were based.

The resins were also placed in the hydroxide state by treatment with base after the conditioning procedure. Rinsing with carbon dioxide free water was continued to an effluent conductance of  $10^{-6}$  mho.

The moisture content of the chloride resin was determined by drying in a desiccator over phosphorus pentoxide; constant weight was attained in about 3 weeks. With oven drying at 100° the same, constant weight was attained within 24 hours. The hydroxide form was dried only in the desiccator, as it decomposed partially at the elevated temperature.

Quaternary base anion exchange resins which contain the ethanolic group are not stable in the hydroxide form, but decompose quite slowly to an amine.<sup>6</sup> Gilwood and Utermohlen<sup>6</sup> measured the stability of various resins in the hydroxide state at both room temperature and 100°, and observed that the ethanolic substituted quaternary ammonium resins are unstable relative to the purely aliphatic substituted ones. All types of resins are considerably more stable as salts of mineral acids than in the hydroxide state. However, even the decomposition of the ethanolic type resins is slow at room temperature, requiring several weeks to become measurable. In this investigation, all resins were stored in the salt (chloride) state, and were converted to the base state for use in that form.

(1) The authors wish to thank the Signal Corps, U. S. Army, and the Office of Naval Research for the support given this work.

(2) Taken in part from the dissertation of J. Belle, submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry, Polytechnic Institute of Brooklyn, October, 1951.

(3) R. M. Wheaton and W. C. Baumann, *Ind. Eng. Chem.*, **43**, 1088 (1951).

(4) Gillin D. Jones, *ibid.*, **44**, 2686 (1952).

(5) S. L. Thomas, paper given at the 120th Meeting of the American Chemical Society, New York, September, 1951.

(6) M. E. Gilwood and W. P. Utermohlen, paper presented at the 120th Meeting of the American Chemical Society, New York, Sept. 1951.