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Synergistic Effect in Solvent Extraction—Effect of Oxygen and Nitrogen Containing Organic Bases on the Stability of Zinc(II) and Cobalt(II) β-Diketonate Adducts—

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The effect of the organic Lewis bases acting as a synergist on the extraction of zinc(II) and cobalt(II) with benzoyltrifluoroacetone was studied. *n*-Hexyl alcohol, TBP, TBPO and TOPO were used as oxygen-containing bases, and quinoline, isoquinoline, lepidine, acridine and quinaldine as nitrogen-containing bases. The stability constants between metal chelates and the adduct forming materials in the organic phase were obtained by curve fitting method. The results are summarized as follows: (1) Zinc(II) and cobalt(II) chelates formed adducts including one or two molecules of the bases per metal ion. Adduct formation was carried out successively. (2) The stability of adducts with oxygen-containing organic bases increased in the order, *n*-hexyl alcohol$<$TBP$<$TBPO$\approx$TOPO. This is the same order with that of the basicity of donor oxygen in the compounds. The stability of adducts with nitrogen-containing bases increased in the order, quinaldine$<$acridine$<$quinoline$<$lepidine$<$isoquinoline. In this case, however, the steric effect of the bases preferably contributed to the adduct formation. (3) The overall stability constants of the adducts are affected by the coordination number of the metal ions. Cobalt(II) adducts are more stable than zinc(II) adducts.

In many extraction systems of metal β-diketone chelates, the presence of some neutral organic Lewis bases extremely enhances the extractability. Such phenomena, called "synergistic effect" can be explained by adduct formation between the metal chelates and the Lewis bases. The authors have made a systematic study on synergistic extraction,[1-4)]

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1) T. Shigematsu, M. Tabushi, M. Matsui and T. Honjyo, This Bulletin, **39**, 165 (1966).

2) T. Shigematsu, M. Tabushi, M. Matsui and T. Honjyo, *ibid.*, **40**, 2807 (1967).

3) T. Honjyo, *ibid.*, **42**, 995 (1969).

4) T. Shigematsu, M. Tabushi, M. Matsui and K. Utsunomiya, *Bull. Inst. Chem. Res., Kyoto Univ.*, **45**, 290 (1967).

and reported on the influence of terminal groups of β-diketones in zinc-β-diketone-TOPO system.[4] In the present research, the effect of organic Lewis bases on the synergistic extraction of zinc(II) and cobalt(II) with benzoyltrifluoroacetone was studied, and the stability constants of the adducts were determined.

Experimental

The radioisotopes, zinc-65 and cobalt-60 were supplied by the Radiochemical Centre, Amersham, England, as chlorides in hydrochloric acid solution. They were converted to the perchlorates and diluted with 0.01 M perchloric acid to make stock solutions. Sodium perchlorate was prepared by dissolving sodium carbonate in perchloric acid and purified by recrystallization from water. Benzoyltrifluoroacetone (BFA) was obtained from the Dojindo Co. Organic bases; TOPO (tri-*n*-octylphosphine oxide), TBPO (tri-*n*-butylphosphine oxide), *n*-hexyl alcohol, quinoline, isoquinoline, lepidine, quinaldine and acridine were obtained commercially. TBP was purified by washing successively with a dilute sodium hydroxide solution, a dilute hydrochloric acid solution and a saturated sodium chloride solution, followed by centrifugation. All the other reagents were GR grade materials and used without further purification.

Experimental procedure was almost the same as previously described.[1-4] Five milliliters of aqueous solution containing zinc(II) or cobalt(II) ions (a few ppm), sodium perchlorate (0.1 M) and acetic acid (0.01 M) were adjusted to a desired pH, and shaken with 5 m*l* of benzene solution containing 0.05 M benzoyltrifluoroacetone and various amount of organic bases, for one to three hours, at 20±1°C. After separating two phases, 2 m*l* of each of the phases was pipetted into test tubes (14 mm in diameter), and radioactivity was measured with a NaI(Tl) well-type scintillation counter. The pH values of the aqueous layers after the extraction were again measured, and the data were used for plotting the distribution curves.

Theoretical

The extraction constants of metal chelates, K, and the stability constants of adducts, β_n, were calculated by the equations

$$K = [MR_2]_o[H^+]^2/[M^{2+}][HR]_o^2, \tag{1}$$

$$\log K = \log D - 2\log [HR]_o - 2pH, \tag{2}$$

$$\beta_n = [MR_2L_n]_o/[MR_2]_o[L]_o^n, \tag{3}$$

$$\log D^*/D = \log(1+\sum_{n=1}^{n}\beta_n[L]_o^n), \tag{4}$$

where D and D^* were the distribution ratios in the absence or presence of organic bases, M stood for metal, HR for β-diketone and L for organic bases; and [ ] and $[\ ]_o$ designated the concentration of the chemical species in the aqueous and organic phase, respectively.

The equilibrium concentration of the bases, $[L]_o$, can be assumed to be equal to the initial concentration, C_L, in the case of oxygen-containing bases, because the amount of metal ions is negligibly small and the bases are scarcely distributed to the aqueous phase. However, nitrogen-containing bases can form the cationic species such as LH^+ in acidic aqueous solution, and accordingly the $[L]_o$ value may not be the same with, but lower than the C_L value. Using the dissociation constant, $K_{LH} = [H^+][L]/[LH^+]$, and the partition coefficient, $P_L = [L]_o/[L]$, the relation between these two concentrations may be given as follows:

$$C_L = [L]_o(1+P_L^{-1}+P_L^{-1}K_{HL}^{-1}[H^+]) \tag{5}$$

The $\log P_L$ values of quinoline and isoquinoline are about 2 at 20±2°C and the pK_{LH} values are 4.85 (quinoline) and 5.14 (isoquinoline) (Ref. 5). In the pH region studied (pH 4.5—6.0), more than 90 per cent of the base must be present in organic phase, and therefore, the error caused by using C_L for $[L]_o$ can be neglected. The $\log P_L$ and pK_{LH} values of the other three bases are unknown or uncertain. However, as they are almost insoluble in water, and their K_{LH} values may not be so low as to cover their very high P_L, we might assume that the situation is similar to the case of quinoline and isoquinoline.

Results and Discussion

Fugures 1 and 2 show the $\log D$ *vs.* pH plots and the $\log D$ *vs.* $\log [HR]_o$ plots in the extraction of zinc(II) and cobalt(II) with BFA only. All the plots give an almost straight line with a slope of 2, indicating that over all extraction equilibrium can be written as follows:

$$M^{2+} + 2HR(org) \rightleftharpoons MR_2(org) + 2H^+ \tag{6}$$

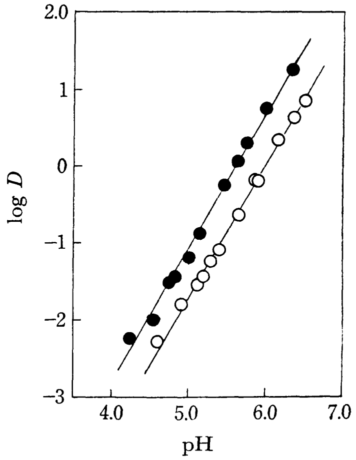

Fig. 1. Variation of the distribution ratio of zinc(II) (—●—) and cobalt(II) (—○—) as a function of pH.
Organic phase: 0.05 M BFA in benzene
Aqueous phase: 0.1 M NaClO$_4$

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[5] H. M. N. H. Irving and N. S. Al-Niaimi, *J. Inorg. Nucl. Chem.*, **27**, 1671 (1965).

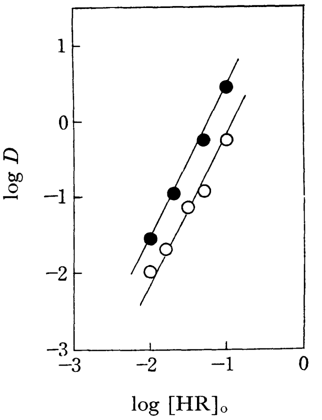

Fig. 2. Variation of the distribution ratio of zinc(II) (—●—) and cobalt(II) (—○—) as a function of chelate ligand concentration.
Organic phase: BFA in benzene
Aqueous phase: 0.1M $NaClO_4$, pH=5.5

The extraction constants, K, can be calculated by Eq. (2).

The change in the distribution ratio of zinc and cobalt resulting from the addition of organic Lewis bases is shown in Figs. 3 and 4, as the log D^*/D vs. log $[L]_o$ plots (actually, log D^*/D vs. log C_L plots). When the metal chelates react with organic bases to form adducts in organic phase, the equilibrium may be written as follows:

$$MR_2(org) + nL(org) \rightleftharpoons MR_2L_n(org) \qquad (7)$$

Since the slope of linear log D^*/D vs. log $[L]_o$ plots or the slope of an asymptote of curved plots indicates the maximum number of the base molecule, it is considered that cobalt BFA chelate forms MR_2L type adduct with TBPO, TOPO, quinaldine and acridine, and both MR_2L and MR_2L_2 type adducts with n-hexyl alcohol, TBP, quinoline, isoquinoline and lepidine; while zinc chelate forms MR_2L_2 type adduct only with n-hexyl alcohol. The stability constants of the adducts were obtained by analyzing the plots in Figs. 3 and 4 with the curve fitting method.[6] The log β_1, log β_2 and log K values are summarized in Table 1.

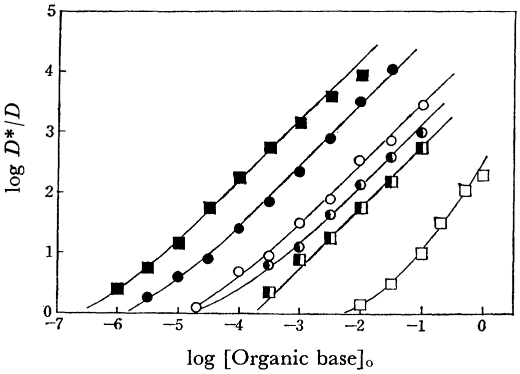

Fig. 3. Variation of the distribution ratio of zinc(II) as a function of the organic base concentration.
Solvent: benzene BFA: 0.05M
Organic base: —●— Isoquinoline, —◐— Quinaldine, —○— Quinoline, —■— TBPO, —◧— TBP, —□— n-Hexyl alcohol

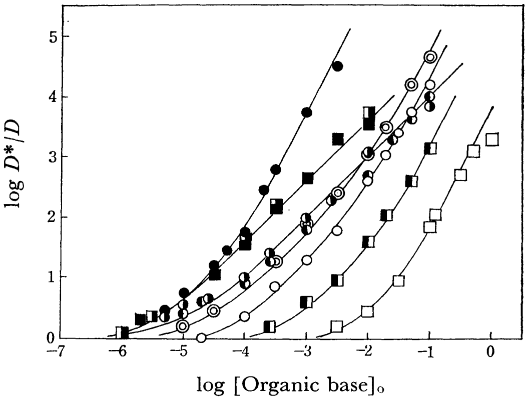

Fig. 4. Variation of the distribution ratio of cobalt(II) as a function of the organic base concentration.
Solvent: benzene BFA: 0.05M
Organic base: —●— Isoquinoline, —◐— Quinaldine, —◑— Acridine, —◎— Lepidine, —○— Quinoline, —■— TBPO, —◨— TOPO, —◧— TBP, —□— n-Hexyl alcohol

TABLE 1. EXTRACTION CONSTANTS OF ZINC(II) AND COBALT(II) BFA CHELATES AND STABILITY CONSTANTS OF THEIR ADDUCTS WITH SOME ORGANIC BASES

	Zn(II) log K=−9.9		Co(II) log K=−10.5	
Organic base	log β_1	log β_2	log β_1	log β_2
n-Hexyl alcohol	1.45	2.90	2.20	3.80
TBP	3.75	*	3.45	5.20
TBPO	6.20	*	5.60	*
TOPO	6.24**	*	5.70	*
Quinoline	4.50	*	4.20	6.40
Isoquinoline	5.45	*	5.50	9.80
Lepidine	—	—	4.80	6.80
Quinaldine	4.10	*	4.80	*
Acridine	—	—	5.00	*

* MR_2L_2 type adduct was not observed.
** Taken from Ref. 4.

The stability of zinc and cobalt adducts with oxygen-containing Lewis bases increases in the order, n-hexyl alcohol<TBP<TBPO≈TOPO, which is the

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[6] T. Sekine and D. Dyrssen, *ibid.*, **26**, 1727 (1964).

same with that of the donating power of lone-pair electron of oxygen atom. In other words, the stability directly corresponds to the basicity of the base. A similar tendency has been observed in rare earth metals-BFA,[1] zinc-TTA[6-8] and europium-TTA systems.[9] In the TTA systems, the increasing order of the stability found in carbon tetrachloride was: hexone$<$TBEP$<$TBP$<$TBPO$\approx$TOPO. From the fact that TBPO adducts as well as the TOPO adducts are stable it may be deduced that the length of hydrocarbon chain of alkyl phosphine oxides or alkyl phosphate does not give important effect on the stability of the adducts.

The over all stability of the adducts with nitrogen containing Lewis bases increases in the order, quinaldine$<$quinoline$<$isoquinoline for zinc, and quinaldine$<$acridine$<$quinoline$<$lepidine$<$isoquinoline for cobalt. The order of stability does not only correlate with the basicity, but results preferably from the steric effect by methyl or phenyl groups of the bases. A similar result has been observed in the adduct formation between cobalt acetylacetonate and pyridine derivatives, where the apparent stability of the adducts increases as, α-picoline$<$2,6-lutidine$<$2,4-lutidine$<$$\beta$-picoline$<$$\gamma$-picoline.[10]

The effect of the basicity of oxygen-containing Lewis bases and the steric effect of nitrogen-containing bases reflect the maximum number of the base molecule involved in the adduct. *n*-Hexyl alcohol forms MR_2L_2 type adduct with both zinc and cobalt chelates, TBP forms the same type adduct with cobalt chelate, but TBPO and TOPO forms only MR_2L type adduct. Steric hindrance appears similarly in the formation of MR_2L_2 type cobalt adduct with nitrogen-containing bases. Maximum mole ratio of the base to cobalt chelate is 2 for quinoline, isoquinoline and lepidine adducts, but 1 for quinaldine and acridine adducts.

In general, cobalt BFA chelate forms more stable adduct than zinc chelate. This may be due to the fact that cobalt ion has a coordination number of six and takes octahedral configuration, while zinc ion has a coordination number of four and usually forms tetrahedral complexes, although octahedral configuration with a coordination number of six should be expected in some cases.

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7) H. M. N. H. Irving and D. N. Edgington, *J. Inorg. Nucl. Chem.*, **27**, 1359 (1965).

8) R. L. Scruggs, T. Kim and N. C. Li, *J. Phys. Chem.*, **67**, 2194 (1963).

9) T. Sekine and D. Dyrssen, *J. Inorg. Nucl. Chem.*, **29**, 1457 (1967).

10) H. Akaiwa and H. Kawamoto, *ibid.*, **29**, 1345 (1967).