

《Original》

Suppression Effect in Some Solvent Extration System

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특정 용매 추출계의 억제효과

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Abstract

The mechanism of the suppression effect of the extraction of microquantities of an element in the presence of macroquantities of another element in some solvent extraction systems is considered.

For the system of metal halide complex acids, it has been revealed that the principal cause of the suppression phenomenon is due to the dissociation of the compounds extracted into the organic phase. The various factors, such as relative value of distribution ratios of the individual micro and macroelements, stability of halide complex anion are discussed, and a equation relating those factors are derived.

요 약

일련의 용매 추출계에서 다량성분원소들이 존재할 때 미량성분원소에 대한 억제효과의 메카니즘에 대해서 검토해 보았다.

할로게노 금속산계에 대해서는 유기상으로 추출된 화합물의 해리가 억제효과의 주된 원인으로 나타났으며 각 미량 및 다량성분의 상대적분배비, 할로겐 착음이온의 안전성등이 억제효과에 미치는 영향등을 계통적으로 살펴 보았으며 이에 대한 관계식을 유도하였다.

Introduction

It turns out that the distribution ratio of individual species does not be affected, in general, by the presence of other extractable species. However, the distribution ratio of the microcomponent may be affected according to

the concentration of macroelements by unequal change of the activity coefficients of two solvent phases⁽¹⁾ or/and by the formation of mixed species with the macro elements.

For the case of coextraction, there are many works reported⁽²⁻⁴⁾ for various extraction systems. Yu. A. Zolotov has reported⁽⁵⁾ some experimental results relating to the suppression

effect of macroelements to the distribution of microelement. It is attempted to study further systematically the suppression effect for the tracer level extraction system of metal halide complex acids.

Experimental

1. Reagents

TBP, supplied by Junsei, Japan, was further purified according to the same method as D.F. Peppard et. al. described⁽⁶⁾. Metallic salts, supplied by Kanto, Japan, were all reagent grade. ^{60}Co , ^{59}Fe , $^{114\text{m}}\text{In}$ and $^{115,115\text{m}}\text{Cd}$ were prepared by neutron irradiation at the Korea Advanced Energy Research Institute. ^{125}Sb was supplied by Radio Chemical Center, England. The radiochemical purity was checked with their γ spectrum and some purification processes were undertaken if necessary.

2. Extraction and Radioassay

Water jacketed double reaction cell (the volume of inner cell was $\sim 10\text{ml}$) was mounted on a motor driven shaking machine and the shaking rate was controlled by means of a transformer. The shaking speed was adjusted to ~ 60 cycles per minutes. The shaking period was kept to 10 min. except the case of extraction rate determination. The concentrations of the microelements in the aqueous solution are estimated as $10^{-5}\sim 10^{-6}\text{M}$ during the extraction operation carried out. 3ml each of pre-equilibrated organic phase and aqueous phase were taken in the cell. The tracer was added just prior to start actual extraction operation. After shaking for pre-determined period, it was transferred into centrifuge cell immediately and the both phase were separated by double centrifuge operation. Distribution ratio was determined by measuring the gamma activities of equal volume of both phases using NaI(Tl) well

type scintillation counter.

Results and Discussion

Table 1. shows the distribution ratios of Co ($\sim 10^{-6}\text{M}$) for the system of 50% TBP-benzene-9N HCl in the case of absence of other elements (D_1) and of presence of macroelements (D_2), Sb, Cd and Fe, respectively.

The concentration of those macroelements were adjusted to 0.1M, 0.5M and 1.0M. The magnitude of D_1/D_2 ratio can be related to the extent of suppression of distribution ratio of microelements due to the presence of macroelements. Table 1. shows that the values of D_1/D_2 increase according to the concentration of macroelements. The sequence of the magnitude of D_1/D_2 , $\text{Fe} > \text{Cd} > \text{Sb}$, corresponds to the sequence of the value of distribution ratio of individual macroelements for the respective extraction system ($D_{\text{Fe}} = \sim 10$, $D_{\text{Cd}} = \sim 5$, $D_{\text{Sb}} = \sim 4$).⁽⁷⁾ In this case the distribution ratio of Co ($D_{\text{Co}} = \sim 0.89$) is smaller than any of the macroelements presence and the suppression effect of Fe is remarkably high, reaching to the order of 10^4 for the case of 1.0 M concentration.

The D_1 and D_2 of In for the extraction system of 25% TBP-benzene-9N HCl are shown in Table 2. The macroelements are Co, Sb and Fe and the concentrations of these macroelements are 0.1M, 0.5M and 1.0M. The sequence of D_1/D_2 is obtained as $\text{Fe} > \text{Sb} > \text{Co}$. This sequence does not correspond to the sequence of their distribution ratios ($D_{\text{Sb}} = \sim 1$, $D_{\text{Fe}} = \sim 0.8$, $D_{\text{Co}} = \sim 0.1$)⁽⁷⁾ which shows marked different tendency from the results of Table 1.

Table 3. shows the D_1 and D_2 of Bi for the systems of 50% TBP-benzene-3N and -8N HCl, respectively.

The macroelements are Sb, Cd and Fe (1.0M). Contrast to the expected marked suppression effect of which has the largest distribution ratio

Table 1. Extraction of Co ($\sim 10^{-6}M$) in the Presence of Macroelements. (50% TBP-Benzene-9N HCl system)

Element	Concentration of macroelement	D ₁	D ₂	D ₁ /D ₂
Sb	0.1M	0.895	0.708	1.264
	0.5M		0.328	2.729
	1.0M		0.119	7.521
Cd	0.1M	0.897	0.762	1.177
	0.5M		0.241	3.722
	1.0M		0.049	18.306
Fe	0.1M	1.285	0.681	0.875
	0.5M		0.013	67.308
	1.0M		0.0001	8750.000

D₁: Distribution ratio of microelement without macroelements.

D₂: Distribution ratio of microelement with macroelements.

Table 2. Extraction of In ($\sim 10^{-6}M$) in the Presence of Macroelements. (25% TBP-Benzene-9N HCl system)

Element	Concentration of macroelement	D ₁	D ₂	D ₁ /D ₂
Co	0.1M	2.874	2.555	1.125
	0.5M		1.916	1.500
	1.0M		1.854	1.550
Sb	0.1M	2.861	2.592	1.104
	0.5M		1.328	2.154
	1.0M		0.462	6.193
Fe	0.1M	2.886	2.673	1.080
	0.5M		0.003	1443.000
	1.0M		0.001	2886.000

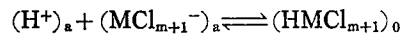
among them ($D_{Fe} \sim 6$ at 3N HCl, $D_{Fe} \sim 10$ at 8N HCl),⁽⁷⁾ Cd shows smaller D_1/D_2 value compared to Sb which has smaller distribution ratio than Cd ($D_{Cd} \sim 1.2$, $D_{Sb} \sim 0.08$ at 3N HCl, $D_{Cd} \sim 7$, $D_{Sb} \sim 5$ at 8N HCl)⁽⁷⁾ and this latter sequence correspond to that of Table 2.

When the extractable species are solvated metal chloride complex acids following expressions are derived. (solvated molecules are neglected for clarity) For the distribution

Table 3. Extraction of Bi ($\sim 10^{-6}M$) in the Presence of Macroelement (1.0M). (50% TBT-Benzene-HCl system)

Conc. of HCl	Sb		Cd		Fe	
	3N	8N	3N	8N	3N	8N
D ₁	0.475	0.127	0.475	0.127	0.475	0.127
D ₂	0.022	0.008	0.415	0.023	0.009	0.0008
D ₁ /D ₂	21.590	15.875	1.145	5.522	52.778	158.750

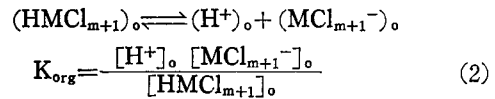
equilibrium



The extraction coefficient, K_{ex} , can be expressed as

$$K_{\text{ex}} = \frac{[HMCl_{m+1}]_{\text{o}}}{[H^+]_{\text{a}} [MCl_{m+1}^-]_{\text{a}}} \quad (1)$$

where the suffix 0 and a denote organic and aqueous phase, respectively. In the organic phase there will be a dissociation equilibrium. (The extent of the dissociation, of course, depends on the dipole character of the organic phase.) The dissociation constant, K_{org} , can be expressed as follow;



The distribution ratio, D_m , can be expressed as follows;

$$D_m = \frac{[HMCl_{m+1}]_{\text{o}} + [MCl_{m+1}^-]_{\text{o}}}{[MCl_{m+1}^-]_{\text{a}} \alpha_{MCl_{m+1}(cl)}} \quad (3)$$

where $\alpha_{MCl_{m+1}(cl)}$ is side reaction coefficient of MCl_{m+1}^- and any possibility of distribution of the chloride complex of more higher order than $HMCl_{m+1}$ is supposed to be negligible.

From the relations of (1), (2) and (3) the following expression is derived.

$$D_m = K_{\text{ex}} \frac{[H^+]_{\text{a}}}{\alpha_{MCl_{m+1}(cl)}} \left\{ 1 + \frac{K_{\text{org}}}{[H^+]_{\text{o}}} \right\} \quad (4)$$

On the other hand, if coexisting macroelement, M^* , also be distributed as similar form to the organic phase and dissociated to some extent the following relation is held according to the principle of electroneutrality.

$$[H^+]_{\text{o}} = [MCl_{m+1}^-]_{\text{o}} + [M^*Cl_{m+1}^-]_{\text{o}} \quad (5)$$

Table 4. Variation of the Distribution Ratio of In with HCl Concentration in the Presence of Macroelements (0.5M). (100% TBP-HCl system)

	Concentration of HCl							
	1N	2N	3N	4N	5N	6N	7N	9N
D ₁	2.89	8.03	9.44	10.39	10.04	10.90	13.29	17.41
D ₂ (with Co)	5.93	9.19	9.38	10.92	9.81	10.93	12.32	15.01
D ₃ (with Sb)	—	—	3.28	6.69	8.05	8.47	10.50	14.45

Table 5. Variation of the Distribution Ratio with the Concentration of the Extractable Species.

Element	Tracer	0.1M+ Tracer	0.3M+ Tracer	0.5M+ Tracer	0.7M+ Tracer	1.0M+ Tracer	Ext. system
Co	0.312	0.297	0.217	0.185	0.167	0.156	25% TBP-9N HCl
Cd	1.447	1.287	0.874	0.844	0.524	0.391	50% TBP-6N HCl
Fe	168.606	125.929	82.782	2.619	1.376	0.769	25% TBP-9N HCl

If

$$[M^*Cl_{m+1}^-]_o \gg [MCl_{m+1}^-]_o$$

Then

$$[H^+]_o = [M^*Cl_{m+1}^-]_o \quad (6)$$

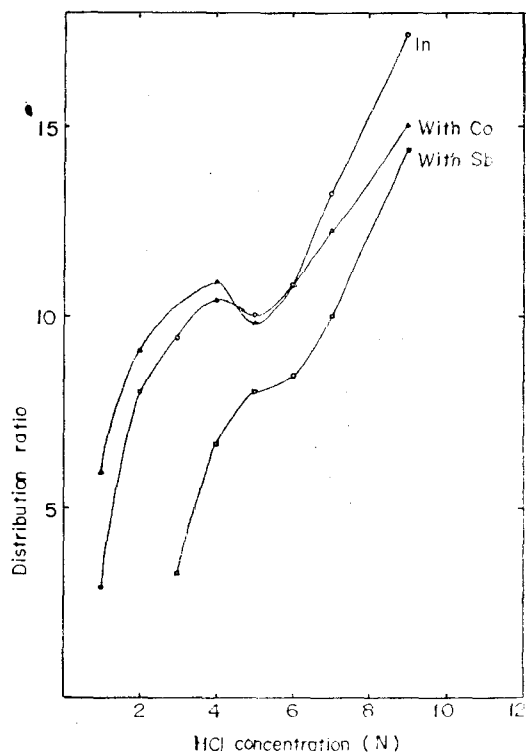
Since, K_{ex} , $\alpha_{MCl_{m+1}(cl)}$, K_{org} and $[H^+]_a$ which are appeared in equation (4) are all constant under a given condition, the value of D_m should be decreased according to the increasing of $[H^+]_o$. and, moreover, the relation (6) shows that the distribution of microelements be suppressed by the coexisting macroelements. Now, it may be easy to explain those experimental results on Table 1, 2 and 3 with the relation (4) as the variation of D_m depends not only on the concentration and/or distribution ratio of macroelements but also on the dissociation constant of those elements in organic phase.

Reviewing the results on Table 2. and 3, it is estimated that the sequence of the dissociation constants in TBP phase is $Fe > Sb > Cd > Co$.

Table 4. and Fig. 1 show the D_1 and D_2 of In as a function of HCl concentration for the 100% TBP extraction system. Here the macroelements are Co and Sb and their concentrations are 0.5M. For the case of Sb, the D_2 curve is suppressed through out whole HCl range, but for the case of Co, the two curves were intersect

at around 4N HCl concentration.

For the latter case, the D_1 curve is suppressed by the D_2 curve up to around 4N and after the range D_2 curve is suppressed as the case of Sb.

**Fig. 1. Variation of the Distribution Ratio of In with HCl Concentration in the Presence of Macroelements.**

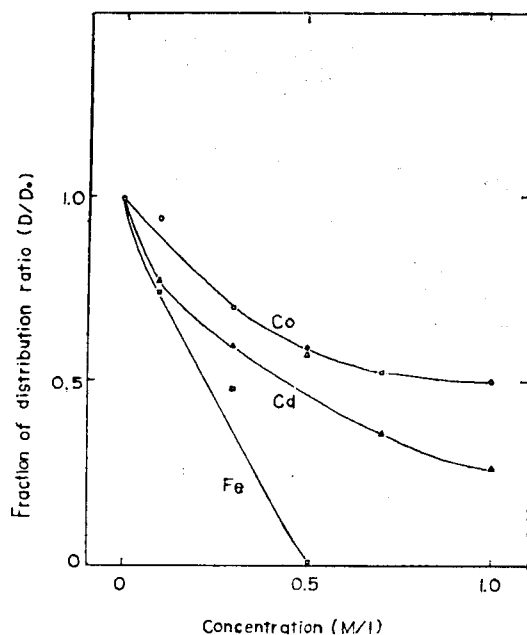


Fig. 2. Variation of the Distribution Ratio with the Concentration of Extractable Species.

This corresponds well to the report⁽⁸⁾ that no appreciable anionic chlorocomplex formation was observed in the aqueous HCl solution of less than 4N.

The enhancement of D_1 is understood as mainly due to the decreasing of the water activity by the Co dissolved in and remaining almost all of them in aqueous phase. ($D_{Co} < 10^{-3}$ at this conditions)

It is expected from the relation (4) that the distribution ratio of any elements will be decreased if the distributed species are dissociated in the organic phase and make the $[H^+]$ increase, even though in the absence of other elements.

This is verified by the results of Table 5. which shows D_1 of Co, Fe (25% (v/v)-TBP-benzene-9N HCl system) and Cd (50% (v/v)-TBP-benzene-6N HCl system) as a function of their concentrations.

Fig. 2 shows the relative decreasing modes of the three elements on Table 5. The graph is drawn by taking D_1 of each elements at

tracer level ($\sim 10^{-6}M$) as unity. The observed sequence of the decreasing modes is $Fe > Cd > Co$ which is excepted from the relation (4).

Conclusion

The extraction of microelements is suppressed by the coexisting macroelements as far as they are distributed to the organic phase as a form of metallic acid which are dissociated to some extent. This suppression effect is a function of the product of the distribution ratio and its dissociation constant of the coexisting elements in organic phase. It is also found that the distribution of some metallic acids is decreased along with the increasing of its concentration even in the absence of other elements and these are expressed with a simple equation.

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