EFFECTS OF TRI-*n*-BUTYLPHOSPHATE AND 2-ETHYL-1-HEXANOL ON THE EXTRACTION OF ZINC WITH DI(2-ETHYLHEXYL)PHOSPHORIC ACID

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Introduction

In metal extraction systems, tri-*n*-butylphosphate (TBP) and 2-ethyl-1-hexanol (EOH) are sometimes intentionally added as a phase modifier in order to overcome third-phase formation or to prevent emulsification.²⁾ In combination with di(2-ethylhexyl)-phosphoric acid (abbreviated as D2EHPA or simply HR), a well-known synergistic effect on the extraction of uranium and several other rare-earth metals has been observed.¹¹⁾

Some papers concerning the effects of TBP and EOH modifiers on the extraction of first-row transition metals with acidic organophosphorus extractants have appeared.^{3,9,12,13)} It was reported that the addition of TBP will reduce the distribution ratios of divalent metals extracted with D2EHPA from nitrate media.^{3,12)} This behavior was qualitatively explained either by the lowering of the thermodynamic activity of D2EHPA by interacting with TBP, or by relating to the structure of the metal complexes and to the availability of TBP for complexation. Komasaawa *et al.*⁹⁾ studied the effect of some higher alcohol diluents on the extraction of cobalt and nickel from nitrate media with D2EHPA. They found that the diluent can coordinate with the extracted metal complex in the Co/D2EHPA system and substitute for the neutral extractant molecules in the nickel complex. The effect caused by the alcohol diluent enhances nickel extraction, achieving the same performance as in cobalt extraction. In addition, Sabot and Bauer¹³⁾ indicated that the extractability for cobalt from perchlorate media always increases but that for nickel slightly decreases when tri-*n*-octylphosphine oxide (TOPO), TBP or EOH was added to a kerosene solution of di(2-ethylhexyl)dithiophosphoric acid. The extent of this effect increases in the order TOPO > TBP > EOH for cobalt extraction and TOPO > EOH > TBP for nickel extraction. However, a

quantitative explanation was also not given in their paper.

In the present work the equilibrium behavior for the extraction of zinc from sulfate media with kerosene solutions of the D2EHPA-TBP or D2EHPA-EOH mixtures was studied.

1. Experimental

D2EHPA, TBP and EOH were the products of Merck-Schuchardt Co., as received without further purification. The purity of the D2EHPA was determined to be 98.5% by potentiometric titration of an 80 vol% ethanol solution of the acid with 0.1 mol/dm³ NaOH in ethanol. The diluent kerosene, from Union Chemical Works Ltd., Taiwan, was washed twice with 20 vol% H₂SO₄ to remove aromatics and then with distilled water several times until it was neutral.^{4,6)} The other inorganic chemicals were supplied by RDH AG, as analytical reagent grade.

The aqueous composition was 0.5 mol/dm³ (Na, H, Zn)SO₄. In the aqueous phase, the initial concentration of zinc ranged from 9.18×10^{-4} to 1.38×10^{-3} mol/dm³, while the initial pH values were 1.86 and 2.46. In the organic phase, the initial formal concentration of the monomeric D2EHPA was from 2.5×10^{-2} to 4.0×10^{-1} mol/dm³, whereas TBP and EOH were both from 1.0×10^{-2} to 1.0 mol/dm³. All experiments were performed at 25°C. The experimental procedure is the same as reported in our previous paper.^{4,6)}

2. Results and Discussion

As the total concentration of zinc is present at trace level, the extraction of zinc with D2EHPA dissolved in kerosene can be represented by the following reaction:^{4,6,14)}

and

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$$K_{2n} = \frac{[\overline{\text{ZnR}_2(\text{HR})_n}][\text{H}^+]^2}{[\text{Zn}^{2+}][\overline{(\text{HR})_2}]^{(n+2)/2}} \quad (2)$$

where K_{2n} is the extraction constant and the overbar indicates the species in the organic phase.

The distribution ratio of zinc is defined as

$$D = \frac{[\overline{\text{ZnR}_2(\text{HR})_n}]}{[\text{Zn}^{2+}]} \quad (3)$$

$$= K_{2n} [\overline{(\text{HR})_2}]^{(n+2)/2} [\text{H}^+]^{-2}$$

The previous study⁶⁾ indicated the value of n to be 1.20, which implied that both complexes $\overline{\text{ZnR}_2(\text{HR})}$ and $\overline{\text{ZnR}_2(\text{HR})_2}$ exist in the organic phase, and the corresponding extraction constants K_{21} and K_{22} are found to be $8.13 \times 10^{-3} (\text{mol}/\text{dm}^3)^{1/2}$ and 3.63×10^{-3} at 25°C , respectively.

The effect of the concentration of TBP and EOH on the distribution ratio of zinc extracted with D2EHPA is shown in **Figs. 1 and 2** respectively. In Fig. 1, the solid curves are obtained as described below. Here the value of D_0 was calculated from Eq. (3) based on the same conditions as for extraction with D2EHPA–TBP and D2EHPA–EOH mixtures, i.e., the same equilibrium aqueous pH and the D2EHPA concentration in the organic phase. As shown in Figs. 1 and 2, whether $S = \text{TBP}$ or EOH , the values of D/D_0 remain unchanged when $[\overline{S}] < 0.01 \text{ mol}/\text{dm}^3$, and decrease moderately with increasing $[\overline{S}]$ when $[\overline{S}] > 0.01 \text{ mol}/\text{dm}^3$. Also, the higher the concentration of D2EHPA present, the less the reduction of D/D_0 .

The extraction system involving alkylphosphoric acids with a neutral modifier or diluent such as TBP generally shows some synergistic or antisnergistic effects.^{3,9,11,12)} This behavior may be due to the neutral modifier being hydrogen bonded to the metal complexes rather than directly coordinated to the metal. It is also believed that an antagonism is present as a result of greater interactions between the phosphoric acid and the neutral modifier.^{11,12)}

In our previous paper,⁶⁾ it was reported that the mole fraction of D2EHPA loaded with zinc was less than 3% in the organic phase under the experimental conditions studied. It seems impossible that the slight reduction in D/D_0 is due to the direct interaction between the neutral modifier TBP or EOH and the metal complex $\overline{\text{ZnR}_2(\text{HR})}$ or $\overline{\text{ZnR}_2(\text{HR})_2}$, since the modifier is in large excess compared to the metal complex in the organic phase.

Alternatively considering the mutual interaction between D2EHPA and the modifier (S) molecules, we have:^{6,8–10)}

Fig. 1. Effect of TBP concentration on the extraction of zinc with D2EHPA in kerosene. $\text{pH}_i = 1.86$. $C_{\text{HR}} (\text{mol}/\text{dm}^3) = 0.4$ (curve 1, $\diamond$), 0.2 (curve 2, $\circ$), 0.05 (curve 3, $\triangle$) and 0.025 (curve 4, $\square$). Solid curves for $E^{1.6}$ are obtained from Eqs. (6) to (9). Data points for D/D_0 are obtained from experiments

Fig. 2. Effect of EOH concentration on the extraction of zinc with D2EHPA in kerosene. $\text{pH}_i = 1.85$. $C_{\text{HR}} (\text{mol}/\text{dm}^3) = 0.4$ ($\diamond$), 0.2 ($\circ$), 0.1 ($\triangle$) and 0.05 ($\square$)

Thus, the equilibrium compositions in the absence of zinc can be obtained by the following mass balance equations:

$$C_{\text{HR}} = \{1 + K_2 K_d^{1/2} [\overline{S}]\} [\overline{\text{HR}}] + \{2K_d + 2K_1 K_d [\overline{S}]\} [\overline{\text{HR}}]^2 \quad (6)$$

$$C_S = \{1 + K_2 K_d^{1/2} [\overline{\text{HR}}] + K_1 K_d [\overline{\text{HR}}]^2\} [\overline{S}] \quad (7)$$

and

$$2\overline{\text{HR}} \rightleftharpoons \overline{(\text{HR})_2}, \quad K_d = [\overline{(\text{HR})_2}] / [\overline{\text{HR}}]^2 \quad (8)$$

where K_d is the dimerization constant of D2EHPA and is taken to be $2.63 \times 10^4 \text{ dm}^3/\text{mol}$ in kerosene.⁴⁾

The values of K_1 and K_2 for D2EHPA–TBP in kerosene are found to be $4.0 \text{ dm}^3/\text{mol}$ and $1.0 (\text{dm}^3/\text{mol})^{1/2}$, respectively.¹⁾ For a given sets of C_{HR} and C_{TBP} , we can obtain the values of $[\overline{\text{TBP}}]$ and $[\overline{\text{HR}}]$ by solving Eqs. (6) to (8). It is assumed that

both $\overline{S(HR)_2}$ and $\overline{S(HR)}$ are inactive for the extraction of zinc. The descending ratio of free dimeric D2EHPA, E , in the presence of modifier is defined by:⁸⁾

$$E = [\overline{(HR)_2}] / [\overline{(HR)_2}]_0 \quad (9)$$

where $[\overline{(HR)_2}]_0$ denotes the equilibrium concentration of dimeric D2EHPA before the addition of the modifier.

The distribution ratio D is proportional to $[\overline{(HR)_2}]^{1.6}$ at the same equilibrium pH, as indicated in Eq. (3). The calculated values of $E^{1.6}$ are shown as solid curves in Fig. 1, which are in good agreement with the values of D/D_0 over the whole range studied. Since the extractability of zinc with TBP alone was negligibly small in our experiment (about 3–4 orders less than that extracted with D2EHPA), it was not surprising that the amount of free D2EHPA would determine the extraction behavior of zinc with D2EHPA–TBP mixture. It should also be noted that the solubility of TBP in the aqueous phase is inferred to be extremely low, since the values of D/D_0 are nearly the same for the aqueous pH values of 1.86 and 2.46.

The above analysis was in accordance with those of Komasaawa *et al.*⁸⁾ and Majdan *et al.*¹⁰⁾ for the extraction of divalent metals by alkylated hydroxyoximes in the presence of alcohol modifiers. They also found that the formation of an alcohol-extractant association complex can describe the reduction in the distribution ratio of divalent metals.

The corresponding constants of the D2EHPA–EOH system are not available from the literature.⁷⁾ Since the extractability of zinc with EOH alone was still negligible, we tried to estimate them from the distribution data, ignoring the aqueous solubility of EOH for simplicity.

It was assumed that the values of $E^{1.6}$ were essentially identical to that of D/D_0 . For given C_{HR} , C_{EOH} and $[\overline{HR}]$, the optimal sets of K_1 and K_2 for the D2EHPA–EOH system are obtained by the least-squares method:

$$F(K_1, K_2) = \sum \{ \Delta[\overline{EOH}]_{jj} \}^2 \quad (10)$$

where $\Delta[\overline{EOH}]$ is the difference in $[\overline{EOH}]$ calculated separately from Eqs. (6) and (7) by assuming an initial set of K_1 and K_2 .

The obtained values of K_1 and K_2 for the D2EHPA–EOH system are $7.61 \pm 1.44 \text{ dm}^3/\text{mol}$ and $0.65 \pm 0.42 (\text{dm}^3/\text{mol})^{1/2}$, respectively. Compared with the corresponding constants for the D2EHPA–TOPO mixture in kerosene of $100 \text{ dm}^3/\text{mol}$ and $30.2 (\text{dm}^3/\text{mol})^{1/2}$, respectively,⁵⁾ it is evident that the reactivity of the neutral modifier with D2EHPA in aliphatic diluent decreases in the order $\text{TOPO} > \text{EOH} > \text{TBP}$, as expected based on the relative tendency of each modifier for hydrogen bonding with

D2EHPA. This result roughly agrees with that of Sabot and Bauer¹³⁾ for the extraction of nickel from perchlorate media with di(2-ethylhexyl)dithiophosphoric acid dissolved in kerosene. Also, Mikhailov *et al.*¹¹⁾ similarly found that *n*-octanol is a more active antagonist than TBP in both benzene and *n*-heptane diluents for the extraction of rare earth metals with di-*n*-butylphosphoric acid.

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Nomenclature

C	= total concentration of a species initially added into the system	[mol/dm ³]
D	= distribution ratio of zinc extracted with D2EHPA–TBP mixture, etc.	[—]
D_0	= distribution ratio of zinc extracted with D2EHPA alone	[—]
E	= descending ratio of dimeric D2EHPA in the presence of TBP or EOH	[—]
K_{2n}	= extraction constants defined in Eq. (2)	[(mol/dm ³) ^{(2-n)/2}]
K_1	= constant defined in Eq. (4)	[dm ³ /mol]
K_2	= constant defined in Eq. (5)	[(dm ³ /mol) ^{1/2}]
K_d	= dimerization constant of D2EHPA defined in Eq. (8)	[dm ³ /mol]
[]	= concentration of species in brackets	[mol/dm ³]

<Superscripts>

— = species in the organic phase

<Subscripts>

i = initial

Literature Cited

- 1) Baes, C. F., Jr.: *Nucl. Sci. Eng.*, **16**, 405 (1963).
- 2) Flett, D. S. and J. Melling: in "Handbook of Solvent Extraction", Lo, T. C., M. H. I. Baird and C. Hanson (Eds.), John Wiley & Sons, Inc., New York (1983), Chapter 24, pp. 269–647.
- 3) Grimm, R. and Z. Kolarik: *J. Inorg. Nucl. Chem.*, **36**, 189 (1974).
- 4) Huang, T. C. and R. S. Juang: *Ind. Eng. Chem. Fundam.*, **25**(4), 752 (1986).
- 5) Ihle, H., H. Michael and A. Murrenhoff: *J. Inorg. Nucl. Chem.*, **25**, 734 (1963).
- 6) Juang, R. S. and Y. T. Chang: *Ind. Eng. Chem. Res.*, **30**(11), 2444 (1991).
- 7) Kolarik, Z.: *Pure Appl. Chem.*, **54**(12), 2593 (1982).
- 8) Komasaawa, I. and T. Otake: *J. Chem. Eng. Jpn.*, **16**(5), 377 (1983).
- 9) Komasaawa, I., T. Otake and Y. Ogawa: *J. Chem. Eng. Jpn.*, **17**(4), 410 (1984).
- 10) Majdan, M., R. P. Sperline, W. G. Gu, W. H. Yu and H. Freiser: *Solvent Extr. Ion Exch.*, **7**(6), 987 (1989).
- 11) Mikhailov, V. A., E. F. Grigoreva and S. K. Kharchenko: *Radiokhimiya*, **9**(2), 149 (1967).
- 12) Nash, K. L. and G. R. Choppin: *J. Inorg. Nucl. Chem.*, **39**, 131 (1977).

- 13) Sabot, J. L. and D. Bauer: *J. Inorg. Nucl. Chem.*, **41**, 767 (1979).
- 14) Sastre, A. M. and M. Muhammed: *Hydrometallurgy*, **12**, 177 (1984).