

Extraction Behavior of Metal Acetylacetonates*

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The extraction behaviors of several metal acetylacetonates with chloroform were studied, and the extraction curves were presented for aluminium, beryllium, cadmium, cerium, cobalt, copper, ferric iron, gallium, hafnium, indium, lead, magnesium, manganese, nickel, strontium, uranium, yttrium and zinc.

Some considerations were made on the relationships between the properties of the central metal ions and the extractability of the chelates. Maximum extraction recovery is correlated with the ionic potential and the ionization potential of the metal, and the pH value for unit distribution ratio decreases linearly with the increase of the ionic potential. These facts may be attributed to that the increase of these potentials rises the bound energy and covalent property of oxygen bond, which is essentially ionic, and so results in the increase of the stability of the chelates and of the solubility into the organic solvent.

INTRODUCTION

Acetylacetone reacts with many metals to form stable chelates, and many of them can be extracted with various organic solvents. Acetylacetone is not only a chelating reagent but also an extracting solvent. Freiser *et al*¹⁻⁶⁾ studied on the extraction of metals with acetylacetone. The authors also investigated on the solvent extraction of metal acetylacetonates, and proposed the methods for the separation and the spectrophotometric determination of beryllium^{7,8)}, uranium^{9,11)}, and ferric iron^{10,11)}. During the investigations, it became evident that the extractability of metal acetylacetonates may be related to the ionic potentials or the ionization potentials of the central metal ions. Although many reports were already published on the relation between the stability of the metal complexes and the properties of metal ions, such as ionic radii, ionization potentials or electronegativities and the studies were made also on the β -diketone chelates¹²⁻¹⁴⁾, studies on the solvent extractions have not been reported.

In the present paper, the relationships between the ionic potentials of metal ions and the maximum per cent extractions of the chelates, the ionization potentials and the maximum per cent extractions, and the ionic potentials and the pH values for the half extractions are discussed respectively.

EXPERIMENTAL

Spectrophotometric, fluorometric and polarographic measurements for the an-

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alytical determinations were made with a Hitachi's Photoelectric Spectrophotometer, Model EPU-2A, a Shimadzu's Universal Fluorometer, Model UF-1, and a Yanagimoto's Polarograph, Model PA-105 respectively. A Horiba's Glass electrode pH meter, Model M, and a Metro's EIT Scalar, Model 6E with G-M tube (TEN 132), were used for pH measurements and radioactivity countings.

In order to obtain the extraction curves for acetylacetonates of metals, such as aluminium, beryllium, cadmium, cerium, cobalt, copper, ferric iron, gallium, hafnium, indium, lead, magnesium, manganese, nickel, strontium, uranium, yttrium, and zinc, the extractions were carried by shaking 50 ml. of aqueous solutions having a constant concentration of acetylacetone, 1 per cent, and various pH values, with 20 ml. of chloroform. Per cent extractions were determined by the measurements of radioactivity, when the radioisotopes were used or by the common chemical analysis, as described in Table 1, after evaporating chloroform solutions and destroying organic materials by fuming with perchloric acid.

Table 1. The analytical method for the determination of the per cent extraction.

Metal	Method	
Al	Fluorometry	(Pontachrome Blue Black R ^{a)})
Be	Spectrophotometry	(Acetylacetone; Eriochrome Cyanine R ^{b)})
Cd	Polarography	
Ce	Radioactivity	(Ce-144)
Co	Radioactivity	(Co-60)
Cu	Spectrophotometry	(Chloro-Complex)
Fe	Spectrophotometry	(Acetylacetone)
Fe	Radioactivity	(Fe-55, 59)
Ga	Fluorometry	(2-Methyloxine ^{c)})
Hf	Radioactivity	(Hf-181)
In	Fluorometry	(2-Methyloxine ^{d)})
Mg	Chelatometry	
Mn	Spectrophotometry	(KMnO ₄)
Ni	Radioactivity	(Ni-63)
Pb	Spectrophotometry	(Chloro-Complex ^{e)})
Sr	Radioactivity	(Sr-89)
U	Spectrophotometry	(Acetylacetone; KSCN)
Y	Radioactivity	(Y-91)
Zn	Radioactivity	(Zn-63)

Reference

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- ^{c)} M. Ishibashi, T. Shigematsu and Y. Nishikawa, *J. Chem. Soc. Japan, Pure Chem. Sec.*, **78**, 1139 (1957).
- ^{d)} M. Ishibashi, T. Shigematsu and Y. Nishikawa, *ibid.*, **77**, 1479 (1956).
- ^{e)} Y. Yamamoto, *This Bulletin*, **36**, 139 (1958).

RESULTS AND CONCLUSION

Extraction curves are shown in Fig. 1-a and Fig. 1-b. Results on the acetylacetonates of aluminium, beryllium, gallium, hafnium, indium, iron and uranium show

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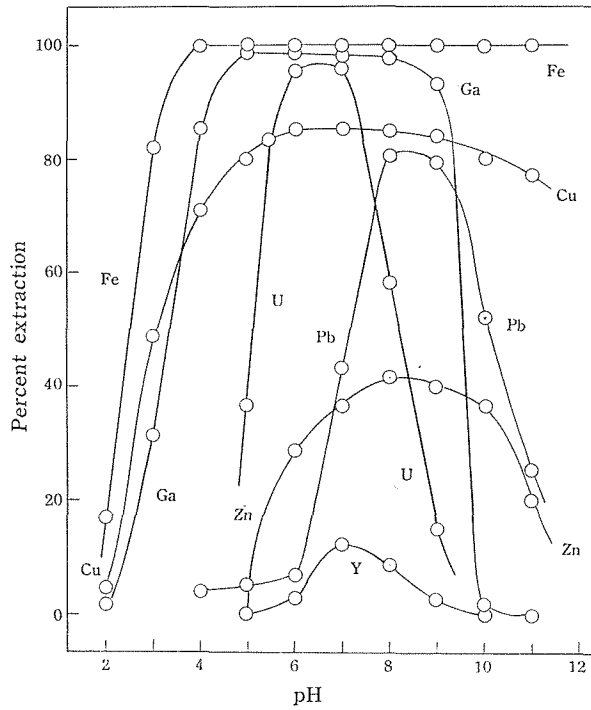


Fig. 1-a. Extraction curves of metal acetylacetonates.

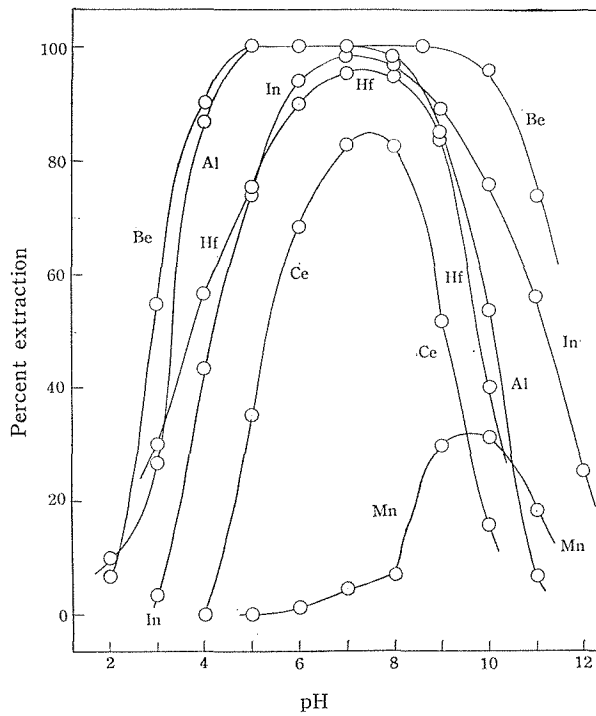


Fig. 1-b. Extraction curves of metal acetylacetonates.

approximately quantitative extraction, while the chelates of cadmium, cobalt, magnesium, nickel and strontium are not extracted at any pH values, and the extraction of the chelates of cerium, copper, lead, manganese and zinc are incomplete.

In Fig. 2, the maximum per cent extractions of metal acetylacetonates are shown as a function of ionic potentials ($\frac{\text{valency}}{\text{ionic radii}^*}$) of the central metal ions. The figure suggests that there may be a positive correlation between the maximum per cent extractions and the ionic potentials: the chelates of metals with higher ionic potentials than 4, are extracted almost completely; the chelates with lower ionic potential than 2.5 are not extracted; within the interval from 2.5 to 4, there is a regular increase in the extractability as the ionic potential increases. The chelates of copper and lead show unexpected extractability, and magnesium with larger ionic potential than that of copper, can not be extracted. This reverse trend between copper and magnesium may be caused by the ionization potential (see Fig. 4), and the irregularity of lead chelate will be discussed later.

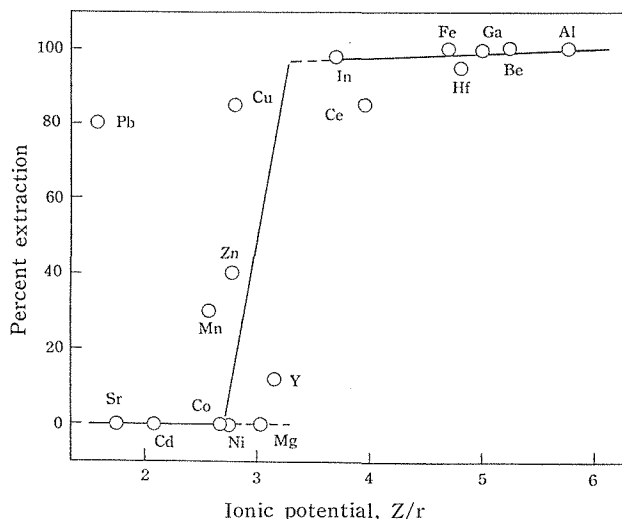


Fig. 2. Relation between the maximum percent extraction and ionic potential.

In Fig. 3, the $\text{pH}_{1/2}$ values (pHs corresponding to unit distribution ratio**) of the extractable chelates having the maximum per cent extraction of 30% or more, are plotted as a function of ionic potentials. As shown in the figure, there is a distinct linear relationship between the $\text{pH}_{1/2}$ values and the ionic potentials. In this relation, however, copper chelate shows irregularity.

Fig. 4 represents the correlation between the maximum per cent extractions for the chelates of bivalent metals and the ionization potentials ($E_{M \rightarrow M^{++}}$)*. As seen in the figure, the extractability increases with the ionization potential, except lead chelate which shows unexpected extractability.

* E. Kordes : Z. Physik. Chem., **B 48**, 91 (1940)

** It corresponds to 28.6% extraction yield in the extraction procedure described above.

*** "Handbook of Chemistry" (1952) Maruzen Co., Tokyo.

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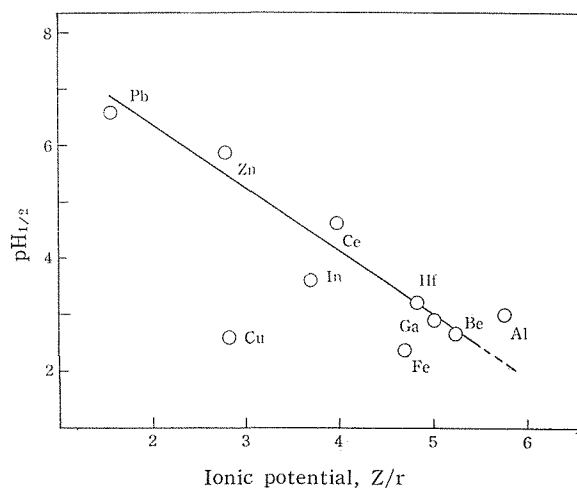


Fig. 3. Relation between $\text{pH}_{1/2}$ and ionic potential.

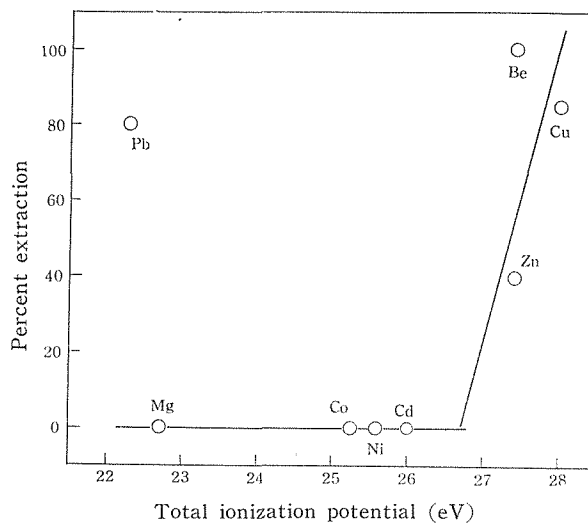


Fig. 4. Relation between the maximum percent extraction and ionization potential.

CONSIDERATION AND DISCUSSION

General Consideration

On the solvent extraction of the metal chelates, the extractability is determined by the formation constant and by the distribution coefficient of the chelates. Because acetylacetonone is oxygen-oxygen donating ligand, it has a marked tendency to form ionic bond, and it is confirmed by the facts that nickel and cobalt acetylacetonates have not planer configurations, but tetrahedral, as proved by the magnetic properties (3.2 and 4.2 Bohr magnetones, respectively) and the absorption spectra, and that ferric acetylacetonate also is para magnetic (the magnetic moment: 5.95 Bohr magnetone) and therefore 3d orbital of iron is not occupied by the bond

formation¹⁵⁾. In comparison with the covalent bond, the ionic bond may be effected greatly by the ionic potential or the ionization potential of the central metal ion. As these potential values increase, the bond energy as well as covalency in the bond of the chelate becomes greater, that is, both the stability of the chelate and the distribution coefficient to organic solvent increase with these potentials. As mentioned above, the extractability are determined by the formation constant and the bistribution coefficient of the chelate, and therefore the increases in the ionic- or ionization potential results in the increases of the maximum per cent extractions and in the decreases of $\text{pH}_{1/2}$ value.

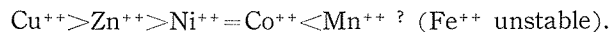
The regularities represented in Fig. 2, Fig. 3 and Fig. 4, can be explained by these considerations. As previously reported by many workers, there is a positive correlation between the stabilities of the chelates and ionic- or ionization potentials, and so the similar features as shown in figures will be observed also when these are expressed as a function of the stability constant.

On Bivalent Cations of the First Transition Series

The stabilities of the complexes of bivalent ions of the first transition elements follow Irving and Williams' order of the stability¹⁶⁾.



regardless of the nature of the coordination ligands. In the solvent extractions of acetylacetonates of these metals, is observed a similar sequence,



Now, the difference of the position of zinc in the both orders, will present an interesting question, and it is considered as follows.

Irving and Williams' order of the stability corresponds essentially to the order of ionic radii of the metal ions, and zinc holds the position between copper and nickel. However, in almost all cases, zinc complexes are less stable than cobalt complexes, and this disorder may be attributed to the fact that zinc complexes are tetrahedral, and therefore some configurational changes occur by the complex formation from octahedral aquo ion, while the complexes of nickel or of cobalt have planer structure and the replacements of the ligands occur in a usual way. For acetylacetonates, such considerations are not required, because nickel and cobalt form tetrahedral chelate as well as zinc, and on the contrary, the order of the ability to form tetrahedral configuration, $\text{Zn}^{++} > \text{Co}^{++} > \text{Ni}^{++} \gg \text{Cu}^{++}$, must be considered to be what was assumed from the stability of the complexes of triaminoethylamine. Thus, it seems that the sequence of the extractabilities described above is reasonable. This assumption might be confirmed by the fact that zinc chelates with toropolone or its derivatives, which are oxygen-oxygen ligands and have similar structures to acetylacetone, are more stable than nickel and cobalt chelates^{17,20)}, although the stability constant of zinc acetylacetonate measured by the pH titration method is slightly less than those of nickel and cobalt.

As shown in Fig. 1, manganese can be extracted at relatively high pH region, (pH 9~10), but it is doubtful whether manganese exists as bivalent ion in this region. Ferrous acetylacetonate is so unstable that it is easily oxidized to ferric chelate and

the oxidation can not be prevented with ascorbic acid*. Thus, it may be concluded that Irving and Williams' sequence of the stability is valid for the extraction of acetylacetonates.

On Anomaly of Copper and Lead

In general, the high stability of copper complexes is attributed to its high ionization potential, and the acetylacetonate is not an exception. This can be proved by the result that the unusual features of copper chelate are observed in Fig. 2 and Fig. 3, but not in Fig. 4.

The anomaly of lead complexes has been discussed by many workers. Mellor and Maley²¹⁾ suggested that the stability order, $\text{Cu} > \text{Ni} > \text{Pb} > \text{Co} > \text{Zn}$, proposed by themselves for salicylaldehyde complexes, was not justified either by the ionic radii or the electronegativities of the metals. The similar disorder is found also in Monk's sequence of the stability²²⁾, $\text{Ni} > \text{Zn} > \text{Pb} \approx \text{Co} > \text{Mn}$, obtained for the chelates with alanine and glycine. The extraction behavior of lead acetylacetonate is the same. It follows Mellor and Maley's or Monk's order of the stability, if one takes account of the configuration of nickel chelate as discussed above. Now, comparing Fig. 2, Fig. 3 and Fig. 4., a question why the irregular behavior of lead acetylacetonate is found in the plots of the maximum percent extractions, but not in those of pH, arises. This observations may suggest the possibility that lead exists as high valent ion in the pH region where the extraction is carried, and this might give a hint to explain the anomaly of lead. In order to answer this question, of course, more detailed investigations must be made, although the valency change of lead might be possible, because of its relatively small third ionization potential.

Freiser and coworker²³⁾ reported that tervalent cobalt can be extracted with acetylacetone, and the result is also explained in term of the ionic potentials of cobaltous (2.65) and cobaltic (4.78). They proposed also a method for the extraction of chromium²⁴⁾, in which chromium was heated with acetylacetone prior to the extraction. Chromium is expected to be extractable from its ionic potential of 4.85, but the formation of inner complex is very slow, because of its inert type electron configuration²⁴⁾, and the latter fact is the reason why the heating in advance is required.

In this research, the consideration was made on the results obtained when chloroform was used as an extracting solvent. Acetylacetonates are also extracted with esters, and for some chelates, ester is superior to chloroform, although in general, the latter is the better solvent. And it is expected that there is a correlation between the structure of the chelate and the nature of the extracting solvent. Further investigation will be carried out on this interesting problem.

SUMMARY

The extraction curves for metal acetylacetonates were obtained, and the behaviors of the chelates were discussed as a function of the ionic- or ionization poten-

* Hydroxylamine can not be used, because it reacts with acetylacetone.

tials of the central metal ions. The increase of ionic or ionization potential results in the rise of the maximum per cent extraction and in the decrease of pH value, and this may be due to the increase in the stability of the chelate and the covalency of the bond which is related to the solubility in organic solvent.

Just after the preparation of this manuscript, W. B. Brown, J. F. Steinbach and W. F. Wanger has published a paper concerning the similar consideration on acetylacetonats of lanthanides: *J. Inorg. Nuclear Chem.*, **13**, 119 (1960).

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