acid, for example, the predominant form involves combination of the alkaline earth cations with both carboxyl groups. In an equilibrium mixture, however, small fractions must be present in which M^{++} is combined with only one carboxyl group; with a carboxyl group and amino group; and with an amino group only. With cations of many of the transition elements, however, chelate formation involving nitrogen predominates.

The ion-exchange data are of interest in themselves and in relation to chromatographic separations. Consider the following exchange reaction of the alkaline earth cations, M^{++}, with the sodium form of the exchanger

$$M^{++} + 2\overline{Na}^+ \rightleftarrows \overline{M}^{++} + 2Na^+ \quad (4)$$
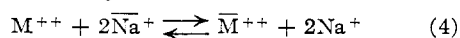
where the bar over the symbol represents the resin phase. The dependence of $K_d(M)$ on concentration changes can be deduced from Donnan membrane or mass action considerations as was done previously.[2] Under the experimental conditions in which $[\overline{Na}^+] \gg [\overline{M}^{++}]$ and $[Na^+] \gg [M^{++}]$ the variation of $K_d(M)$ with ionic strength of the aqueous phase should, neglecting activity coefficients, in both the external solution and resin phases, vary inversely as the square of the Na^+ concentration. In the range $\mu = 0.16$–0.078 this is the case. Thus at $\mu = 0.16$, $K_d(Ba)$ is 9.9 while at $\mu = 0.078$, K_d-(Ba) is found to be 43.6 while the calculated value is $(0.16/0.078)^2 \times 9.9 = 41.5$.

The chromatographic separation of Ra^{++}, Ba^{++} and Sr^{++} by elution with ammonium citrate from columns of Dowex-50 has been reported by Tompkins.[12] From the plate theory[13] the peaks of the published elution curves can be shown to be directly related to the distribution coefficients, K_d, of the elements involved. Thus, by definition, the separation factor, α, is given by the relation[14]

$$\alpha = \frac{K_d(M_1)}{K_d(M_2)} \times \frac{K_f(M_2)}{K_f(M_1)} \quad (5)$$

From the data given in Table I, the separation factor for Ra–Ba is, where $M_1 = Ra^{++}$ and $M_2 = Ba^{++}$

$$\alpha = \frac{12.6}{11.3} \times \frac{350}{229} = 1.11_5 \times 1.52_8 = 1.7 \quad (6)$$

From the ratio of the peaks of the elution curve shown in reference 12 the separation factor found is 2.3. This approximate agreement between the calculated and observed values is actually better when activity coefficient corrections are made since the solutions employed in the column experiments were 0.5 M ammonium citrate ($\mu = 3.0$).

Under the experimental conditions the separation factor α', corrected for activity coefficients in the external solution phase only, is

$$\alpha' = \alpha \times \frac{\gamma_{M_1}\,\gamma_{M_1}\,\gamma_{M_2A}}{\gamma_{M_2}\,\gamma_{M_2}\,\gamma_{M_1A}} = \alpha \times \left(\frac{\gamma_{M_1}}{\gamma_{M_2}}\right)^2 \frac{\gamma_{M_2A}}{\gamma_{M_1A}} \quad (7)$$

It is easily shown that the calculated value of α' made at $\mu = 0.16$ is too low when approximate activity coefficient corrections are made. Similar calculations have been made for Ba–Sr, and Ra–Sr separations. The corrections are all in the proper

(12) E. R. Tompkins, THIS JOURNAL, **70**, 3520 (1948).

(13) S. W. Mayer and E. R. Tompkins, *ibid.*, **69**, 2866 (1947).

(14) B. H. Ketelle and G. E. Boyd, *ibid.*, **69**, 2800 (1947).

direction and order of magnitude since[15] $\gamma_{Sr^{++}} > \gamma_{Ra^{++}}$ and presumably $\gamma_{Ba^{++}} > \gamma_{Ra^{++}}$ while M_1A and M_2A, e.g., $(SrCit)^-$ can be considered[2] to behave as the monovalent ion, $(H_2Cit)^-$.

The author wishes to acknowledge the technical assistance of Mr. Roman V. Lesko. The adenylic and cytidylic acids were kindly furnished by Dr. Waldo E. Cohn.

(15) R. H. Stokes, *Trans. Faraday Soc.*, **44**, 295 (1948).

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Ion Exchange as a Separations Method. VIII. Relative Elution Positions of Lanthanide and Actinide Elements with Lactic Acid Eluant at 87°

BY LEON WISH, EDWARD C. FREILING AND LELAND R. BUNNEY

Because lactic acid has been shown to be a more selective eluant than citric acid for the ion-exchange separation of lanthanides,[1] its selectivity for the trivalent actinide elements appeared to merit investigation. Consequently, a number of column studies have been made of the elution of Am, Cm, Cf and element 99 from Dowex-50 cation-exchange resin with pH 3 lactate solutions at a temperature of 87°.

Since β-emitting isotopes of the lanthanides and α-emitting isotopes of Am, Cm, Cf and 99 were available, it was possible to obtain data on any desired combination of elements from a single run. Thus, the position of any given actinide peak could be readily determined, even though it were superimposed upon a background of lanthanide activities.

Finally, a simple correlation between the relative elution positions of homologs in the lanthanide and actinide series has been determined.

Experimental

Radioactive tracers were used to determine the relative elution positions of all elements except Dy, which was obtained from Dy_2O_3 of $>98\%$ purity.[2] All other apparatus and materials have been previously described.[3] The procedure used to make these separations and to determine the distribution of β-emitting isotopes was essentially the same as that of Freiling and Bunney.[3] However, advantage was taken of the insensitivity of C ratios obtained with lactic acid[1] in order to adjust the eluting conditions to obtain either more accurate data or more rapid elutions. The α-activity in each actinide fraction was most conveniently and rapidly determined by collecting small samples of eluate on Pt discs, drying on a hot plate, destroying the organic residue with successive additions and evaporations of fuming HNO_3, and counting in an alpha scintillation counter. By this technique the appearance of microgram amounts of Dy in the eluate could also be detected.

Results and Discussion

A quantitative summary of the results is made in Table I by listing, for each element studied, the C ratio[1,4] to Eu. As in the case of 0.25 M citric

(1) S. W. Mayer and E. C. Freiling, THIS JOURNAL, **75**, 5647 (1953).

(2) Purchased from the Johnson, Mathey and Co., Ltd.

(3) E. C. Freiling and L. R. Bunney, THIS JOURNAL, **76**, 1021 (1954).

(4) S. W. Mayer and E. R. Tompkins, *ibid.*, **69**, 2866 (1947). The C value of a solute is equal to the number of free column volumes of eluting agent which have passed through the resin bed when the concentration of the solute in the eluate is a maximum.

acid at pH 3.5,[5,6] Am is found to elute almost in coincidence with Pm, while Cm appears between Sm and Pm. Cf, however, elutes between Dy and Tb with citric acid, but with lactic acid it falls between Tb and Gd.

TABLE I

C RATIOS OBTAINED FOR LANTHANIDE AND ACTINIDE ELEMENTS RELATIVE TO Eu USING LACTIC ACID AT pH 3.0 AND 87°

Element	C ratio to Eu	Element	C ratio to Eu
Ho	0.28 ± 0.03[a]	Bk	0.87[b]
Dy	.40 ± .03	Eu	1.000
99	.40 ± .03	Sm	1.28 ± 0.03
Tb	.52 ± .03	Cm	1.58 ± .03
Cf	.63 ± .03	Am	2.00 ± .03
Gd	.845 ± .005	Pm	2.06 ± .03

[a] Standard deviation. [b] Calculated from equation 3.

The superiority of lactic acid to citric acid for separating the trivalent actinide elements is demonstrated by the C ratios (or separation factors) shown in Table II. These data indicate that lactic acid offers a 4% increase in separation per column stage.

TABLE II

A COMPARISON OF SEPARATION FACTORS OBTAINED WITH LACTIC AND CITRIC ACID ELUANTS AT 87° FOR Am, Cm AND Cf

	Citric acid	Lactic acid
C_{Am}/C_{Cm}	1.21[a]	1.27
C_{Cm}/C_{Cf}	2.42[a]	2.51

[a] Calculated from the results of Street, Thompson and Seaborg.[6]

According to the data of Thompson, Seaborg and co-workers,[5,6] the relative elution positions of lanthanide and actinide homologs may be related almost as well by a logarithmic as by a linear equation. Thus, if C_{Ac} is the C value of any trivalent actinide element and C_{La} is the C value of its lanthanide homolog, the linear relationship

$$C_{Ac}/C_{Eu} = 2.13(C_{La}/C_{Eu}) - 0.507 \qquad (1)$$

gives a goodness of fit[7] of 0.008, while the logarithmic equation

$$C_{Ac}/C_{Eu} = 1.64(C_{La}/C_{Eu})^{1.53} \qquad (2)$$

gives a goodness of fit of 0.010.

With lactic acid, however, the logarithmic equation

$$C_{Ac}/C_{Eu} = 1.99(C_{La}/C_{Eu})^{1.26} \qquad (3)$$

with a fit of 0.009 is considerably better than the linear equation

$$C_{Ac}/C_{Eu} = 2.20(C_{La}/C_{Eu}) - 0.236 \qquad (4)$$

with a fit of 0.029.

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(5) S. G. Thompson, B. B. Cunningham and G. T. Seaborg, *ibid.*, **72**, 2798 (1950).

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

(7) R. Livingston, "Physico Chemical Experiments," The Macmillan Co., New York, N. Y., p. 35.

The Purification and Some Physical Properties of Nitromethane

BY CHARLES J. THOMPSON,[1a] HAROLD J. COLEMAN[1a] AND R. VERNON HELM[1b]

In order to make available high-purity nitromethane for thermodynamic measurements, a commercially prepared sample was purified by chemical and physical means to better than 99.9 mole per cent. as determined by the freezing point method. In addition to the thermodynamic properties reported by McCullough, *et al.*,[2] values for freezing point, density, refractive index, viscosity and surface tension were determined on the purified nitromethane. This paper describes the purification procedures and presents values for the latter properties.

Purification.—The nitromethane was a commercially purified sample obtained from Commercial Solvents Corporation. Most of the impurities had been removed, but further necessary purification was effected by a combination of chemical and physical means. The method employed, with only minor deviations, was suggested by John A. Reddick of Commercial Solvents Corporation,[3] and resulted in a sample of better than 99.9 mole per cent. purity as determined by the freezing point method of Rossini.[4]

The nitromethane was given three successive washings with each of the following reagents in order: 25 g. each of sodium bicarbonate and sodium bisulfite per liter of water; 5% sulfuric acid solution and water. Each treatment was accomplished by violent agitation in a separatory funnel. A 2.5-liter sample of the washed nitromethane and 850 ml. of water were charged to an Oldershaw perforated-plate column with a rectifying section 137 cm. in length. After refluxing for 1 hour, 10 ml. of distillate was removed at total takeoff. Refluxing and distillate removal were repeated at 30-minute intervals until the head temperature remained constant, when an additional 10 ml. was collected. All distillate obtained to this point was discarded. The distillation was then continued at a reflux ratio of 5:2 until an increase in head temperature of 1° was observed. The nitromethane then was separated from the azeotropic distillate, which was an immiscible nitromethane–water mixture. This nitromethane was charged to a vacuum-jacketed Podbielniak "Heli-Grid" packed column with a rectifying section 22 mm. by 122 cm. All of the water remaining in the sample was removed by alternate refluxing at 100 mm. pressure and product removal at total takeoff until the boiling point of nitromethane (101.2°) was reached. The coolant to the head condenser was then shut off, and the nitromethane vapors were allowed to flush out the remaining traces of water in both the head and takeoff tube. Refluxing was continued for two hours, 25 ml. of distillate was collected and discarded, and the remainder of the charge was distilled at a reflux ratio of 90:1.

The glassware and column packing were acid washed, and the material was handled in an inert atmosphere and in the absence of strong light. The purified nitromethane was stored under vacuum in glass ampoules containing boric acid and given a vapor-phase transfer immediately before property measurements were made.

Physical Properties

Refractive Index.—Refractive indices (Table I) were measured with a Bausch & Lomb Precision oil refractometer, Abbe type, by procedures previously described.[5] Data

(1) (a) Petroleum Experiment Station, Bureau of Mines, Bartlesville, Okla.; (b) Petroleum and Oil Shale Experiment Station, Laramie, Wyo.

(2) J. P. McCullough, D. W. Scott, R. E. Pennington, I. A. Hossenlopp and Guy Waddington, paper presented at Kansas City ACS Meeting, March 23–April 1, 1954.

(3) Private communication.

(4) F. D. Rossini, *Anal. Chem.*, **20**, 110 (1948).

(5) W. E. Haines, R. V. Helm, C. W. Bailey and J. S. Ball, *J. Phys. Chem.*, **58**, 270 (1954).