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The Synergistic Effect in Solvent Extraction. The Effect of Carboxylic Acid on the Solvent Extraction of Europium(III) with Benzoyltrifluoroacetone

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The effects of carboxylic acids, such as formic, chloroacetic, acetic, propionic, butyric and caproic acid, on the extraction of europium with benzoyltrifluoroacetone were studied. The extraction is enhanced by the adduct formation between metal chelates and carboxylic acids in the organic phase, while it is hindered by the formation of metal-complex ions with anions of carboxylic acids in the aqueous phase. Caproic acid acts as an organic Lewis base and shows the synergism, but formic and chloroacetic acids have a masking effect. Acetic acid, propionic acid, and butyric acid behave both as synergists in the organic phase and as masking agents in the aqueous phase. Caproic acid forms more stable adducts than does *n*-hexyl alcohol, and the composition of the chelate adduct is estimated to be $Eu(BFA)_3 \cdot 2CH_3(CH_2)_4COOH$.

As a general procedure for the extraction of metal chelates, a suitable buffer solution is added to the aqueous phase in order to minimize the pH change during the extraction. However, the use of a buffer solution sometimes causes an abnormal distribution of metals as a result of the synergistic effect and the masking effect.

Acetic acid enhances the extraction of thorium with TTA,[1,2] but inhibits the extraction of lanthanum with TTA[3] or that of uranium[4] and europium[5] with benzoyltrifluoroacetone; it was also observed that the slope of log *D vs.* pH plots decreased upon the addition of acetic acid.[5]

In the present research, the effect of such carboxylic acids as formic, chloroacetic, acetic, propionic, butyric, and caproic acid on the extraction of europium with benzoyltrifluoroacetone in benzene was studied, and the extraction behavior was explained by the adduct formation of the carboxylic acid molecules with europium chelates in the organic phase, and by the complex formation of the acid anions with europium ions in the aqueous phase.

Experimental

Materials. The europium-152, 154 was obtained from the Radiochemical Center, Amersham. The radioisotope was purified by extracting it with 0.05 M benzoyltrifluoroacetone in benzene at pH 5, by back-extracting into 0.1 M perchloric acid, and by evaporating almost to dryness. The residue was dissolved with 0.1 M perchloric acid to make a stock solution. The benzoyltrifluoroacetone was obtained from the Dojindo Co., Ltd. The sodium perchlorate was prepared by adding sodium carbonate to perchloric acid and by subsequent recrystallization from water. All the other reagents were of the G. R. grade and were used without further purification.

Procedure. The experimental procedures were almost the same as have previously been described.[5] Ten milliliters of an aqueous solution containing a few ppm europium ions, 0.1 M sodium perchlorate, and carboxylic acid in a given concentration were shaken with 10 *ml* of 0.05 M benzoyltrifluoroacetone in benzene for one hour at 25±1°C: Each of the carboxylic acids except caproic acid was added in the aqueous phase; caproic acid was added to the organic phase. Aliquots (2 *ml*) of the two phases were pipetted into test tubes, and the distribution ratio of europium was estimated from the gamma counts, as measured with a NaI(Tl) well-type scintillation counter. The pH of the aqueous layer was measured again after the extraction. The partition of the carboxylic acids, such as acetic, propionic, butyric, and caproic acid, between benzene and water was estimated by titrating an aqueous solution containing 0.1 M or 1 M carboxylic acid with a standard sodium hydroxide solution before and after shaking with benzene. The pH of the aqueous layer during the distribution measurement was near 3; therefore, more than 99% of the carboxylic acids may exist in the neutral form. As will be described below, formic acid and chloroacetic acid did not act as synergists, but only as masking agents in the aqueous phase; therefore, the partition was not measured in these cases.

Theoretical

When the predominant species in the organic phase are MR_3, $MR_3 \cdot HA$, $MR_3 \cdot 2HA$, $\cdots$, and when those in the aqueous phase are M^{3+}, MA^{2+}, $MA_2{}^+$, $\cdots$, the distribution ratio of the metal is written as follows:

$$D^* = \frac{\sum_0^m [MR_3 \cdot mHA]_o}{\sum_0^n [MA_n{}^{(3-n)+}]} \tag{1}$$

where M stands for the metal; MR_3, for the chelate with a chelating agent, HR, and HA, for a carboxylic acid, and where [ ] and $[\ ]_o$ indicate the concentration of the relevant chemical species in the aqueous and organic phases respectively.

By introducing the distribution ratio in the absence of the carboxylic acid, *D*, the equation can be reduced to;

$$\frac{D^*}{D} = \frac{1+\sum_1^m \beta_m [HA]_o{}^m}{1+\sum_1^n k_n [A^-]^n} \tag{2}$$

or;

$$\log D^* - \log D = \log \{1+\sum_1^m \beta_m [HA]_o{}^m\}$$
$$- \log \{1+\sum_1^n k_n [A^-]^n\} \tag{3}$$

where β_m is the overall stability constant of the adducts formal between the metal chelate and the carboxylic acid, and where k_n is that of the metal complexes with the carboxylic anion; these stability constants are expressed as:

$$\beta_m = \frac{[MR_3 \cdot mHA]_o}{[MR_3]_o [HA]_o{}^m} \tag{4}$$

$$k_n = \frac{[MA_n{}^{(3-n)+}]}{[M^{3+}][A^-]^n} \tag{5}$$

When the acid dissociation constant of the carboxylic acid, K_A, the partition coefficient of the acid in molecular form, K_d, and the dimerization constant in the organic phase, K_p, are known, the concentration of the monomer species in the organic phase, $[HA]_o$, and of the anionic species in the aqaqueous phase, $[A^-]$, are given from the total concentration of the carboxylic acid, C_{HA}, by the following equations:

$$[HA]_o = \frac{-K_b \sqrt{K_b{}^2+8K_d{}^2 \cdot K_p C_{HA}}}{4K_d \cdot K_p} \tag{6}$$

$$[A^-] = \frac{K_A(-K_b+\sqrt{K_b{}^2+8K_d{}^2 \cdot K_p C_{HA}})}{4K_d{}^2 \cdot K_p \cdot [H^+]} \tag{7}$$

where:

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1) R. A. Day, Jr., and R. W. Stoughtom, *J. Am. Chem. Soc.*, **72**, 5662 (1950).

2) G. Goldstein, O. Menis and D. L. Manning, *Anal. Chem.*, **32**, 400 (1960).

3) O. Menis, T. C. Rains and J. A. Dean, *ibid.*, **31**, 187 (1959).

4) T. Shigematsu, M. Tabushi and M. Matsui, This Bulletin, **37**, 1333 (1964).

5) T. Shigematsu, M. Tabushi, M. Matsui and T. Honjyo, *ibid.*, **39**, 165 (1966); *ibid.*, **40**, 2802 (1967).

$$K_d = \frac{[\mathrm{HA}]_o}{[\mathrm{HA}]}, \quad K_p = \frac{[(\mathrm{HA})_2]_o}{[\mathrm{HA}]_o{}^2}$$

and:

$$K_b = 1 + \frac{K_\mathrm{A}}{[\mathrm{H}^+]} + K_d$$

If the largest portion of the carboxylic acid is distributed into the organic phase, the concentration of the monomer species is obtained by the following equation:

$$[\mathrm{HA}]_o = \frac{-1+\sqrt{1+8K_pC_\mathrm{HA}}}{4K_p} \tag{8}$$

Results and Discussion

The effect of acetic acid on the extraction of europium with benzoyltrifluoroacetone is shown in Fig. 1. With an increase in the concentration of acetic acid, the extraction must be carried out in the higher pH region, and the log *D* *vs.* pH plot curves concavely. The effect of other carboxylic acids are shown in Fig. 2 (formic and chloroacetic acid), Fig. 3 (propionic acid), Fig. 4 (*n*-butyric acid), and Fig. 5 (caproic acid). Caproic acid enhances, while formic and chloroacetic acid hinder, the extraction. In these cases, the log *D* *vs.* pH plots are parallel to that obtained in the absence of the carboxylic acids. Propionic acid and *n*-butylic acid increase the extractability in the lower pH region, but decrease the extractability in the higher pH region, indicating convexly-curved log *D* *vs.* pH plots. Figure 6 presents the change in the distribution ratio of europium as a function of the caproic acid concentration. As is shown in the figure, a straight line with a slope of 1 is obtained when the log D^*/D values are plotted against log C_HA, but the slope becomes 2 if they are plotted against log $[\mathrm{HA}]_o$. This fact indicates that two moles of caproic acid react with one mole of europium benzoyltrifluoroacetonate to form the $\mathrm{MR_3 \cdot 2HA}$-type adduct in benzene, although it is not clear whether caproic acid reacts as the monomer or as the dimer. The overall stability constant of the adduct was esti-

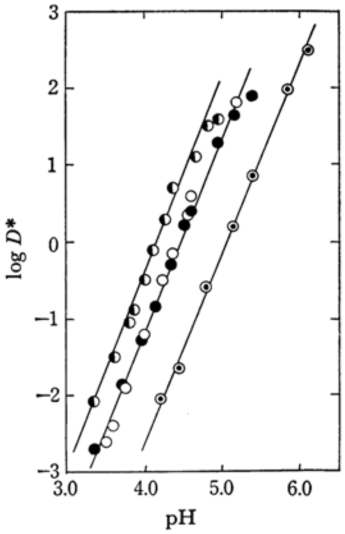

Fig. 2. The distribution ratio of europium(III) as a function of pH in the presence of chloroacetic or formic acid.
Molarity of chloroacetic acid: -◐- none, -○- 0.1 M; formic acid: -◐- none, -●- 0.1 M, -⊙- 1.0 M

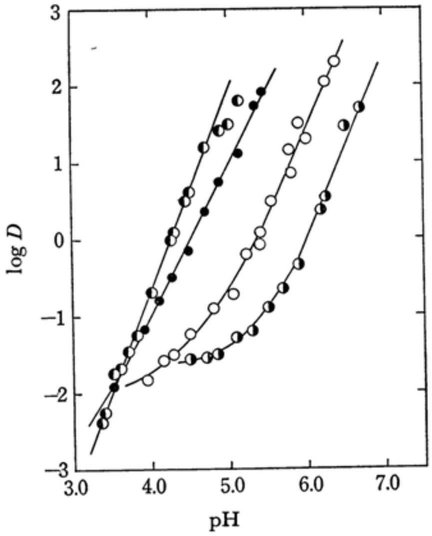

Fig. 1. The distribution ratio of europium(III) as a function of pH in the presence of acetic acid.
Molarity of acetic acid: -◐- none or 0.01 M, -●- 0.1 M, -○- 1.0 M, -◑- 5.0 M

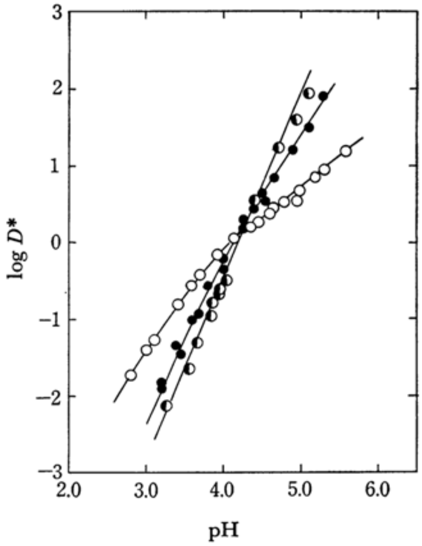

Fig. 3. The distribution ratio of europium(III) as a function of pH in the presence of propionic acid.
Molarity of propionic acid: -◐- none or 0.01 M, -●- 0.1 M, -○- 1.0 M

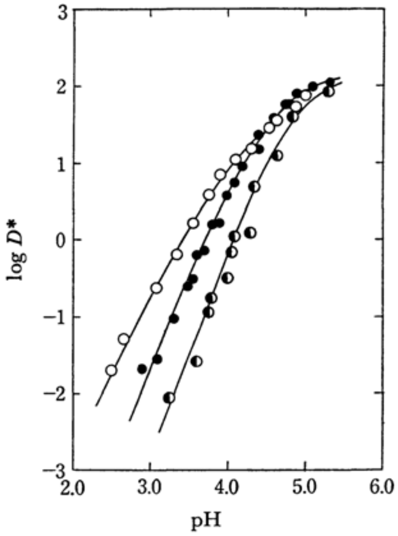

Fig. 4. The distribution ratio of europium(III) as a function of pH in the presence of *n*-butyric acid.
Molarity of *n*-Butyric acid: -◐- none or 0.01 M, -●- 0.1 M, -○- 1.0 M

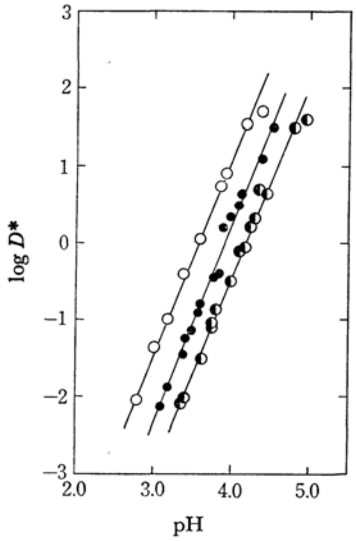

Fig. 5. The distribution ratio of europium(III) as a function of pH in the presence of caproic acid.
Molarity of caproic acid: -◐- none or 0.001 M, -●- 0.01 M, -○- 0.1 M

mated to be log $\beta_2=5.20$. From this value, it may be expected that caproic acid forms more stable adducts with europium benzoyltrifluoroacetonate than does *n*-hexyl alcohol (log $\beta_2=3.10$). In the cases of acetic, propionic, and *n*-butyric acid, some correlation may be observed between the bend point of the log D *vs.* pH plots and the pK_A value of the carboxylic acid, and between the strength of the synergistic effect and the partition ratio (including K_d and K_p) of the acid. In order to examine why the curious extraction behavior resulted from the distribution equilibrium expressed by Eq. (1), the rough theoretical extraction curves were obtained from the equations described above by introducing various constants of carboxylic acids, which are summarized in Table 1. The K_d and K_p values of *n*-butyric acid were lacking; K_p was assumed to be the same as the values of acetic and propionic acid, and K_d was estimated from the partition of 1 M *n*-butyric acid (Ex=72.7%). The extractabilities of acetic and propionic acid obtained experimentally in the present research

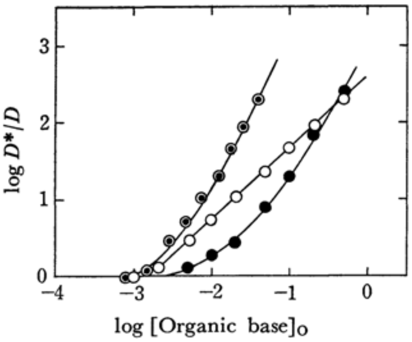

Fig. 6. Variation of the distribution ratio as a function of organic base concentration.

Caproic acid : -○- (log D^*/D *vs.* log C_{HA} plot)
-⊙- (log D^*/D *vs.* log $[HA]_O$ plot)
n-Hexylalcohol: -●- (log D^*/D *vs.* log [*n*-Hexylalcohol]$_0$ plot)

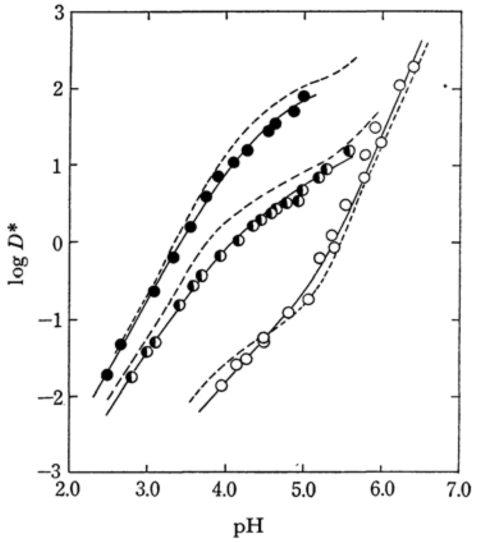

Fig. 7. The extraction curves of europium(III) with benzoyltrifluoroacetone in the presence of 1 M carboxylic acid.
——: experimental, - - -: calculated
Carboxylic acid: -○- Acetic acid, -◐- Propionic acid, -●- *n*-Butyric acid

Table 1. The constants used for the approximate calculation

Carboxylic acid	K_A	K_d	K_p	β_2	k_1		k_2		% Extrn. of carboxylic acid			
					0.1 M	1 M	0.1 M	1 M	0.1 M		1 M	
									Calcd	Exp.	Calcd	Exp.
Acetic acid	1.8×10^{-5}	1×10^{-2} a)	1.3×10^{2} a)	1×10^{5} e)	2×10^{2} b)	1×10^{2} f)	8×10^{3} b)	2×10^{3} f)	2	1.7	3	2.5
Propionic acid	1.3×10^{-5}	5×10^{-2} a)	1.3×10^{2} a)	1×10^{5} e)	1.7×10^{2} b)	8.5×10 f)	6×10^{3} b)	1.5×10^{3} f)	10	9.3	33	30.0
n-Butyric acid	1.5×10^{-5}	1.9×10^{-1} d)	1.3×10^{2} c)	1×10^{5} e)	1.4×10^{2} f)	7×10 f)	4×10^{3} f)	1×10^{3} f)	42.5	42.5	73	72.7 g)

a) Ref. 6, b) Ref. 7.

c) The value was assumed to be the same with that of acetic and propionic acid.

d) The value was estimated from the K_p value c) and the extractability g).

e) The values were assumed from β_2 of caproic acid.

f) The values were assumed from the data presented by Ref. 7.

g) The extractability was used for calculating the K_d value. d)

were in good agreement with those calculated from the K_d and K_p values previously reported.6) Also, in the partition of 0.1M *n*-butyric acid, the extractability obtained experimentally agreed well with that derived from the asumed K_d and K_p values. The β_2 values of these acids were uncertain, so $\log \beta_2=5$ was used, the data of caproic acid being referred to. The k_1 and k_2 values used were based on the data in the literature.7)

Typical calculated extraction curves are indicated in Fig. 7, along with the experimental curves. Since many of the equilibrium constants were roughly estimated, and since the concentration was used instead of the activity in the calculation, the resulting curves were, of course, mere approximations. However, they may not be very wrong, for the vertical scale is logarithmic. Both the extraction curves, those calculated and those experimentally obtained, show a similar shape in each carboxylic acid; this fact indicates that the extraction behavior of europium benzoyltrifluoroacetonate in the presence of carboxylic acid can be explained by Eq. (1). For formic and chloroacetic acid, the first term of Eq. (3) is negligible and only the masking effect appears, while the second term can be neglected and the synergism is observed in the case of caproic acid.

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6) M. Davies, P. Jones, K. Patnaik and E. A. Moywyn-Hughes, *J. Chem. Soc.*, **1951**, 1249.

7) S. P. Sinha; "Complex of the Rare Earths," Pergamon Press, London (1966), pp. 38, 41, 46.