DOUBLE SYNERGISTIC EFFECTS AND EXTRACTION KINETICS OF A MICELLE MIXED EXTRACTANT SYSTEM[①]

I DOUBLE(KINETIC AND THERMODYNAMIC) SYNERGISTIC EFFECTS AND EXTRACTION MECHANISMS

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ABSTRACT

The equilibria and kinetic characteristics of a micelle mixed extractant system-D_2EHPA-MPA(MPA-monoalkyl phosphoric acid with long carbon chain and micellization) in extraction of the Al^{3+} ions were studied. It was found that the system has double synergistic effects on the extraction of the Al^{3+} ions. The compositions of the synergistic complexes were determined and the synergistic reaction equations were obtained.

Key words: D_2EHPT-MPA mixed system double synergistic effects extraction kinetics extraction mechanism micelle mixed extractant system

1 INTRODUCTION

In the recent years, we found an important phenomenon that when compared with the two single extraction systems, because of its double synergistic effects and lowering interfacial activity, the mixed extraction system composed of dialkyl phosphoric acid and monoalkyl phosphoric acid has the advantages of high reaction rate and good interfacial properties[1-3], which will help improve the existing extraction processes and develop new technologies. In the mixed extraction system of D_2EHPA-MPA-Al^{3+}, we found there exist two regimes, i. e. micelle range and non-micelle range, and there occur double synergistic effects in the non-micelle range. The kinetic characteristics in the micelle and non-micelle ranges are different[4]. In order to make clear the extraction kinetics in the micelle range, it is necessary to research the double synergistic effects and equlibria characteristics of the extraction of the Al^{3+} ions. These have yet to be reported in the world but will be reported in this paper.

2 EXPERIMENTAL

All the chemical reagents, apparatus, extractants and their purifications, the determination of the Al^{3+} ions and the extractants, the research methods of the extraction kinetics and equilibria and their data processing used in this paper are the same as those

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in refs. [1,4—7]

The experimental conditions were chosen according to the studies of the interfacial chemistry of various mixed extraction systems.

3 RESULTS AND DISCUSSION

3.1 *Micellization and Interfacial Adsorption Behaviours of MPA in the Micelle Mixed Extraction System*

The MPA in the mixed extraction system of the D_2EHPH-MPA still has micellization[1,4]. Therefore, there also exist two regimes which are called non-micelle and micelle ranges.

In the non-micelle range, the interfacial tension(γ) sharply decreases and the interfacial pressure sharply increases with increasing [MPA]. This shows that the adsorption of the MPA increases sharply, and that only the MPA monomers can adhere at the interfaces. But in the micelle range, because the MPA forms reversal micelle in the bulk organic phase, with increasing [MPA], the values of γ and π tend to decrease or increase gradually and eventually reach equilibria. Consequently, the adsorption of the MPA monomers at the interfaces increases very little, and there occur different reactions for the MPA extracting the Al^{3+} ions in the micelle and non-micelle ranges.

3.2 *Double Synergistic Effects*

In the micelle range, the studied mixed extraction system has double synergistic effects on the extraction of the Al^{3+} ions. From our study (Figs. 1 and 2), it is known that $k_m > k_1 + k_2$, $D_m > D_1 + D_2$, where k_m ($[D_2EHPA]=0.2$ mol/L, [MPA] varies) and D_m ([MPA] = 0.14 mol/L,

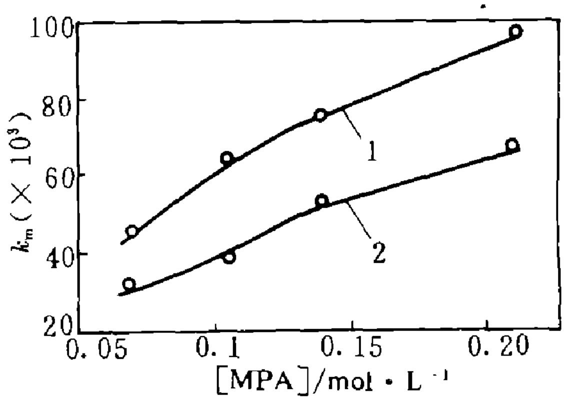

Fig. 1 Kinetic synergistic effects of the micelle mixed extraction system
1— k_m; 2— $k_1 + k_2$

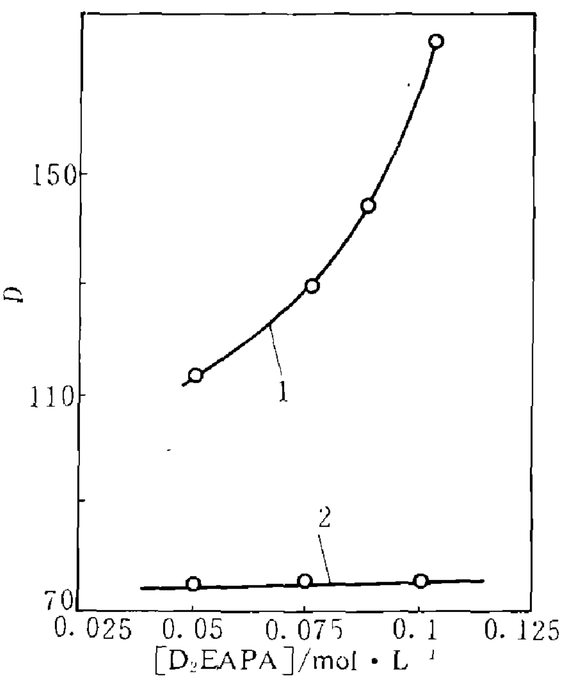

Fig. 2 Thermodynamic synergistic effects of the micelle mixed extraction system
1— D_m; 2—$D_1 + D_2$

$[D_2EHPA]$ varies) are the reaction rate constant and distribution coefficient of the mixed extraction system respectively; k_1 (single D_2EHPA system, $[D_2EHPA]=0.2$ mol/L), k_2 (single MPA system, [MPA] varies) are the reaction rate constants of both the single extraction systems; D_1 (single D_2EHPA system, $[D_2EHPA]$ varies), D_2 (single MPA system, [MPA]=0.14 mol/L) are the distribution coefficients of both the single extraction systems. We also found the mixed extraction systems composed of monoalkyl and dialkyl phorsphoric acids have double synergistic effects on the extraction of M^{3+} ions in such systems as

D_2EHPA-MEHPA-Fe^{3+},
EHEHPA-MEHPA-Fe^{3+},
D_2EHPA-MEHPA-Al^{3+},
D_2EHPA-H_2RPA-Al^{3+},
D_2EHPA-MPA-Fe^{3+} (non-micelle range),
D_2EHPA-MPA-Fe^{3+} (micelle range),
D_2EHPA-MPA-Ga^{3+} and so on[1-5,8-11].

The reason why the micelle mixed extraction system can accelerate the extraction reaction of the Al^{3+} ions is that the much faster formation of the synergistic complexes in the mixed extraction system replaces the slower dehydration process which controls the extraction rate of the Al^{3+} ions in the single extraction system D_2EHPA- Al^{3+}; when compared with the MPA, the accelerating mechanism of the mixed micelle extraction system is also connected with the formation rate of the synergistic complex. The accelerating mechanism and characteristics will be further discussed in part Ⅱ of this paper.

3. 3 *Extraction Mechanisms*

3. 3. 1 The Compositions of the Synergistic Complexes

With the other experimental conditions unchanged, influences of the [D_2EHPA] and [MPA] in the mixed and both single extraction systems on the distribution coefficient (D) of the Al^{3+} ions were studied. $\ln D_s \sim \ln[D_2EHPA]_F$, $\ln D_s \sim \ln[MPA]_F$ curves were plotted (F represents the free concentration of the extractants) and two straight lines were obtained (Figs. 3,4).

For the micelle mixed extraction systems (Fig. 3), the slops of curves 1 and 2 are 1.07 ($\approx$1) and 2.02 ($\approx$2). For non micelle extraction systems (Fig. 4), the slopes of curves 1 and 2 are 1.94 ($\approx$2) and 1.07 ($\approx$1). Therefore, the molar ratios of the synergistic complexes are

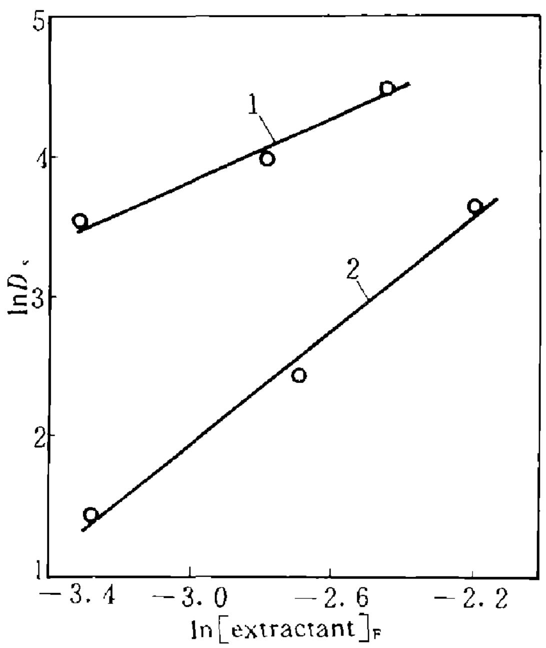

Fig. 3 $\ln D_s$ vs ln[extractant]$_F$ curves of the micelle mixed extraction systems
([Al^{3+}]=0.4 g/L, pH=1, T=25 ℃)
1—$\ln D_s$ vs ln[D_2EHPA]$_F$ curve, [MPA]=0.14 mol/L;
2—$\ln D_s$ vs ln[MPA]$_F$ curve, [D_2EHPA]=0.05 mol/L

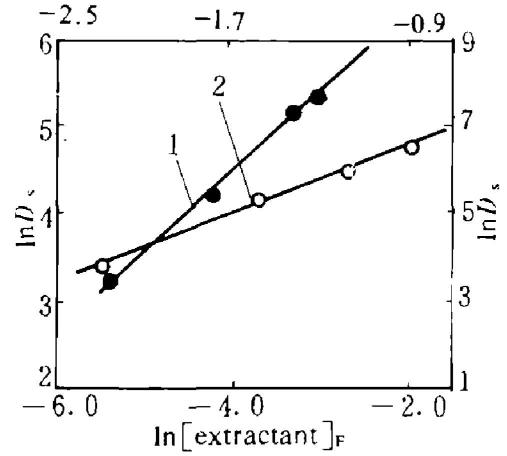

Fig. 4 $\ln D_s$ vs ln[extractant]$_F$ curves of the non-micelle mixed extraction system
([H^+]=0.0398 mol/L, [Al^{3+}]=0.169 g/L, T=25 ℃)
1—$\ln D_s$ vs ln[MPA]$_F$, [D_2EHPA]=0.2 mol/L;
2—$\ln D_s$ vs ln[D_2EHPA]$_F$, [MPA]=0.05 mol/L

$D_2EHPA : MPA : Al^{3+} = 1:2:1$ for the micelle mixed extraction systems; and $D_2EHPA : MPA : Al^{3+} = 2:1:1$ for the non-micelle mixed extraction systems.

The compositions of the synergistic complexes obtained above are in agreement with those determined by the saturation method. Therefore, the synergistic complex forming in the micelle mixed extraction system has different compositions from that forming in the non-micelle mixed extraction system.

3.3.2 The Nuclear Magnetic Relaxation (NMR) Study of the Synergistic Complexes

The ^{31}P NMR spectra study of the synergistic complexes was made on the mixed extraction system D_2EHPA-MPA and the complexes with different [Al]. Before extraction, there exists a single peak at 1.5 ppm caused by the extractant MPA. The single peak at 0.43 ppm is caused by the D_2EHPA extractant. The higher the concentration of the complex is, the larger the chemical displacement toward the higher magnetic field intensity is. This phenomenon is caused by the bonding between the aluminum atoms and the P = O bonds in the MPA and D_2EHPA, and that hydrogen atom in the P—OH bond is replaced by aluminum atom in varying degrees. The electron atomsphere density of the phosphorous atomic nucleus increases in varying degrees. Therefore, the P = O bonds both in the MPA and D_2EHPA form bonding with the aluminum, and one OH^- ion in the MPA or D_2EHPA was replaced by an Al^{3-} ion and an synergistic complex was formed.

3.3.3 Synergistic Reaction Equations

(1) Micelle Extraction System. As mentioned above, MPA in D_2EHPA-MPA mixed extraction system also has micellization just as it exists as a single extraction system, and the controlling reaction in the extraction of the Al^{3+} ions in the micelle mixed extraction system occurs inside the micelle phase. Therefore, in the extraction process of the Al^{3+} ions, the MPA takes part in the extraction reactions in the micelle state.

From the above studies of the interfacial chemistry, NMR and kinetic controlling mechanism in combination with the synergistic complex compositions, equation (1) was obtained.

$$[Al^{3+}]_B + 2[H_2(MPA)_n]_O + [(HA)_2]_O \rightleftharpoons [Al(HMPA)_2 \cdot 2(H_2MPA)_{n-1} \cdot HA_2]_O + 3[H^+]_B \quad (1)$$

where B and O represent the aqueous phase and organic phase respectively; $(H_2MPA)_n$ represents the MPA micelle; n is the polymeric number which is connected with the experimental conditions and it is a constant under certain conditions; $(HA)_2$ represents the dimer D_2EHPA.

(2) Non-micelle Extraction System. We have proved that the controlling reactions in the non-micelle mixed extraction systems occured at the interfaces and the MPA exists in monomers[1]. Therefore, the MPA monomers took part in the extraction reaction.

Consequently, an equation like equation (1) can be obtained.

$$[Al^{3+}]_B + [H_2MPA]_O + 2(HA)_O \rightleftharpoons Al(HMPA) \cdot A_2]_O + 3[H^+]_B \quad (2)$$

where H_2MPA represents an MPA monomer, HA an D_2EHPA monomer.

In addition, it should be noted that there still exist liquid-liquid interfacial reactions in the micelle range. The values of γ and π decreases or increases only a little with increasing [MPA]. This dose not mean that the MPA monomers do not adhere to the interfaces but that the adsorption amount increases very little. Strictly speaking, besides the micelle reaction zone, there is also liquid-liquid reaction zone in the micelle range, but the former is dominant. The reactions in liquid- liquid interfacial reaction zone can also be expressed in equation(2).

From the above studies, it is clear that the compositions of the synergistic complexes in the micele and non-micelle mixed extraction systems are different, so the two systems have different equilibrium mechanisms.

4 CONCLUSIONS

(1) The new micelle mixed extractant system D_2EHPA-MPA has double synergistic effects on the extraction of the Al^{3+} ions.

(2) The compositions of the Al^{3+} bearing synergistic complexes in the micelle and non-micelle mixed extractant systems are different.

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