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1960

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## Abstract

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## CHEMISTRY

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# STUDY OF THE COMPLEX FORMATION OF CERTAIN $\alpha$-HYDROXY ACIDS WITH YTTRIUM AND CERIUM

Complex compounds with certain $\alpha$-hydroxy acids are used in the chromatographic separation of mixtures of rare-earth elements ($^{1-3}$). However, the literature contains no data that would make it possible to substantiate the optimal structure and composition of the hydroxy acid employed. We have studied the complex formation of yttrium and cerium, taken in the form of microquantities of carrier-free radioisotopes, with aliphatic $\alpha$-hydroxy acids having different numbers of carbon atoms—glycolic, lactic, $\alpha$-hydroxybutyric, $\alpha$-hydroxyvaleric, and $\alpha$-hydroxycaproic acids. Commercial preparations of glycolic and lactic acids were used in the work; $\alpha$-hydroxybutyric acid ($^{4}$), $\alpha$-hydroxyvaleric acid ($^{5}$), and $\alpha$-hydroxycaproic acid ($^{6}$) were synthesized.

As the solid phase, KU-2 cation exchanger was used, with grain sizes of 0.25–0.50 mm and an approximate DVB content of 8%. The specific activity of the working solutions containing $Y^{91}$ or $Ce^{144}$ was about 6000 counts/ml • min and was measured with an end-window counter.

The distribution coefficients of $Y^{3+}$ and $Ce^{3+}$ between the resin and the solution were studied under static conditions. For this purpose, the radioactivity was measured in the initial solution and in the same solution after equilibrium with the resin had been established. The ion exchanger was used in the Na form. Solutions of complex-forming substances of various concentrations, from $10^{-3}$ to $2 \cdot 10^{-1}$ $M$, were used. The concentration of the complex-forming anion was varied by neutralizing the initial solution of the given acid (of constant concentration) with different amounts of NaOH. The concentration of the anion participating in complex formation was determined as the sum of the concentration of the neutralized acid and, on the other hand, the anions arising from dissociation of the remaining acid under the given conditions. The ionic strength was kept constant ($\mu = 0.2$) with $NaClO_4$.

Several series of experiments were carried out with glycolic, lactic, $\alpha$-hydroxybutyric, and $\alpha$-hydroxyvaleric acids, separately for $Y^{91}$ and $Ce^{144}$, with a constant total acid concentration equal to 0.005 $M$, 0.05 $M$, or 0.2 $M$. The added NaOH solutions had concentrations of, respectively, 0.01, 0.1, and 0.4 $N$. In addition, an experiment was performed with different total

Fig. 1

Figure 1: Fig. 1

acid concentrations but at constant pH, which gave results analogous to the preceding ones.

The distribution coefficient $\varphi$ was calculated from the formula $\varphi = xv/cm$, where $x$ is the fraction of activity remaining in the resin, $c$ is the fraction of activity in the solution, $v$ is the volume of the solution in ml, and $m$ is the weighed amount of air-dry resin in grams. In carrying out the experiments, a drop of the initial solution of the radioactive element was evaporated to remove the mineral acid, and the residue was treated with a solution of the organic acid of the concentrations indicated above. Into a special shaking test tube, 10 ml of the resulting solution was poured, the ion exchanger was introduced, and a definite amount of NaOH, $NaClO_4$, and water was added to a total volume of 20 ml. The amount of ion exchanger varied from 0.02 to 0.4 g. The temperature in all experiments was maintained at

equal to $20 \pm 1^{\circ}$C. For measurement of radioactivity, 1-ml samples of both the initial solution and the solution after attainment of equilibrium were evaporated to dryness.

The data obtained were plotted as the dependence of $\varphi$ on $[A^-]$ (the concentration of the addend anion). The quantities $\varphi^0$ ($\varphi$ for zero addend concentration) were found experimentally. For yttrium $\varphi^0 = 18160 \pm 1200$; for cerium $\varphi^0 = 26170 \pm 2000$. The curves $(\lg \varphi - \lg[A^-])$ are presented in Fig. 1. The stability constants of the complex compounds were calculated by Fronaeus' method (7). It was assumed that in solutions of the given concentration range there exist three types of complex compounds: $MA^{2+}$, $MA_2^+$, $MA_3$, and the simple ion $M^{3+}$. For such a system, the expression for the distribution coefficient takes the form

$$\varphi = \frac{\varphi^0 + l_1\beta_1[A^-] + l_2\beta_2[A^-]^2}{1 + \beta_1[A^-] + \beta_2[A^-]^2 + \beta_3[A^-]^3}, \tag{1}$$

where $\beta_1$, $\beta_2$, and $\beta_3$ are the overall stability constants of the complex compounds $MA^{2+}$, $MA_2^+$, and $MA_3$; $l_1$ and $l_2$ are the distribution coefficients of the cationic complex compounds.

**Fig. 1.** Dependence of the distribution coefficient ($\varphi$) on the concentration of the addend anion $[A^-]$. $2_Y$—yttrium-glycolic acid system; $3_Y$—yttrium-lactic acid system; $4_Y$—yttrium-$\alpha$-hydroxyisobutyric acid system; $5_Y$—yttrium-$\alpha$-hydroxyisovaleric acid system; $2_{Ce}$, $3_{Ce}$, $4_{Ce}$, and $5_{Ce}$—the same for systems with the cerium ion.

From the obtained data on the dependence of $\varphi$ on $[A^-]$, the function was calculated

$$\Phi_1 = \left(\frac{\varphi^0}{\varphi} - 1\right)\frac{1}{[A^-]},$$

the limit of which is

$$\lim_{[A^-]\to 0} \Phi_1 = \beta_1 - l, \quad \text{where} \quad l = \frac{l_1\beta_1}{\varphi^0}.$$

Then the function

$$f = \beta_1\Phi_1 - \beta_2 - \beta_3[A^-]$$

or, in another form,

$$f = \frac{\frac{\varphi^0}{\varphi}\{(\beta_1 - l)[A^-] - 1\} + 1}{[A^{-2}]}$$

with the limit

$$\lim_{[A^-]\to 0} f = f^0.$$

The equation

$$\frac{\Delta f}{[A^-]} = \beta_1\frac{\Delta\Phi_1}{[A^-]} - \beta_3, \tag{2}$$

where $\Delta f = f - f^0$ and $\Delta\Phi_1 = \Phi_1 - \Phi_1^0$, corresponds to a straight line from which $\beta_1$ and $\beta_3$ can be determined graphically. On the basis of these data, from the equation $f^0 = \beta_1\Phi_1^0 - \beta_2$, the value of $\beta_2$ can also be found.

Using the data of Fig. 1, corrected values of $\varphi$ for each value of $[A^-]$ were taken from the $\varphi$-$[A^-]$ curves. They were treated as indicated above. As an example, Fig. 2 gives the results of calculations by equation (2) for yttrium $\alpha$-hydroxyisobutyrate, according to which $\beta_1 = (1.3\pm0.1)\cdot10^3$; $\beta_2 = (4.0\pm0.6)\cdot10^5$; $\beta_3 = (2.0\pm0.6)\cdot10^7$. On the basis of these data, the content of the various forms of complex compounds as a function of addend concentration was calculated (Fig. 3).

In the same way, data were obtained for the stability constants of the complex compounds of Y and Ce with the acids studied (Table 1).

Fig. 2. Graphical representation of the equation

$$\frac{\Delta f}{[A^-]} = \beta_1 \frac{\Delta \Phi_1}{[A^-]} - \beta_3$$

for yttrium $\alpha$-hydroxybutyrate.

Fig. 3. Content of complex compounds of yttrium and $\alpha$-hydroxybutyric acid of various composition as a function of ligand concentration.
1 –ion $Y^{3+}$, 2 –$YA^{2+}$, 3 –$YA_2^+$, 4 –$YA_3$.

The literature contains similar data. According to Paramonova ($^9$), the constant of $YLac_2^+$ is equal to $9.1 \cdot 10^4$, or according to ($^{10}$), $5.0 \cdot 10^4$. The stability constant of $YLac^{2+}$ is $3.7 \cdot 10^2$ (all for ionic strength, $\mu = 0.2$). In work ($^{11}$), the following values were found for

**Table 1**

Stability constants ($\beta$) of complex compounds of cerium and yttrium

with some $\alpha$-hydroxy acids

| $\beta$ | Glycolic acid | Lactic acid | $\alpha$-Hydroxybutyric acid | $\alpha$-Hydroxyvaleric acid |
|---|---|---|---|---|
| Y $\beta_1$ | $(6.1 \pm 0.4) \cdot 10^2$ | $(6.8 \pm 0.5) \cdot 10^2$ | $(1.3 \pm 0.1) \cdot 10^3$ | $(4.0 \pm 0.3) \cdot 10^2$ |
| Y $\beta_2$ | $(5.1 \pm 0.7) \cdot 10^4$ | $(8.5 \pm 1.0) \cdot 10^4$ | $(4.0 \pm 0.6) \cdot 10^5$ | $(9.0 \pm 1) \cdot 10^4$ |
| Y $\beta_3$ | $(1.0 \pm 0.3) \cdot 10^6$ | $(6.0 \pm 2.0) \cdot 10^6$ | $(2.0 \pm 0.6) \cdot 10^7$ | $< 1 \cdot 10^6$ |
| Ce $\beta_1$ | $(2.7 \pm 0.3) \cdot 10^2$ | $(2.7 \pm 0.3) \cdot 10^2$ | $(2.7 \pm 0.3) \cdot 10^2$ | $(1.7 \pm 0.2) \cdot 10^2$ |
| Ce $\beta_2$ | $(1.3 \pm 0.3) \cdot 10^4$ | $(1.3 \pm 0.3) \cdot 10^4$ | $(2.2 \pm 0.4) \cdot 10^4$ | $(3.2 \pm 0.6) \cdot 10^3$ |
| Ce $\beta_3$ | $(2.0 \pm 1.0) \cdot 10^5$ | $(2.0 \pm 1.0) \cdot 10^5$ | $(2.0 \pm 1.0) \cdot 10^5$ | $(6.0 \pm 3.0) \cdot 10^4$ |

ionic strength $\mu = 0.5$: $YLac^{2+}$ $-4.36 \cdot 10^2$, $CeLac^{2+}$ $-2.42 \cdot 10^2$ and $2.82 \cdot 10^2$, $CeLac_2^+$ $-5.32 \cdot 10^3$.

It may be concluded that the strength of the bond of the hydrogen ion with the acid residue in the series of monobasic $\alpha$-hydroxy acids is directly proportional to the strength of the bond of the rare-earth ions in the complex compounds formed by these acids. This dependence is clearly manifested in the series: glycolic –lactic –$\alpha$-hydroxybutyric acids. For these acids, as in the corresponding complex compounds of yttrium, we observe a relatively large difference in the values of the dissociation constants. In the case of $\alpha$-hydroxyvaleric acid, which, in terms of proton-bond strength, lies between lactic and $\alpha$-hydroxybutyric acids, closer to lactic acid, an anomalous shift in the strength of the complex compound with yttrium toward a less stable complex is observed. The strength of the rare-earth salts of $\alpha$-hydroxyvaleric acid is evidently influenced, to a considerable extent, by the factor of the size of the addend. In the formation of complex compounds, steric hindrance and the very fact of the large distance between the centers of the interacting ions lead to a decrease···

Fig. 4. Dependence of $\lg \varphi$ for Y and Ce on the number of carbon atoms in the addends (the values of $\lg \varphi$ correspond to $\lg[A^-] = -1.5$). The lower curve is the dissociation constants of $\alpha$-hydroxy acids.

Figure 2: Fig. 4. Dependence of $\lg \varphi$ for Y and Ce on the number of carbon atoms in the addends (the values of $\lg \varphi$ correspond to $\lg[A^-] = -1.5$). The lower curve is the dissociation constants of $\alpha$-hydroxy acids.

in strength, in comparison with the preceding member of the series of $\alpha$-hydroxy acids [8]. This effect is even more sharply manifested in the properties of complex compounds with cerium, which, apparently, is connected with the larger size of $Ce^{3+}$. In the case of the formation of cerium complexes with glycolic and lactic acids, the effects of the factors of the volume of the addend, on the one hand, and the strength of the proton bond, on the other hand, apparently compensate each other. The strength of the bond of cerium with $\alpha$-hydroxyisobutyric acid, in comparison with the corresponding value for the yttrium complex, is very strongly weakened. Finally, the $Ce^{3+}$ complex with $\alpha$-hydroxyvaleric acid is so weak in comparison with the yttrium complex that, evidently, in this case the factor of the volume of the addend already proves to be decisive.

**Fig. 4.** Dependence of $\lg \varphi$ for Y and Ce on the number of carbon atoms in the addends (the values of $\lg \varphi$ correspond to $\lg[A^-] = -1.5$). The lower curve is the dissociation constants of $\alpha$-hydroxy acids.

In Fig. 4, where additional data for $\alpha$-hydroxycaproic acid are given, it is seen what role is played by the factor of the volume of the addend. Comparison with the values of the dissociation constants shows that the character of the change in $\varphi$ for yttrium and cerium for the first three acids corresponds well to the change in the values of the dissociation constants; for the last two,* weakening of the complex bond occurs because of the volume of the addend. In cerium, owing to the large magnitude of its own volume, this influence is not so clearly manifested.

For practical selection of optimal conditions for the chromatographic separation of trace amounts of rare-earth elements, the following conclusion may be drawn: the greater the strength of the proton bond in an $\alpha$-hydroxy acid, i.e., the weaker the acid, the higher the value of the separation coefficient of the rare-earth elements. From this point of view the best eluent is $\alpha$-hydroxyisobutyric acid, since there is no reason to expect that the following members of the $\alpha$-hydroxy acid series will be stronger complex-formers (or, correspondingly, weaker acids). Some improvement in the separation ability should be expected for $\alpha$-hydroxyvaleric acid, where, owing to the large volume of the addend, a sharp drop in the strength of the cerium complex is observed.

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Received

18 IV 1960

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* The dissociation constants of glycolic, lactic, and $\alpha$-hydroxyisobutyric acids were taken from the literature. For $\alpha$-hydroxyvaleric and $\alpha$-hydroxycaproic acids these values were determined by us by the method of potentiometric titration with accuracy sufficient for the present case.

*Note: Figure translations are in progress. See original paper for figures.*

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