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THE ROLE OF EXTRACTANT COMPONENTS IN THE SYNERGIC EXTRACTION OF Ge WITH LIX 63/OPAP

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ABSTRACT

Extraction of Ge from sulfuric acid solution was studied for the synergic extractant pair 5,8-diethyl-7-hydroxy-6-dodecanone oxime (LIX 63) and octylphenyl acid phosphate (OPAP). These studies were undertaken by the U.S. Bureau of Mines to enhance selective extraction of metals by determining mechanisms of synergic extraction. In equilibrium shakeout tests, Ge extraction was measured for LIX 63 with each of the two components of OPAP--monoalkyl (MOPPA) and dialkyl (DOPPA)--in the presence of a modifier, isodecanol, in isooctane diluent. Mechanistic models are proposed for each of the two systems. The fit of the assumed models to the data is consistent with the conclusion that extraction synergy results from the formation of several mixed extractant complexes. In both systems, Ge extraction increases with increasing sulfuric acid concentration. MOPPA generally is a stronger Ge extraction synergist than DOPPA, but MOPPA experiences higher solubility losses to the aqueous phase.

INTRODUCTION

The U.S. Bureau of Mines is studying solvent extraction of Ge from sulfuric acid leach solutions of ores and zinc processing residues. The first commercially important Ge extractant was the α-hydroxyoxime LIX 63 (DeSchepper *et al.*, 1975, 1976). High extractant concentrations were necessary, however, and extraction was effective only for highly acidic Ge-bearing solutions. The feed acid requirement was later lowered (DeSchepper *et al.*, 1984a) by adding an 8-hydroxyquinoline synergist, either Kelex 100 or LIX 26. An organic phase containing, for example, 99% (v/v) LIX 63 and 1% (v/v) LIX 26 thus extracted Ge from low-acid solution, but total extractant requirement was still high.

As well as working as a Ge extraction synergist for LIX 63, Kelex 100 is the other commercially important Ge extractant (Cote *et al.*, 1980). Phase separation is slow for Kelex 100 organic phase/stripping solution, but this problem can be minimized by elevating stripping temperature to at least 40° C (DeSchepper *et al.*, 1984b).

Recently, a phosphatic synergist was proposed for LIX 63 (Boateng *et al.*, 1990). In this process, the addition to LIX 63 of di-2-ethylhexyl phosphoric acid (DEHPA) alone, or in combination with its monoalkyl form (MEHPA), lowered the organic phase extractant concentration requirement to under 10% (v/v). At the same time, the Bureau studied another phosphate synergist, octylphenyl acid phosphate (OPAP), and proposed a Ge extraction process based on the LIX 63/OPAP pair (Harbuck *et al.*, 1991).

Although the active components of OPAP have been identified (Arnold, 1977), no reports were found that identified which component is the more active Ge extraction synergist. Therefore, this study was initiated to determine the role of the OPAP components in synergic Ge extraction with LIX 63, and to find the chemical stoichiometry of the extracted Ge complexes.

EXPERIMENTAL

Extractants were purified from commercially available products (reference to specific products or manufacturers does not imply endorsement by the Bureau of Mines). The anti-form of 5,8-diethyl-7-hydroxy-6-dodecanone oxime was purified from LIX 63 (Henkel Corp.) using a copper-oximate precipitation method (Keeney *et al.*, 1984). Commercial OPAP (Albright & Wilson Americas Inc.) was separated into its purified primary active components, typically found in equal proportions: a dialkyl (DOPPA) species and a monoalkyl (MOPPA) species, according to a published method (Arnold, 1977). Extractants were dissolved in isooctane containing 10% (v/v) isodecanol and adjusted to desired concentrations 0.005 *M* to 0.100 *M*. Isodecanol was added to promote solubility of MOPPA and DOPPA in isooctane and also to provide the well-documented phase separation enhancement of long-chain alcohols.

Stock Ge solution was made up to 0.027 *M* by dissolving Ge powder (99.999%) (Alfa Inorganics) in 0.5 *M* H_2O_2 containing 0.1 *M* NH_4OH and then boiling to destroy peroxide and drive off ammonia. Desired Ge and acid levels were reached by diluting with water and adding reagent-grade H_2SO_4. Initial Ge concentration was usually 0.0027 *M*. A

higher concentration (0.0063 *M*) was used for a few tests where low Ge extraction was expected. Except where indicated, H_2SO_4 concentration was 100 g/L.

Equilibrium shakeouts were performed with equal volumes of each phase in separatory funnels shaken on an orbital shaker for 30 minutes at ambient temperature. After phase disengagement, the layers were separated and filtered. To reduce aqueous entrainment, the organic layer was filtered through phase separation paper.

Aqueous raffinates were analyzed for Ge by inductively coupled plasma spectroscopy and for phosphate by ion chromatography. Organic samples were digested in sealed plastic bottles in a microwave oven using 14% HF in concentrated HNO_3. Resulting solutions were analyzed for Ge by atomic absorption spectrophotometry. Extraction is reported as the distribution ratio, D(D = $[Ge]_{org}/[Ge]_{aq}$), or as percent extraction.

RESULTS AND DISCUSSION

Equilibrium extraction of Ge was measured independently for LIX 63 and for each component of OPAP--MOPPA and DOPPA. Neither OPAP component extracts measurable quantities of Ge, even under optimized conditions. From 100 g/L H_2SO_4, 0.1 *M* LIX 63 extracts only 4% of the contained Ge, however, a mixture of 0.05 *M* DOPPA and 0.05 *M* LIX 63 effects 20% Ge extraction, and when MOPPA is substituted for DOPPA, Ge extraction rises to 50%.

To understand why Ge extraction increases for the mixed extractants, equilibrium data were fitted by mechanistic models that were defined by a system of simultaneous, nonlinear equations using an equation-solving program on a personal computer. Equations were developed describing the extraction of Ge with LIX 63 alone, and as mixed extractant complexes that contain Ge, LIX 63, MOPPA or DOPPA, and HSO_4^-.

The principal method of evaluation of the extraction mechanism is slope analysis, where the log of the distribution ratio, D, is plotted against the log of the concentration of the extractant of interest. In such a plot, the slope indicates the stoichiometry of the variable extractant. Non-integer slopes usually indicate multiple extracted complexes, with different stoichiometries (Penner *et al.*, 1991). To provide slope analysis data, several series of shake-out tests were conducted in which only one extractant concentration was varied, with all others held constant.

Another technique is the continuous variation method, where the concentrations of two extractants are varied so that their sum is constant (Penner *et al.*, 1991). When

synergic extraction occurs, the continuous variation plot shows a distinct maximum for a mixture of the extractants. When a single mixed extraction complex is involved, the composition of the mixture at the maximum indicates the stoichiometry of the extraction complex.

The research was conducted in two independent parts, the LIX/MOPPA series, and the LIX/DOPPA series, because preliminary extraction tests with all three extractants present indicated no interaction between DOPPA and MOPPA. The evaluation process involved assuming chemical reactions, entering consequent mass action expressions and material balance equations into a commercial equation-solving program, and adjusting equilibrium constants until the calculated extraction fit experimental data within experimental uncertainty.

The LIX 63 system

Although Ge extraction with MOPPA or DOPPA alone was insignificant, a small but measurable Ge extraction was found for LIX 63, at higher acid concentrations. Extraction data for LIX 63 alone are plotted in Figure 1. The corresponding slope of log D vs. log [LIX 63] is 1.4 and, with respect to log $[H_2SO_4]$ (not shown), is 1.7. Because the slopes are non-integers, two reactions are proposed for Ge extraction with LIX 63 (HL):

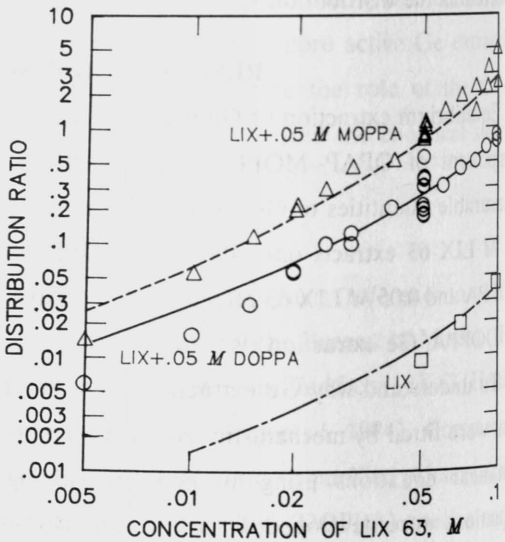

Fig. 1—Slope analysis showing effect of LIX 63 concentration (alone or with 0.05 *M* MOPPA or DOPPA) on Ge extraction. Lines indicate extraction predicted by model.

$$Ge(OH)_4 + \overline{HL} \overset{K_1}{\rightleftharpoons} \overline{Ge(OH)_3L} + H_2O, \quad (1)$$

$$Ge(OH)_4 + 2\,\overline{HL} + H^+ + HSO_4^- \overset{K_2}{\rightleftharpoons} \overline{Ge(OH)L_2(HSO_4)} + 3\,H_2O, \quad (2)$$

with the equilibrium constants $K_1 = 0.12$ and $K_2 = 2.8$. The overbar indicates species in organic solution.

The MOPPA/LIX system

In the MOPPA/LIX system, the slope of log D vs. log [MOPPA] is 1.0 (Fig. 2); with respect to log [LIX 63] is 1.4 (Fig. 1); and with respect to log $[H_2SO_4]$ is 0.65. Reactions are proposed with mixed-species products containing both LIX 63 and MOPPA (HM):

$$Ge(OH)_4 + \overline{HL} + \overline{HM} + H^+ + HSO_4^- \overset{K_3}{\rightleftharpoons} \overline{Ge(OH)LM(HSO_4)} + 3\ H_2O, \quad (3)$$

$$Ge(OH)_4 + 2\ \overline{HL} + \overline{HM} \overset{K_4}{\rightleftharpoons} \overline{Ge(OH)L_2M} + 3\ H_2O, \quad (4)$$

with the equilibrium constants $K_3 = 75$ and $K_4 = 5500$.

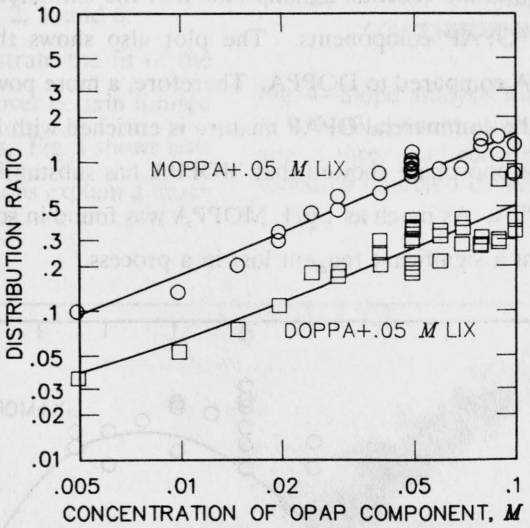

Fig. 2—Slope analysis format showing effect of OPAP component concentration (with 0.05 *M* LIX 63) on Ge extraction. Lines indicate extraction predicted by the model.

The DOPPA/LIX system

In the DOPPA/LIX system, the slope of log D vs. log [DOPPA] is 1.0 (Fig. 2), with respect to log [LIX 63] is 1.5 (Fig. 1), and with respect to log $[H_2SO_4]$ is 1.2. Thus, the following reactions with mixed LIX 63 and DOPPA (HD) products are proposed:

$$Ge(OH)_4 + \overline{HD} + \overline{HL} \overset{K_5}{\rightleftharpoons} \overline{Ge(OH)_2DL} + 2\ H_2O, \quad (5)$$

$$Ge(OH)_4 + \overline{HD} + 2\ \overline{HL} + H^+ + HSO_4^- \overset{K_6}{\rightleftharpoons} \overline{GeDL_2(HSO_4)} + 4\ H_2O, \quad (6)$$

with the equilibrium constants $K_5 = 45$ and $K_6 = 1200$.

Figure 3 uses the continuous variation format to show the synergic effect of LIX 63 with the components of OPAP, where the concentrations of both LIX 63 and MOPPA or DOPPA are varied so their sum is 0.10 *M*. Although the figure demonstrates relatively large experimental uncertainty, the maxima can be seen on the LIX 63 side of the plot. This supports the reaction assumptions that the extracted complexes contain more LIX 63 than OPAP components. The plot also shows the superior synergy exhibited by MOPPA compared to DOPPA. Therefore, a more powerful Ge extractant can be prepared if the commercial OPAP mixture is enriched with MOPPA. However, raffinate analysis for phosphate showed that MOPPA has substantially higher aqueous solubility than DOPPA. As much as 1 g/L MOPPA was found in some raffinates. This level could represent a significant reagent loss in a process.

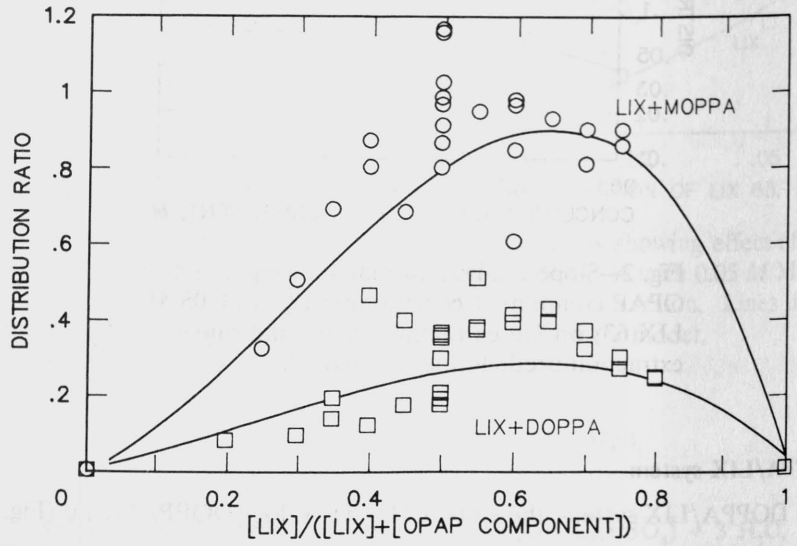

Fig. 3—Continuous variation format showing the extraction of Ge for constant total extractant concentration (0.01 *M*). Line shows extraction predicted by model.

Sulfuric acid effect

The effect of acid concentration on Ge extraction was surprising, because high acid levels usually depress the extraction of most cationic metals. Instead of inhibiting the extraction, it enhances the extraction, although differently in each of the systems studied. To fit a model to Figure 4 data, bisulfate anions are included in the product complexes in the proposed reactions shown in equations 2, 3, and 6.

Figures 1-4 illustrate the fit of the model to the data over certain limited ranges of conditions. Fig. 5 shows how the proposed reactions explain a much broader data range.

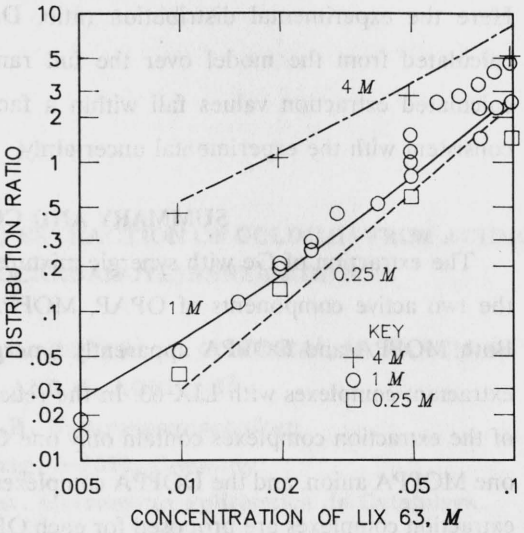

Fig. 4—Slope analysis format showing effect of LIX 63 concentration at 0.05 *M* MOPPA and at three acid concentrations. Corresponding modeled curves are also shown.

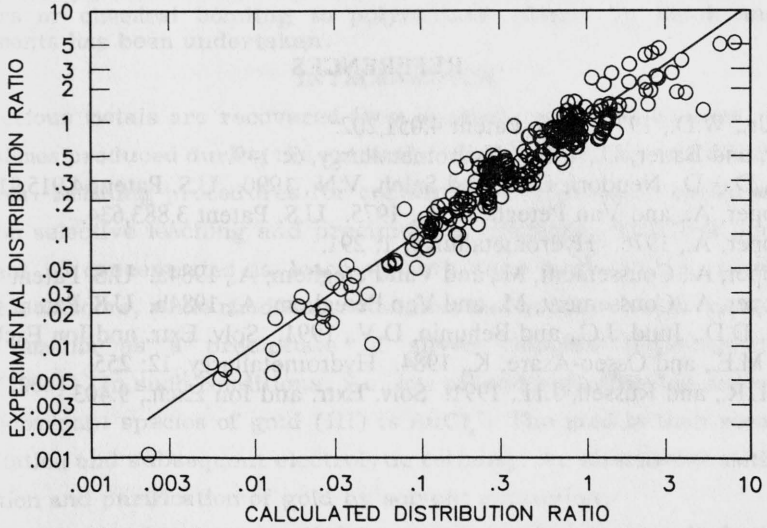

Fig. 5—Comparison of experimental extraction of Ge over full range of conditions tested, with extraction predicted by the model. Perfect fit is indicated by line.

Here the experimental distribution ratio, D, is compared to the distribution ratio calculated from the model over the full range of conditions used. Nearly all the calculated extraction values fall within a factor of two of the experimental results, consistent with the experimental uncertainty.

SUMMARY AND CONCLUSIONS

The extraction of Ge with synergic mixtures of LIX 63 and OPAP was studied. Of the two active components of OPAP, MOPPA was found to be a stronger synergist. Both MOPPA and DOPPA apparently synergize extraction of Ge by forming mixed extractant complexes with LIX 63. In the reactions that appear to best fit the data, all of the extraction complexes contain only one Ge atom, the MOPPA complexes contain one MOPPA anion, and the DOPPA complexes contain one DOPPA anion. Two mixed extraction complexes are proposed for each OPAP component system--one species with one LIX 63 anion and a second species with two LIX 63 anions. In addition, acid enhances extraction by contributing a bisulfate anion to some of the product species. The identification of the MOPPA component of OPAP as the stronger synergist shows how a fundamental understanding of extraction chemistry can predict ways of improving metal extraction.

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