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The Solvent Extraction of Europium Ions with Benzoyltrifluoroacetone. The Synergistic Effect of Oxygen- and Nitrogen-containing Solvents

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The synergistic effect of many kinds of oxygen- and nitrogen-containing solvents on the extraction of europium ions with benzoyltrifluoroacetone in *n*-hexane has been studied. The addition of alcohols, esters, ketones, amines and heterocyclic compounds enhances the extraction, and in general, the solvents with longer carbon chain, especially alcohols and amines, have the larger synergistic effects. At a constant benzoyltrifluoroacetone concentration, the logarithm of the distribution coefficient is linear with pH. The slope of the log D vs. pH plot is about 1.5 in the extraction with 0.05 M benzoyltrifluoroacetone in *n*-hexane, but it is 2 in the presence of 0.04 M oxygen-containing compound and 3 in the presence of 0.04 M nitrogen-containing compound. It may be considered that europium benzoyltrifluoroacetonate forms some adducts with these oxygen- or nitrogen-containing Lewis bases, and that the coordination of nitrogen-containing Lewis bases to the chelates is stronger than that of oxygen-containing ones. Since the solvent extraction of neodymium and lutetium ions with β-diketones is performed as well as that of europium ions, it seems to be a favorable procedure for the extraction of rare earth ions with β-diketones to utilize the adduct formation between β-diketonates and active oxygen- or nitrogen-containing Lewis bases.

The nature of the organic solvent is important in the extraction of metal ions with a suitable chelating reagent.[1] Here the neutral chelate compounds may be extracted into the organic phase, there forming addition compounds with some molecules of water, a solvent and/or an uncoordinated chelating reagent.

In the case of the extraction with such an inert solvent as benzene, chloroform, carbon tetrachloride, *n*-hexane and cyclohexane, the addition of an active oxygen- or nitrogen-containing solvent to the extraction system often increases the extraction. This phenomenon, the synergistic effect of the solvent, may be attributed to the formation of adducts or solvates between the metal chelates and the polar oxygen- or nitrogen-containing solvents. This synergistic effect of the solvent has been observed in the solvent extractions of thorium TTA chelates in the presence of tri-*n*-octylamine[2] and acetic acid[3]; in the solvent extractions of copper(II) and zinc(II) TTA or β-isopropyltropolone chelates in the presence of TBP or hexone,[4] and in the solvent extraction of alkali earth oxinates in the presence of *n*-butyl amine.[5] The synergistic effect has also appeared in the thorium TTA and phosphate ester systems,[2,6] the uranyl DBP-TBP system,[7] and the actinide TTA, TBP and TBPO systems.[8] The chelating reagent also reacts as a donor molecule in the case of a UO_2R_2HR-type complex with uranium(VI) and TTA.[9-11]

On the other hand, there have been severa- investigations of the adduct or solvate formation by the crystallization of chelates, such as the halomethane solvates of tervalent metal acetylacetonates[12]; the solvates of the rare earth acetylacetonates with water and methanol[12,13]; the adducts of copper(II) β-diketonates with heterocyclic bases[14]; the adducts between UO_2 β-diketonates and amine, ammonia, water, ketones or alcohols,[15-17] and europium(III) dibenzoylmethide

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adducts with a number of oxygen- and nitrogen-containing Lewis bases.[18)]

During the course of the authors investigations of the extraction of many metal ions with β-diketones,[11,19-23)] it has been found that rare earth and uranyl β-diketonates are extracted better with a polar oxygen-containing solvent, such as butyl acetate, than with chloroform or benzene. It may be inferred that rare earth β-diketonates form adducts with the active solvents as well as uranyl chelates do.

In this paper, the synergistic effect of a number of oxygen- and nitrogen-containing solvents on the extraction of europium ions with a fluorinated β-diketone, benzoyltrifluoroacetone in *n*-hexane, will be studied, and the usefulness of this effect in the extraction of rare earth(III) ions with β-diketones will be discussed.

Experimental

Apparatus.—Radioactivity countings were made with a Kobe Kogyo NaI(Tl) (4.45 cm. × 5.08 cm.) well-type scintillation counter, model PS-300, connected to a transistorized scaler, model SA-230. A Hitach-Horiba glass electrode pH meter, model M-3, was used for the pH measurements.

Materials.—The radioisotopes of neodyminum-147, europium-152, 154 and lutetium-177 were supplied from ORNL, U. S. A. or from The Radiochemical Center, Amersham, England.

The benzoyltrifluoroacetone was obtained from the Dojindo Co., Ltd., Research Laboratories.

The chloroform was purified by washing it with a diluted sodium hydroxide solution, water, a diluted hydrochloric acid solution and three portions of water, followed by distillation. The butyl acetate was washed with water and distilled. The ethers were shaken with an aqueous ferrous sulphate solution. The furan was refluxed with cuprous chloride and then distilled. All the other reagents were reagent-grade materials and were used without further purification.

Procedure.—The extractions are made by shaking 10 ml. of the aqueous sample solution with 10 ml. of the organic solvent. The aqueous sample solution, adjusted to a desired pH, contains europium ions in the concentration of about 1 p. p. m. (^{152,154}Eu 2—3 × 10^4 c. p. m.), sodium chloride and acetic acid in each 0.1 molar concentration respectively. When the effect of the nitrogen-containing solvent is investigated, the material is added to the aqueous solution to make a 0.04 M solution. The organic solvent phase is composed of 0.05 M benzoyltrifluoroacetone and a 0.04 M oxygen-containing compound in the studies of the effect of an oxygen-containing solvent.

The aqueous and the organic phase are taken into a 50 ml. separating funnel and then shaken for 15 to 30 min. Two milliliters of each of the two phases are then pipetted into test tubes (14 mm. in diameter); the gamma activities are measured with the NaI scintillation counter, and the pH values of the aqueous phase after the extraction are obtained with the pH meter.

Results

The distribution ratio, *D*, and the per cent of extraction, %*E*, were calculated by the following equations;

$$D=\frac{\gamma\text{-count rate per 2 ml. of the org. phase}}{\gamma\text{-count rate per 2 ml. of the aq. phase}}$$

$$\%E=(D/(1+D))\cdot 100$$

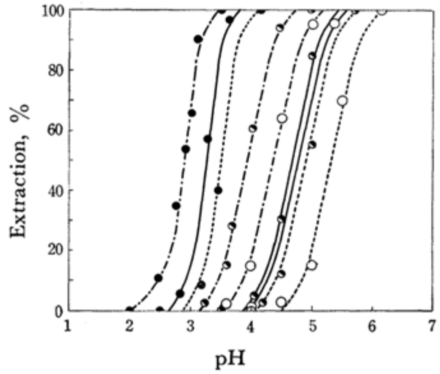

Fig. 1. Extration of rare earth(III) benzoyltrifluoroacetonate.

Rare earth: ⋯⋯ neodymium, —— europium, —·— lutetium
Solvent: —●— butyl acetate, —◐— benzene, —○— chloroform

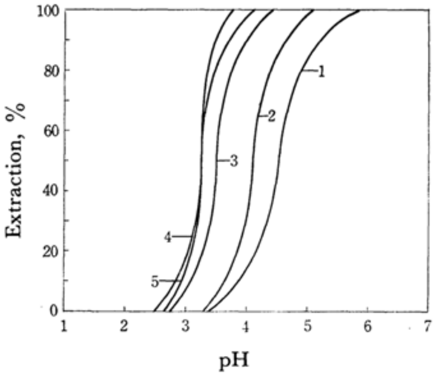

Fig. 2. Extraction of europium benzoyltrifluoroacetonate.

Solvent: *n*-hexane, BTFA: 5×10^{-2} M,
Concentration of added butyl acetate
1 None
2 6.0×10^{-2} M
3 7.6×10^{-1} M
4 3.0 M
5 Pure butyl acetate

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The extraction curves for neodymium-, europium- and lutetium-benzoyltrifluoroacetonates with butyl acetate, chloroform and benzene are shown in Fig. 1. From the figure, it may be seen that the extraction of rare earth benzoyltrifluoroacetonates is performed better with butyl acetate than with chloroform or benzene. Figure 2 represents the extraction behavior of the europium chelate in mixed solvents which are prepared by changing the concentration of butyl acetate using *n*-hexane as the diluent. The extraction is much enhanced, even at a low concentration of butyl acetate such as 0.06 M.

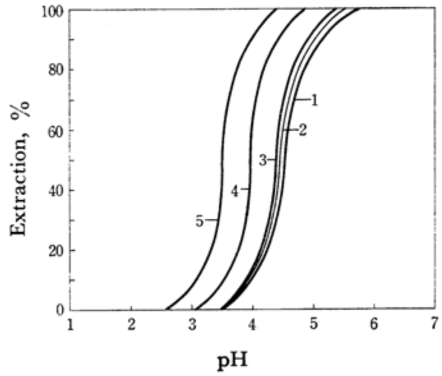

Fig. 3. Extraction of europium benzoyltrifluoroacetonate.
Solvent: *n*-hexane BTFA: 5×10^{-2} M
Molarity of added alcohol: 4×10^{-2} M
1 None or ethyl alcohol
2 *t*-Butyl alcohol
3 *n*-Butyl alcohol, *s*-butyl alcohol, isobutyl alcohol or benzyl alcohol
4 *n*-Amyl alcohol or isoamyl alcohol
5 *n*-Hexyl alcohol, *n*-octyl alcohol, *n*-decyl alcohol or dodecyl alcohol

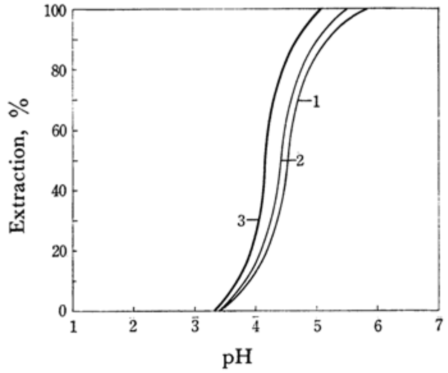

Fig. 4. Extraction of europium benzoyltrifluoroacetonate.
Solvent: *n*-hexane BTFA: 5×10^{-2} M
Molarity of added ester: 4×10^{-2} M
1 None
2 Methyl acetate
3 Ethyl acetate, butyl acetate, amyl acetate or hexyl acetate

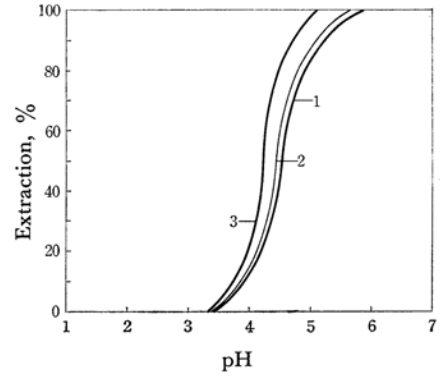

Fig. 5. Extraction of europium benzoyltrifluoroacetonate.
Solvent: *n*-hexane BTFA: 5×10^{-2} M
Molarity of added ketone: 4×10^{-2} M
1 None or acetone
2 Diethyl ketone
3 Methyl isobutyl ketone, methyl *n*-amyl ketone methyl *n*-hexyl ketone or heptyl methyl ketone

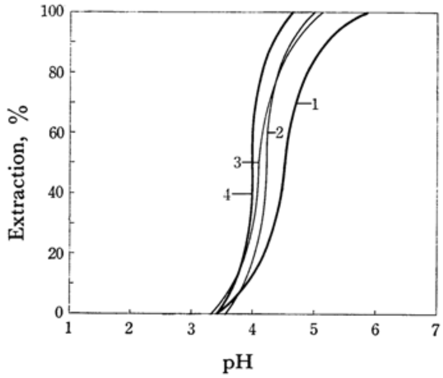

Fig. 6. Extraction of europium benzoyltrifluoroacetonate.
Solvent: *n*-hexane BTFA: 5×10^{-2} M
Molarity of added heterocyclic compound: 4×10^{-2} M
1 None, furan or pyrrole
2 Pyrrolidine
3 Tetrahydrofuran
4 Pyridine or piperidine

The effects of alcohols, esters, ketones and ethers have also been investigated according to the above-described procedure; the extraction curves obtained in the presence of 0.04 M oxygen-containing compounds are shown in Fig. 3 (alcohols), Fig. 4 (esters) and Fig. 5 (ketones). Figure 3 indicates that the higher alcohols have the larger solvent effects. Esters and ketones show effects similar to those of alcohols, although the effect of the latter is much greater than that of the former. Ethers do not have such an influence. The effect of heterocyclic bases has also been studied; the results are shown in Fig. 6. Furan and pyrrole do not exert any effects, whereas tetrahydrofuran, pyrrolidine, pyridine and piperidine increase the extraction. As is shown in Fig. 7, amines have the same effect as alcohols, and the presence of amines and other nitrogen-containing Lewis bases causes a steeper rise in the extraction curves than does that of oxygen-containing compounds.

This fact becomes more evident from the results in Fig. 8, which presents the slope of the log-*D* vs. pH plot obtained at 0.05 M benzoyltrifluoroacetone. When the extraction is carried out using *n*-hexane as the extracting solvent, the slope of the log *D* vs. pH plot is about 1.5. This slope is 2 in the extraction using *n*-hexane containing 0.04 M oxygen-containing compounds as the extracting solvents, and 3 in the presence of 0.04 M nitrogen-containing Lewis bases.

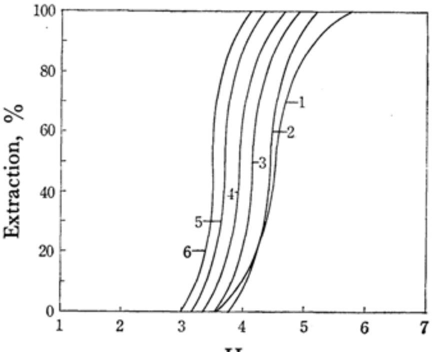

Fig. 7. Extraction of europium benzoyltrifluoroacetonate.
Solvent: *n*-hexane BTFA: 5×10^{-2} M
Molarity of added amine: 4×10^{-2} M
1 None
2 Ethyl amine
3 *t*-Butyl amine
4 *n*-Butyl amine
5 *n*-Hexyl amine
6 Octyl amine

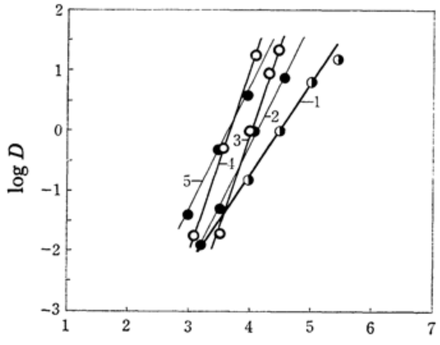

Fig. 8. Variation of the distribution ratio, *D* as a function of pH.
Solvent: *n*-hexane BTFA: 5×10^{-2} M
Molarity of added Lewis base: 4×10^{-2}
Slope: 1 None (1.5)
2 Tetrahydrofuran (2.0)
3 Pyridine (3.0)
4 *n*-Hexyl amine (3.0)
5 *n*-Hexyl alcohol (2.0)

Discussion

The extraction of rare earth benzoyltrifluoroacetonates improves in the order of lutetium, europium, and neodymium, as is shown in Fig. 1. Generally, the stability of rare earth β-diketonates increases with the decrease in the ionic size, that is, with the decrease in basicity,[24-26] while their extraction is enhanced with the decreasing basicity of the central metal ions.[27] The results in Fig. 1 are in agreement with these facts.

Table I shows the shifts of the $pH_{1/2}$s of the extraction caused by the addition of several sorts of oxygen- or nitrogen-containing compounds (Lewis base). In general, the $pH_{1/2}$ shifts seem to enlarge with the increase in the length of the carbon chain of the base. These effects of the carbon cahin length could be ascribed to the decreasing solubility of the higher base in water.

The role of these Lewis bases in the extraction behavior of the chelate can be explained as follows. If a neutral metal chelate extracted reacts with a Lewis base to form the adduct compound, the concentration of the chelate in the organic phase decreases. Then the overall extraction equilibrium of the metal chelate shifts in the direction that favors the rise of the distribution ratio (organic/aqueous) of the metal.

Table I suggests an attractive technique for the solvent extraction of rare earth ions. By utilizing the adduct formation between rare earth benzoyltrifluoroacetone chelate and Lewis bases, the extraction can be undertaken at a lower pH region.

The differences found among the solvent effects of alcohols, esters, ketones and ethers are probably due to the basicity of the oxygen atoms in the solvent molecules. Figure 6 suggests that lone-pair electrons of furan and pyrrole participate in the resonance stabilization of the molecule, whereas lone-pair electrons of tetrahydrofuran, pyrrolidine, pyridine and piperidine are utilized in the adduct formation.

The difference observed between the solvent effect of oxygen- and nitrogen-containing Lewis bases may be attributed to the differences in the donating power of the active oxygen and nitrogen atoms in the molecules, indicating that the bonding of the former to the metal chelates is weaker than that of the latter.

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Table I. Shift of $pH_{1/2}$ of the extraction curve obtained by the addition of 4×10^{-2} M oxygen- and nitrogen-containig solvent or Lewis base to water - *n*-hexane extraction system

Organic solvent of Lewis base	$-\Delta pH_{1/2}$	Organic solvent or Lewis base	$-\Delta pH_{1/2}$
n-Hexane	—	Diethyl ketone	0.16
Ethyl alcohol	0	Methyl isobutyl ketone	0.39
n-Butyl alcohol	0.19	Methyl *n*-amyl ketone	0.42
s-Butyl alcohol	0.16	Methyl *n*-hexyl ketone	0.43
t-Butyl alcohol	0.09	Heptyl methyl ketone	0.45
Isobutyl alcohol	0.18	Ethyl ether	0
n-Amyl alcohol	0.64	Isopropyl ether	0
Isoamyl alcohol	0.63	Furan	0
n-Hexyl alcohol	1.10	Tetrahydrofuran	0.41
n-Octyl alcohol	1.11	Pyrrole	0
n-Decyl alcohol	1.12	Pyrrolidine	0.25
Dodecyl alcohol	1.12	Pyridine	0.50
Benzyl alcohol	0.16	Piperidine	0.50
Methyl acetate	0.17	Ethyl amine	0.05
Ethyl acetate	0.44	*t*-Butyl amine	0.35
n-Butyl acetate	0.49	*n*-Butyl amine	0.53
n-Amyl acetate	0.54	*n*-Hexyl amine	0.80
Hexyl acetate	0.55	Octyl amine	1.03
Acetone	0		

The bondings of the donor molecules (including water molecules) to the metal chelates have been widely studied by various methods; they have generally been classified into two groups; (1) donor molecules bond to the coordinated chelating reagents by dipole-dipole interaction or hydrogen bonding,[12] and (2) donor molecules coordinate directly to the central metal ions.[17,18] Both monomers and dimers of the chelates also exist in a non-aqueous solution.[13,28,29] There are several pieces of evidence that rare earth β-diketonates have coordination numbers greater than six,[30] and the coordination number of seven may be expected from the fact that one water molecule is always tightly held on the crystal of rare earth β-diketonates.[12,13,31] From the results in Fig. 6 and Fig. 7, it might be considered that nitrogen-containing Lewis bases substitute with the water molecule directly coordinated to central metal ions, although more detailed experiments must be undertaken before a definite conclusion can be reached.

At any rate, it is evident that the adduct formation with Lewis bases is favorable for the solvent extraction of rare earths as the benzoyltrifluoroacetone chelates; it is also probable that a similar advantage can be expected in some other cases of the extraction of metal β-diketonates, which show a poor extractability in the absence of adduct-forming materials.

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