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O. Vojtěch and Academician Vikt. I. Spitsyn

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Abstract

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O. Vojtěch and Academician Vikt. I. Spitsyn

THE INFLUENCE OF AN ORGANIC SOLVENT ON THE SEPARATING ABILITY OF α-HYDROXYISOBUTYRIC ACID

As we showed earlier (^{1}), the separating ability of certain monobasic α-hydroxy acids in chromatography depends to a large extent on their dissociation constants. With an increase in the strength of the proton bond in the acid, the strength of the complex bond of these acids with rare-earth elements also increases, and at the same time their separating ability. It is known that the dielectric constant of the medium strongly affects the degree of dissociation of acids. It is therefore of interest to investigate the change in the stability of complexes of this kind in mixed solvents.

The properties of the complexes of cerium and yttrium α-hydroxyisobutyrate in dioxane–water mixtures were studied. Dioxane is convenient for this purpose, since it mixes with water in all proportions and thus gives mixtures with a broad range of dielectric constants. In the work, α-hydroxyisobutyric acid was used; it was synthesized by the method of hydrolysis of acetone cyanohydrin with hydrochloric acid. It was purified by recrystallization from benzene. The dioxane was distilled over metallic sodium.

In our study, tracer amounts of the radioactive isotopes Y^{91}, Ce^{144}, Pm^{147}, and Nd^{147} of satisfactory radiochemical purity were used. In static experiments, a KU-2 ion exchanger was used (with grain size 0.25–0.50 mm in the sodium form), and for chromatographic separation, KPS-200 ion exchanger in the ammonium form was used. The experiments performed showed that the curves of the dependence of the distribution coefficients of yttrium and cerium between the ion exchanger and the solution on the concentration of addend in dioxane-water solutions are similar to the curves obtained in aqueous solution. Series of experiments were carried out in solutions containing 20 and 45% dioxane at a temperature of 20 ± 1°C. A constant ionic strength $\mu = 0.2$ was maintained by means of sodium perchlorate. The distribution coefficients of yttrium and cerium (φ) were then measured for an addend (α-hydroxyisobutyrate) concentration of $\lg[A^-] = -2.04$, as a function of the dioxane content in the solution. The data obtained are presented in Table 1. As follows

Table 1

Distribution coefficients and stability constants of yttrium and cerium

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

α-hydroxyisobutyrate complexes in aqueous-dioxane solutions

Dioxane content in solvent, %	Yttrium $\lg\varphi$	Yttrium $\lg K_{YA^{++}}$	Cerium $\lg\varphi$	Cerium $\lg K_{CeA^{++}}$	$\lg\frac{K_{YA^{++}}}{K_{CeA^{++}}}$	Dioxane content in solvent, %	Yttrium $\lg\varphi$	Yttrium $\lg K_{YA^{++}}$	Cerium $\lg\varphi$	Cerium $\lg K_{CeA^{++}}$	$\lg\frac{K_{YA^{++}}}{K_{CeA^{++}}}$
0	2.59	3.15	3.65	2.43	0.72	30	1.19	4.00	2.78	3.03	0.97
5	2.35	3.30	3.56	2.55	0.75	40	0.59	4.34	2.42	3.25	1.09
10	2.15	3.43	3.43	2.62	0.81	50	–	–	2.06	3.47	–
20	1.63	3.74	3.14	2.80	0.94	60	–	–	1.79	3.63	–

was to be expected, the separation coefficient of yttrium and cerium (α) increases as the dielectric constant decreases. On the basis of the experimentally found relationship between φ and the stability constants of the MA^{++} complexes (^{2}), an approximate estimate was made of the stability constants of the cerium and yttrium α-hydroxyisobutyrate complexes (YA^{++} and CeA^{++}; A – α-hydroxyisobutyrate), the values of which are also given in Table 1. Irving and Rossotti, in (^{3}), give an equation expressing changes in the con-

Fig. 1. Dependence of the logarithm of the ratio of the stability constants of the YA^{++} and CeA^{++} complexes on the mole fraction of dioxane in the solution (n_x)

Fig. 2. Change in the separation coefficient of promethium and neodymium (α) as a function of the dioxane content in the eluant

Fig. 3. Lowering of the peak maxima of the elution curves for Y, Pm, and Nd as a function of the dioxane content in the eluant

stants of stability of complexes as a function of the mole fraction (n_x) of the organic solvent in the solution. Transforming this equation for the case of com-

Fig. 3

Figure 3: Fig. 3

plexes of two metals similar in properties (for example, Y and Ce) with one and the same addendum, we obtain an equation of the following form:

$$\ln \frac{K_{YA^{++}}}{K_{CeA^{++}}} = A + \frac{n_x}{RT} B + \ln C, \tag{1}$$

where the left-hand side of the equation is the ratio of the stability constants of the yttrium and cerium complexes in the mixed solvent, A is the same ratio for pure water, B is a coefficient depending on the change in the free energy of the system upon transition from the aqueous to the organic phase, and C is the ratio of activity coefficients, which for metals similar in properties is approximately equal to 1. In the case where the coefficient B depends linearly on n_x, the equation takes the form of a straight line, as occurs in our case (Fig. 1).

From Fig. 1, as well as from equation (1), it follows that the admixture of an organic solvent substantially increases the separation coefficient of a pair of rare-earth elements.

To verify the indicated regularity under dynamic conditions, we carried out a series of experiments on the chromatographic separation of yttrium, promethium, and neodymium. The separation was performed on a column 100 mm long and 2.5 mm in diameter, filled with KRS-200 resin. The eluant was ammonium α-hydroxyisobutyrate, neutralized to pH $\sim$ 5.5, with various dioxane contents, fed into the column under slight external pressure. Drops of eluant flowing out of the column were collected on a continuously moving tape and evaporated under an infrared lamp, after which their activity was measured. A series of experiments was carried out with different concentrations of addendum in the eluant, with a dioxane content in the solution of 0–60%. With increas-

As the proportion of dioxane in the solution changes, the surface tension changes greatly, and therefore so does the volume of the drops; this was taken into account when comparing the experimental data.

The logarithmic dependence of the positions of the maxima of the elution-curve peaks on the concentration of the addend is linear in character. As could be expected from the data on separation coefficients obtained under static conditions, with an increase in the proportion of dioxane the degree of separation also increases under dynamic conditions. However, with a strong increase in the dioxane concentration (above 50%), a decrease in the separation coefficient is again observed, as can be seen from Fig. 2. This phenomenon apparently occurs owing to a slowing of the motion of ions possessing a large hydrated shell. It is also reflected in Fig. 3, where, on a semilogarithmic scale, data are given on the position of the maxima of the elution curves of yttrium, promethium, and neodymium as a function of the dioxane content in the solution. The concentration of ammonium α-hydroxyisobutyrate in the eluant in this case was equal to 0.06 M. The observed phenomena can be explained precisely only after a more detailed study of the dynamic features of such systems.

In conclusion, it may be stated that, with an increase in the proportion of an organic solvent of low dielectric constant—in the present case dioxane—the stability constant of the yttrium and cerium α-hydroxyisobutyrate complexes increases greatly. At the same time the separation coefficient also increases, in accordance with the linear equation (1). An increase in the separation coefficient is also observed under chromatographic separation conditions, with a maximum at a dioxane content of 50% in the eluant.

Moscow State University
named after M. V. Lomonosov

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