Chelating Agents Applied to Ion-exchange Separations of Americium and Curium[1]

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Recent investigations of cation-exchange column separations of the rare earths have extended the original citrate elutions to include elutions with a variety of chelating agents, such as lactate,[2,3] glycolate,[2] malate,[2] and ethylenediaminetetraacetic acid (EDTA).[2,4] At the same time no comparable studies of elution of the trivalent actinides with other than citrate solutions have been reported. The present report concerns results on tartrate and lactate elutions of two actinides very difficult to separate, namely, americium and curium, from investigations begun in 1950.[5] Tartrate and lactate agents were selected on the basis of the reported[6] large separation factors with the rare earths. It has also been possible to compare the relative efficiencies of chelating agents forming five- and six-membered rings from data obtained with lactate and other related ions.

Experimental

The ion-exchange column used for the separations (similar to columns used for citrate elutions described elsewhere[7,8]) was made by packing 2 mm. capillary tubing with 17 cm. of 250–500 mesh Dowex-50 resin (12% cross-linkage[9]), from which the fine and coarse particles had been carefully removed. The final Dowex-50 resin fraction from the grading process settled about one cm. per minute in water. The column could be operated at 87° by circulating trichloroethylene vapor (b.p. 87°) in a surrounding jacket in the standard manner.[8] The chelating agent solutions were prepared by titrating solutions of the respective acids to the desired *p*H with ammonium hydroxide using a Beckman *p*H meter.

The tracers eluted were the α-emitting Cm^{242} and Am^{241} and the β-emitting $Eu^{152,154}$ and Pm^{147}. These were absorbed on about 50 microliters of resin, settled on top of the column from <0.1 *M* acid solution, and eluted with the desired chelating solution. The actinide peaks were defined by gross α-counting and α-pulse analysis of platinum plates on which the drops of eluting solution from the column were collected, evaporated and flamed. The multi-channel α-pulse analyzer[10] frequently enables one to detect fractions of a percentage of one α-emitting isotope in the presence of large amounts of another if the α-particles are of sufficiently different energy. Thus it is ideally suited to the study of column separations of the α-active actinides. The rare earth peaks were defined by gross β-counting and absorption curves of the same plates.

Equilibrium experiments were also made with americium in order to determine the relative strengths of the various chelating ions as well as to aid in the selection of optimum conditions for column elutions. In these experiments, 10 to 20 ml. of the chelating solution containing americium tracer were equilibrated at 25 or 87° with 0.01 to 0.5 g. of the Dowex-50 resin in the ammonium form. Alpha assays of the solution before and after equilibration were used to determine the partition of americium between resin and solution phases in terms of distribution coefficients.[6] The distribution coefficient is defined as follows.

Distribution coefficient (K_d) = (c./m./g.) resin phase/(c./m./ml.) soln. phase, where c./m. refers to the α counts per minute due to Am^{241}. Since the ammonium ion concentration was not carefully measured and it has a rather large effect on the equilibrium distribution, only the relative magnitudes of the distribution coefficients are of significance for the interpretation of the strengths of the chelate complexes.

Results and Discussion

Two very satisfactory ion-exchange methods of separating the actinides resulted from these studies. The first employed 0.1 *M* tartaric acid adjusted with ammonium hydroxide to a *p*H of 4.0 and used a flow rate of one drop per eight minutes (0.15 $cm.^3/cm.^2$-min.). The column elutions were made at room temperature. A typical elution curve using this tartrate solution is shown in Fig. 1. In this elution, a separation factor (defined in the usual manner[3]) of 1.30 was obtained between americium and curium. The factor is calculated by dividing the number of drops to the highest point of the americium peak by the drops to the highest point of the curium peak, after subtracting a free column volume of about eight drops in both cases, and is equal to the ratio of the distribution coefficient of americium to that of curium in the tartrate solution. Less than 0.2% by activity of americium was found in samples corresponding to the curium peak, from the front edge to the dip between the peaks. The contamination of samples corresponding to the entire americium peak with curium activity was likewise less than 0.2%. These room tem-

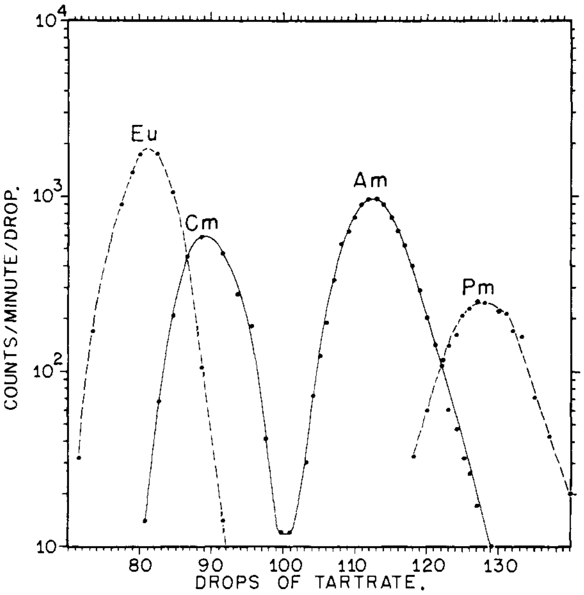

Fig. 1.—Tartrate elution of actinide and rare earth tracers at room temperature (0.10 *M* tartrate, *p*H 4.0, 1 drop/8 min.): ----, β-counting; —, α-counting.

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[2] S. W. Mayer and E. C. Freiling, This Journal, **75**, 5647 (1953).

[3] E. C. Freiling and L. R. Bunney, *ibid.*, **76**, 1021 (1954).

[4] F. H. Spedding, J. E. Powell and E. J. Wheelwright, *ibid.*, **76**, 612 (1954).

[5] Recently L. Wish, E. C. Freiling and L. R. Bunney (*ibid.*, **76**, 3444 (1954)) have also reported favorable elution separations of americium and curium as well as californium and 99 using *p*H 3 lactate solutions.

[6] E. R. Tompkins and S. W. Mayer, *ibid.*, **69**, 2859 (1947).

[7] K. Street, Jr., S. G. Thompson and G. T. Seaborg, *ibid.*, **72**, 4832 (1950).

[8] S. G. Thompson, A. Ghiorso and G. T. Seaborg, *Phys. Rev.*, **80**, 781 (1950).

[9] Dow Chemical Company, Midland, Michigan.

[10] A. Ghiorso, A. H. Jaffey, H. P. Robinson and B. B. Weissbourd, "The Transuranium Elements: Research Papers," McGraw-Hill Book Co., Inc., New York, N. Y., 1949, Paper No. 16.8, National Nuclear Energy Series, Plutonium Project Record, Vol. 14B.

perature tartrate elutions represent the best one-step separations of americium and curium yet reported. The only disadvantage of this method was in the long time required for elution (*ca.* 16 hours).

A second method, capable of yielding americium–curium separations in a considerably shorter time (less than two hours), employed 0.4 *M* lactic acid adjusted with ammonium hydroxide to a *p*H of 4.6 and a flow rate of one drop per one to three minutes (1.2–0.4 cm.^{3}/cm.^{2}-min.). These elutions were carried out at 87°. A typical example of the performance of this column is given in Fig. 2b. In this latter case, a separation factor of 1.19 was obtained between americium and curium, with a cross contamination (defined as before) this time of about 2%. For comparison of the effect of temperature, a room temperature elution with lactate solution using a column operated at a much slower flow rate (to ensure equilibrium) of one drop every eight minutes is also shown in Fig. 2a. On the basis of the superior separations obtained with the lactate elution solutions, they have been rather extensively employed at this Laboratory for actinide separations and were recently of use in demonstrating the existence, production and separation of the recently reported new elements 99 and 100.[11]

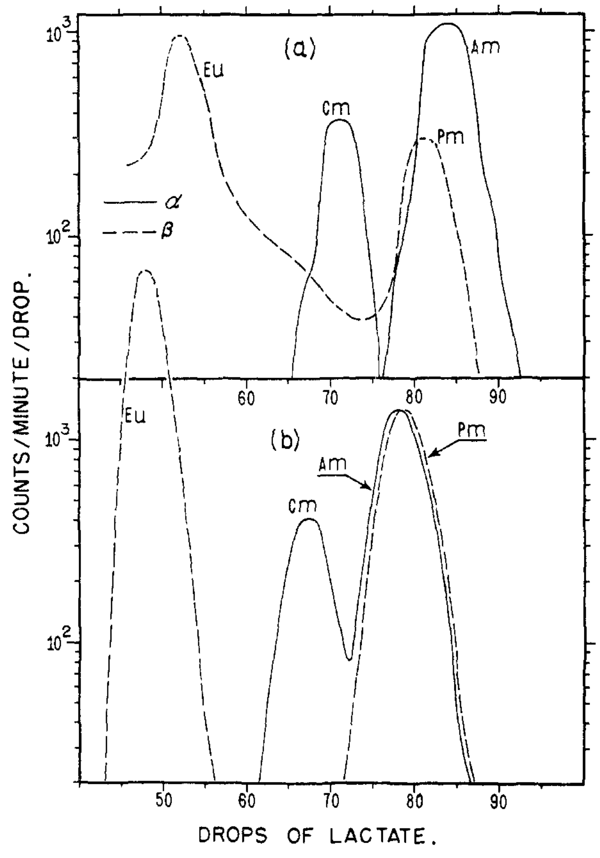

Fig. 2.—Lactate elutions of actinide and rare earth tracers: (a) 0.37 *M* lactate, *p*H 4.1, 1 drop/8 min., room temperature; (b) 0.40 *M* lactate, *p*H 4.6, 1 drop/3 min., 87°: ----, β-counting; —, α-counting.

In the course of trying to select the optimum conditions for elution and separations, some conclusions were made which bear on the nature of the effective chelating ions. When tartrate elutions were run at 87°, the large separation factors observed at room temperature disappeared. For example, elution with 0.1 *M* tartaric acid adjusted to *p*H 4.3 resulted in a separation factor between americium and curium of only 1.07. However, increasing the ratio of singly ionized to doubly ionized tartrate ions (which are the abundant species at *p*H 4) by lowering the *p*H (simultaneously increasing the tartaric acid concentration to maintain the previous elution time), caused the separation factor to increase steadily to a value of 1.20 with 0.8 *M* tartaric acid at *p*H 2.8. Thus, the singly ionized tartrate ion is more effective for separations even though it forms a weaker chelate complex. The latter statement can be illustrated by the fact that the americium distribution coefficient in 0.05 *M* tartaric acid adjusted to *p*H 4 (tartrate$^=$/tartrate$^-$ = 0.9) was found to be 20 times as large as the distribution coefficient in 0.05 *M* acid adjusted to *p*H 5 (tartrate$^=$/tartrate$^-$ = 9.0). At both *p*H values the acid is almost completely dissociated, the only difference being in the ratios of the ions. A similar conclusion that the singly ionized chelate ion is more effective had also been reached previously from the use of citric acid.[6]

A study of four related chelating acids also was made to determine the relative efficiencies of five- and six-membered chelate rings on the basis of the stability of the chelate formed as well as on the ability to induce large separation factors. The data indicate that lactate ion forms a stronger chelate (five-membered ring) with americium than does the hydracrylate ion (six-membered ring). For purposes of comparison, it will suffice to describe two distribution coefficient determinations. Simple calculations show that 0.4 *M* lactic acid and 0.7 *M* hydracrylic acid both adjusted to *p*H 5 have about the same dissociated ion concentrations; yet the value of K_d for americium in the lactate solution is 10 and that for the hydracrylate solution 2600, indicating that the formation constant for the americium–lactate chelate is much larger than that for the other chelate (assuming that the formula for the chelates is the same in both cases). At the same time, column elutions with both agents indicated that the lactate ion caused larger separation factors.

In the same way, the equilibrium experiments indicate that although α-alanine (five-membered ring) forms chelates with americium in solution above *p*H 6, β-alanine (six-membered ring) shows little tendency to do so. In this case, determinations of the values of K_d for americium as a function of *p*H in one molar solutions of the acids showed that the K_d with α-alanine dropped from 4000 at *p*H 6 to 100 at *p*H 9.5, whereas the values of K_d with β-alanine were at least above the upper limit of detection of 10,000 in this *p*H range. From this study of the four hydroxy and amino acids, it appears that the five-membered ring forms a more stable chelate and also causes larger separation factors. On this basis, the large separation factors obtained with tartrate ion (capable of forming two five-membered chelate rings) are to be expected.

(11) A. Ghiorso, S. G. Thompson, G. R. Choppin and B. G. Harvey, *Phys. Rev.*, **94**, 1080 (1954).

In the same manner, it might be predicted that the effective chelate formed with citrate ion employs the one five-membered ring available. The problem of the relative stabilities of five- and six-membered chelate rings has been discussed by Martell and Calvin.[12] The present results are in accord with the conclusions described there.

The author wishes to express his appreciation to Professor G. T. Seaborg and Dr. K. Street, Jr., for guidance in this work.

[12] A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds," Prentice-Hall, Inc., New York, N. Y., 1952, p. 134.

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Effect of Diluents on Burning Velocities in Hydrogen–Bromine Mixtures

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In earlier reports, the results of measurements made by using a special Bunsen-type burner to determine the burning velocities of hydrogen–bromine mixtures for different compositions[1] and temperatures[2] have been summarized. Some measurements of the effects of diluents on flame velocities in tubes have also been reported.[3]

These experiments have been extended to determine, by the burner method, the effects of diluents such as nitrogen, argon and helium on the burning velocities.

Experimental

The materials, apparatus and procedure were essentially the same as described in the earlier reports,[1,2] except that an additional gas line was provided so that an inert gas might be introduced into the burner along with the hydrogen.

The burning velocities were determined, as described before, from the gas flow velocities and the area of the flames.

Results

The colors of the flames and the ranges of shape observed were similar to those for hydrogen–bromine mixtures,[1] but not necessarily for corresponding bromine–hydrogen ratios. There was a distinct tendency toward greater *relative* stability for the bromine-rich mixtures in the presence of the diluents, though the total range of composition for stable flames was decreased. Shapes of flames in the region of 50 mole % bromine in the presence of diluents were, for example, comparable to those observed for 45–46% bromine in the absence of diluents. These effects on stability are illustrated in Table I, which shows the range between flash-back and blow-off for various proportions of nitrogen in the hydrogen.

TABLE I

	Flash-back		Blow-off	
N_2/H_2	H_2/Br_2	Gas flow veloc., cm./sec.	H_2/Br_2	Gas flow, veloc., cm./sec.
0.053	1.40	39.8	1.66	44.1
.111	1.30	39.4	1.55	43.7
.177	1.20	38.8	1.42	42.8
.250	1.06	37.4	1.27	41.6

(Br_2 flow = 4.4×10^{-4} mole/sec.)

The flames were, however, generally more difficult to work with in the presence of diluents, showing more tendency to flicker. It was not possible to work with more than 25% diluent in the hydrogen. Figure 1 shows comparative data on burning velocities for an initial temperature of 50°. (It is apparent that the lines as drawn have no absolute significance. They are sketched in simply to call attention to the general trends of values.) Measurements were also made for initial temperatures of 200°. Under these conditions, the mixtures containing diluent all gave values well below those for hydrogen–bromine mixtures. For mixtures with 34 mole % bromine, for example, the burning velocity for a hydrogen–bromine mixture was 80 cm./sec. That for a mixture with helium replacing 25% of the hydrogen was 53 cm./sec. For argon and nitrogen the corresponding values were, respectively, 46 and 35 cm./sec.

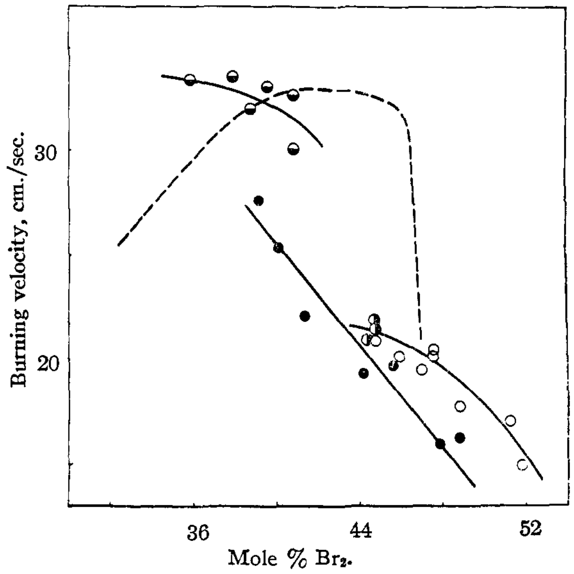

Fig. 1.—Effects of diluents at 50°: ---, no diluent; ○, N_2/H_2 = 0.28; ◑, N_2/H_2 = 0.33; ●, A/H_2 = 0.33; ⊖, He/H_2 = 0.33.

For mixtures of low bromine content, helium dilution tended consistently to increase the burning velocity, and with 11% helium in hydrogen, the burning velocities were higher for all mixtures tested. For 44 mole % bromine, for example, the burning velocity with helium added is around 34 cm./sec., whereas that for hydrogen alone plus bromine is down to about 20 cm./sec.

Discussion

In general, the effects of the diluents on burning velocities are consistent with the effects observed earlier on flame velocities in tubes.[3] They also show the same trends and relative magnitudes as those reported by Wheatly and Linnett for acetyl-

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[1] S. D. Cooley, Jas. A. Lasater and R. C. Anderson, THIS JOURNAL, **74**, 739 (1952).

[2] S. D. Cooley and R. C. Anderson, *Ind. Eng. Chem.*, **44**, 1402 (1952).

[3] H. R. Garrison, J. A. Lasater and R. C. Anderson, "3rd Symposium on Combustion," Williams and Wilkins Co., Baltimore, 1949, p. 155.