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# MONOLAYER BEHAVIOR OF HYDROXYOXIME EXTRACTANTS

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## ABSTRACT

Efforts to elucidate solvent extraction mechanisms in hydrometallurgical systems have generally been hindered by a lack of physico-chemical data pertaining to the interfacial properties of organic-soluble extractants and their metal complexes. In an effort to address this situation, a Langmuir film balance was used to characterize the interfacial properties of purified metal extractants spread as monomolecular films at the air/water interface. This interfacial system was used as a model for studying the interactions of the extractant films with the aqueous phase. The metal extractants used in this study were: the anti-isomer of 5,8-diethyl-7-hydroxy-6-dodecanone oxime (DEDO, the active extractant in LIX63, Henkel), and the anti-isomer of 2-hydroxy-5-nonylbenzophenone oxime (HBPO, the active extractant in LIX65N, Henkel). Both equilibrium and dynamic film properties of single component and mixed monolayers were examined. The effects of aqueous phase copper ion on the equilibrium properties of these extractant monolayers were also investigated.

## INTRODUCTION

As a separation technology, solvent extraction was first used in the field of analytical chemistry where a wide range of extractant reagents was available for

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trace metal analysis. These reagents, however, were not suitable for commercial scale operations because of their high cost, high aqueous solubility, and the difficulty of stripping the metal from the organic phase. Today, more than a dozen extractants are in commercial use. Many of the reagents, originally developed for the nuclear industry, are finding new applications in the recovery of metals such as cobalt, iron, tungsten, vanadium, europium, niobium, zirconium, and hafnium (1,2). The extractants used in analytical chemistry applications are characteristically of low molecular weight (100-200 daltons). In some cases they are readily soluble in water and form their metal complexes in the bulk aqueous phase; the complexes are subsequently recovered by extraction into an organic phase. Extractants for hydrometallurgical applications, on the other hand, have been designed to minimize reagent losses to an aqueous phase. Aqueous solubilities in the parts-per-million range are attained through the presence of high molecular weight hydrocarbon radicals (1,2).

It is generally recognized that, as the extractant molecular weight is increased, the reaction site for metal complexation will tend to move from the bulk aqueous phase towards the oil/water interface (3). There is however, no consensus regarding the actual reaction locale of a given metal-extractant system. For example, reaction mechanisms which have been proposed for Cu-hydroxyoxime systems include: metal complexation in the bulk aqueous phase, in an aqueous zone adjacent to the oil/water interface, and at the oil/water interface (3,4).

One particular system for which there has been little agreement on extraction mechanism is Cu-LIX64N. The commercial extractant LIX64N consists of a mixture of the aliphatic hydroxyoxime LIX63 and the aromatic benzophenone oxime LIX65N (5). In this reagent mixture, a small amount of LIX63 (1 vol%) is known to act as a catalyst for improving the extraction kinetics of LIX65N without affecting the extraction equilibrium (5,6). The formation of mixed-ligand complexes has been featured in a number of interfacial extraction mechanisms that attempt to explain the catalytic role of LIX63. It is in this light that a study of the monolayer properties of the anti-isomer of 5,8-diethyl-7-hydroxy-6-dodecanone oxime (DEDO, the active extractant in LIX63), the anti-isomer of 2-hydroxy-5-nonylbenzophenone oxime (HBPO, the active extractant in LIX65N) and their equimolar mixtures was initiated. In this paper the equilibrium and dynamic properties of these monolayer films are reported. In addition, experimental results are presented on the interaction of $Cu^{2+}$ ions with single-component and mixed films.

## EXPERIMENTAL

The metal extraction reagents LIX63 (Lot No. 9F 15933, MX4877) and LIX65N (Lot No. 80K265006) were obtained from Henkel Corp. The active extractants in LIX63 (anti-isomer of 5,8-diethyl-7-hydroxy-6-dodecanone oxime, or DEDO) and in LIX65N (anti-isomer of 2-hydroxy-5-nonylbenzophenone oxime, or HBPO) were isolated as described in the literature (7-9). Elemental analysis of DEDO indicated a minimum purity of 99.6 wt% (molecular weight 271.45), while nonaqueous titration of HBPO gave a purity of 99.7% (Molecular weight 339.5) (10,11).

All monolayer experiments were performed in triplicate at 18 ± 0.1°C using a Lauda film balance which was interfaced to a microcomputer. Pressure-area isotherm and constant-pressure desorption data were obtained as described previously (10-12). All pressure-area isotherms were determined at the highest compression rate permitted with the Lauda film balance (7.5 cm $min^{-1}$) in order to minimize the extent of film dissolution during the measurement of an isotherm. Pressure-area isotherms were reproducible to within ± 1 $Å^2$ $molecule^{-1}$.

## RESULTS AND DISCUSSION

### Extractant Dissolution from Single Component and Mixed Films

Monolayer dissolution from DEDO, HBPO, and DEDO/HBPO films was observed by following the change in film area as a function of time while maintaining a constant surface pressure of 15 mN $m^{-1}$. The desorption profiles of DEDO, HBPO, and an equimolar mixture of the two reagents are shown in Figures 1 and 2 in the form of $\ln (A_t/A_o)$ vs. t and $\ln (A_t/A_o)$ vs. $\sqrt{t}$ plots respectively. ($A_t$ represents the time- dependent film area while $A_o$ represents the total film area at t=0.) The most interesting aspect of the dynamic behavior of these materials is that the initial desorption rate [defined as $-d \ln (A_t/A_o)/dt$] from pure DEDO monolayers was approximately 10 times greater than the desorption rate from pure HBPO monolayers. This large difference in the desorption rates is surprising in light of the fact that the molecular weights of the two extractants are similar (and hence their diffusion coefficients are comparable, assuming they are both monomeric in the aqueous diffusion layer).

Previous studies (10-12) of the dissolution of HBPO monolayers have shown that these films follow the diffusion-controlled dissolution mechanism described by Ter Minassian-Saraga (13). During the first 25-30 minutes, the change in the logarithmic normalized film area [$d \ln (A_t/A_o)$] is directly proportional to the square-root of time (t), while the concentration of solute within the aqueous diffusion zone increases. At steady-state, a fixed concentration gradient is established, and the change in logarithmic film area [$d \ln (A_t/A_o)$] becomes proportional to t. However, the desorption kinetics of DEDO and the mixed film did not follow a diffusion-controlled mechanism as indicated by the absence of a linear $\ln (A_t/A_o)$- $\sqrt{t}$ relationship. Apparently, more than one kinetic process takes place during the constant pressure desorption of monolayers containing DEDO.

The anomalous behavior of DEDO is unlikely to be due to monolayer collapse since this mechanism shows a characteristic increase in the rate of film loss with time (11,14), a kinetic profile associated with an ever-increasing number of critical nuclei within the monolayer film (14). At this time, the most probable explanation is the coupling of dissolution and evaporation processes in DEDO-containing films. Evaporation in HBPO monolayers, on the other hand, would be inhibited by the strong interactions between the benzene rings and the aqueous subphase. In a somewhat similar fashion, the data of Brooks and Alexander (15) showed that the evaporation rate of a $C_{18}$ alcohol from a spread monolayer film can be reduced to zero by the presence of a single double bond in the R-chain (i.e., oleyl alcohol).

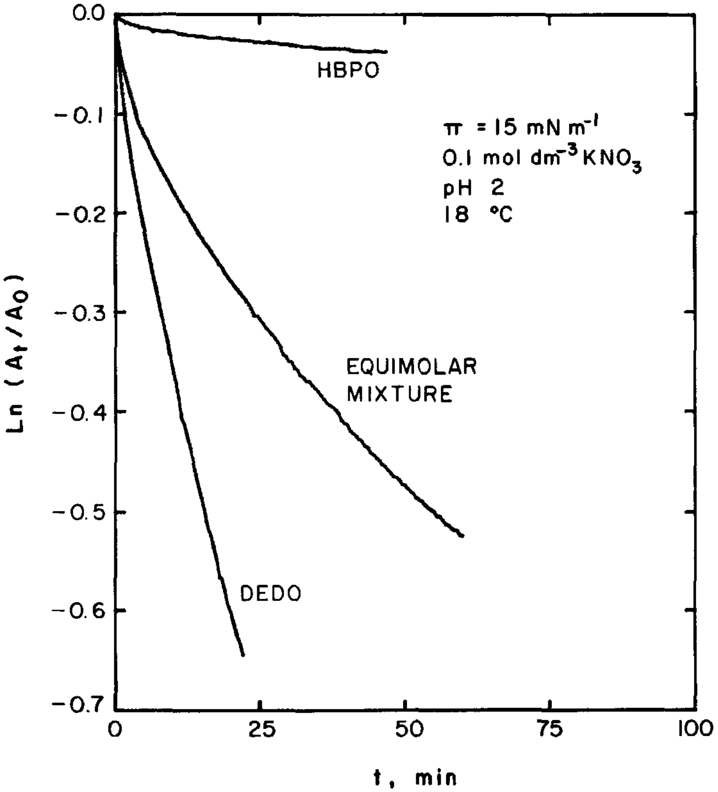

Figure 1. Constant pressure desorption of HBPO, DEDO, and HBPO/DEDO monolayers.

## PRESSURE-AREA ISOTHERMS

The pressure (Π) - area (A) isotherms of HBPO, DEDO, and their equimolar mixture are shown in Figure 3. The shape of the isotherm for HBPO (Curve A) indicates that this extractant forms a liquid-condensed film (16) when the molecular area is reduced to about 66 Å$^2$ (designated by $A_T$). The compacted nature of the film molecules in this region is indicated by a low surface compressibility (given by $d\ln A/d\Pi$) of 0.008 m mN$^{-1}$ (cf 0.024 m mN$^{-1}$ for DEDO). An apparently slow rate of collapse to the thermodynamically stable bulk phase results in the formation of a metastable film at surface pressures up to 7 mN m$^{-1}$ above the equilibrium spreading pressure ($\Pi_e$) of 23 mN m$^{-1}$ (11). Continued film compression beyond

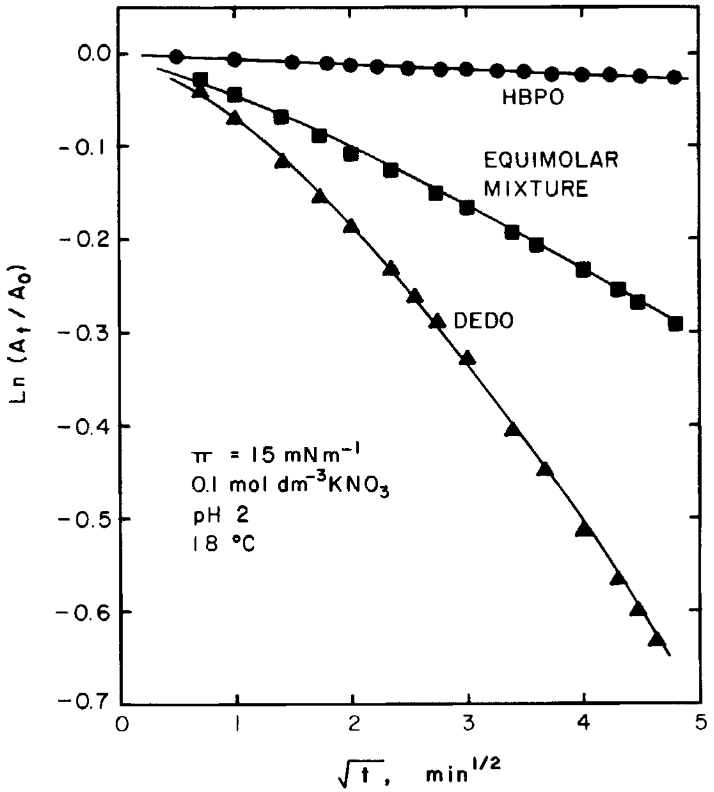

Figure 2. Constant pressure desorption of HBPO, DEDO, and HBPO/DEDO monolayers. A straight line is an indication of nonsteady-state dissolution.

a limiting molecular area of 50 Å$^2$ led to film fracture as demonstrated by the appearance of a plateau in the Π-area curve.

The Π-A isotherm of DEDO (Curve C) exhibits a surface compressibility of 0.024 m mN$^{-1}$ within the steepest region of the isotherm and is characteristic of a liquid-expanded film (16). The high compressibility of DEDO monolayers is typical of spread films of molecules with R-chain branching. A gaseous/liquid film transition in DEDO monolayers is indicated by a region of constant film pressure (see insert Fig. 3) at large interfacial molecular areas. Condensation to the liquid phase is completed at a film pressure of about 2.5 mN m$^{-1}$ and corresponds to a molecular area of 107 Å$^2$. This point is designated as $A_T$ in Curve C. Within the

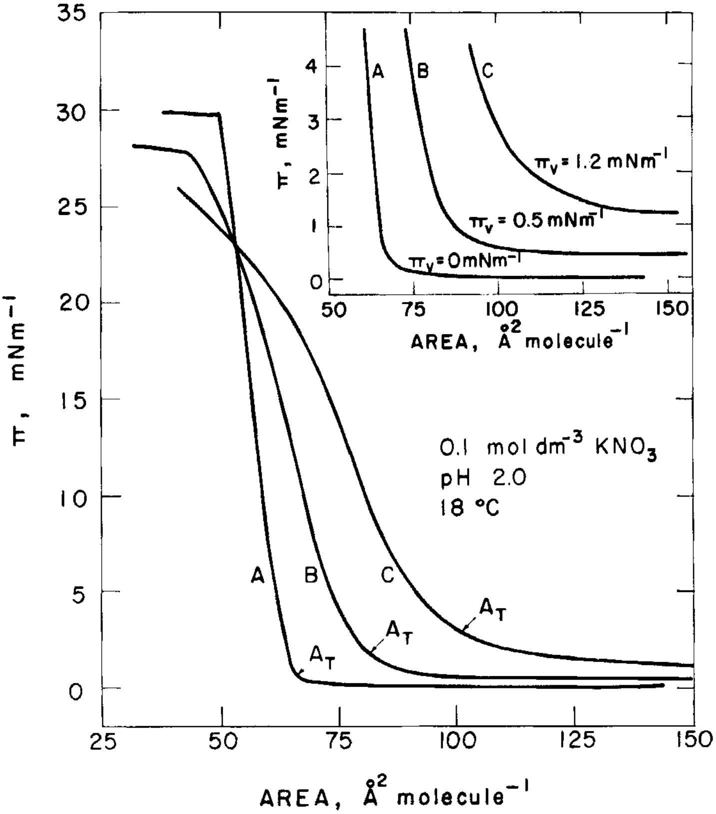

Figure 3. Π-area isotherms of HBPO (A), an equimolar mixture of HBPO/DEDO (B), and DEDO (C). The compression rate was 7.5 cm $min^{-1}$.

transition region, DEDO films can be expected to be inhomogeneous with liquid portions surrounded by a gaseous film (16).

The Π-area isotherm of an equimolar mixture of DEDO/HBPO (Curve B) reflects certain characteristics found in the isotherms of the pure components. For example, the mixed film has a surface compressibility of 0.017 m $mN^{-1}$ which is the mean compressibility of the individual components. While the mixed film is liquid-expanded, it exhibits a collapse behavior similar to that of the HBPO monolayer; the limiting molecular area at film collapse is 43 $Å^2$ $molecule^{-1}$ which is lower than the corresponding limiting area of pure HBPO (53 $Å^2$) indicating that film loss had occurred during monolayer compression. The molecular areas which mark the transition to the liquid phase in both DEDO and HBPO monolayers are

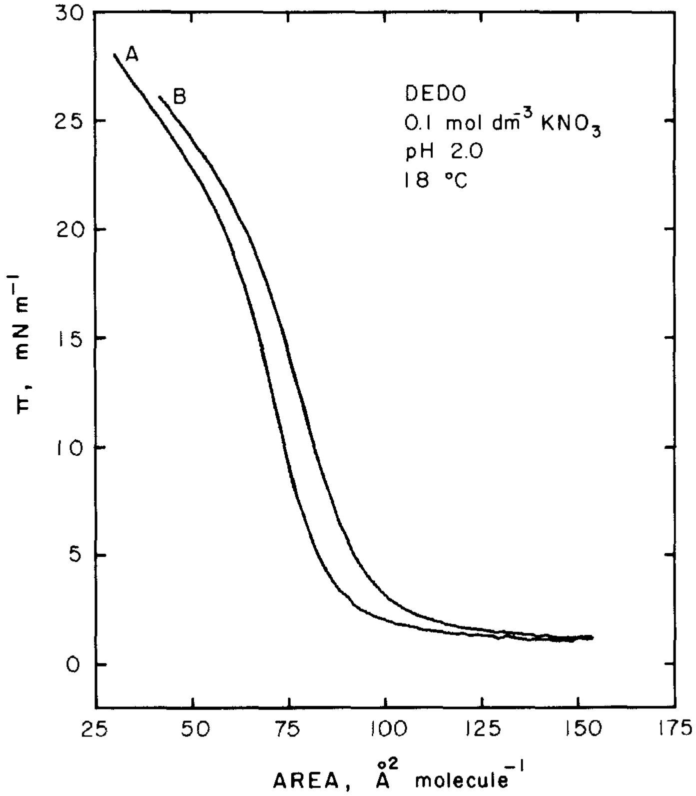

Figure 4. Π-area isotherms of DEDO; (A) was obtained on a 0.1 mol dm$^{-3}$ $Cu(NO_3)_2$ subphase, while (B) was obtained in absence of $Cu(NO_3)_2$.

~100 Å$^2$ and 66 Å$^2$ respectively. The corresponding molecular area for the equimolar mixture is 85 Å$^2$. Within experimental error, this is equal to the numerical average of the values for the pure components.

In addressing the question of miscibility in the mixed film, it can be seen in Figure 3 that HBPO causes a lowering of the surface vapor pressure ($\Pi_V$) when the DEDO and the mixed films are compared. The expanded scale of Figure 3 more clearly illustrates this phenomenon. The surface vapor pressure of the mixture is reduced to 0.5 mN m$^{-1}$ from 1.2 mN m$^{-1}$ for the pure DEDO monolayer. The vapor pressure of HBPO is below the sensitivity of the Lauda film balance. The $\Pi_V$ of the equimolar mixture was reduced in close proportion to the mole fraction of DEDO. While it can be concluded that the two extractants are miscible, a more sensitive instrument is needed for performing vapor pressure measurements before

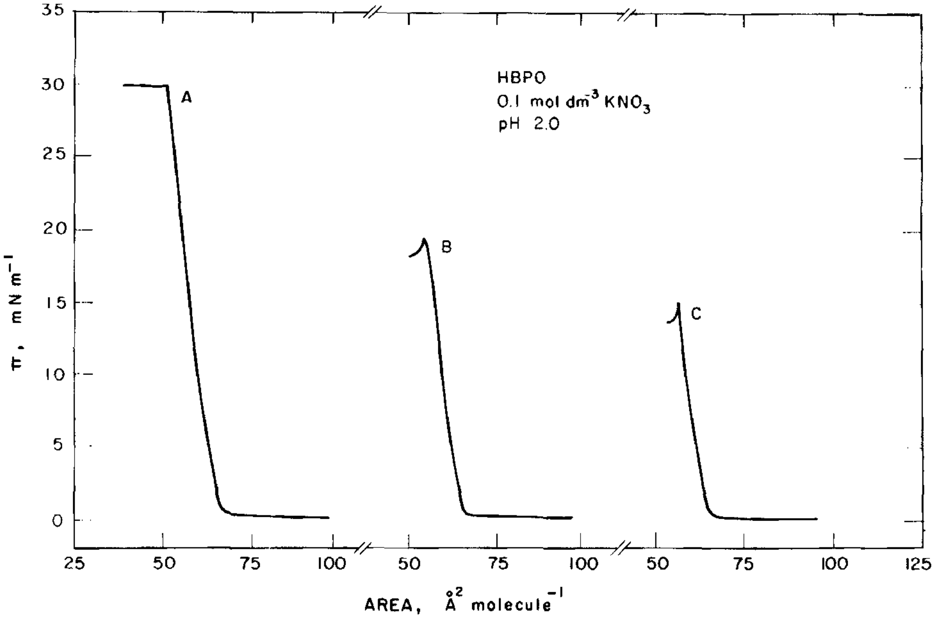

Figure 5. Influence of $Cu(NO_3)_2$ on the collapse pressure of HBPO monolayers. The $Cu(NO_3)_2$ concentrations were: (A) No $Cu(NO_3)_2$ present, (B) 5 mmol $dm^{-3}$, and (C) 10 mmol $dm^{-3}$.

conclusions can be drawn about solution ideality. It should be noted that, if the condensed monolayer phases were immiscible, $\Pi_v$ would be equal to the sum of the vapor pressures for the pure components.

## MONOLAYER INTERACTIONS WITH $Cu^{2+}$ IONS

In Figure 4, the $\Pi$-area isotherm of DEDO spread on an aqueous subphase containing 0.1 mol $dm^{-3}$ $KNO_3$ and 0.1 mol $dm^{-3}$ $Cu(NO_3)_2$ at pH 2.0 is compared with the isotherm which is obtained in the absence of copper. The presence of copper in the aqueous phase resulted in a reduction of the mean molecular area of DEDO from about 100 $Å^2$ to 94 $Å^2$. However, copper had no effect on the surface compressibility of the DEDO film which remained in the liquid-expanded state. It does not appear that the presence of copper resulted in the enhanced dissolution of the DEDO monolayers because in that case the degree to which the isotherm was displaced toward smaller molecular areas would have been a function of surface pressure (16) which it was not. The shift in the isotherms of Figure 4 is therefore interpreted to be the result of a surface interaction between DEDO and copper. Conclusions regarding the stoichiometry of this postulated Cu-

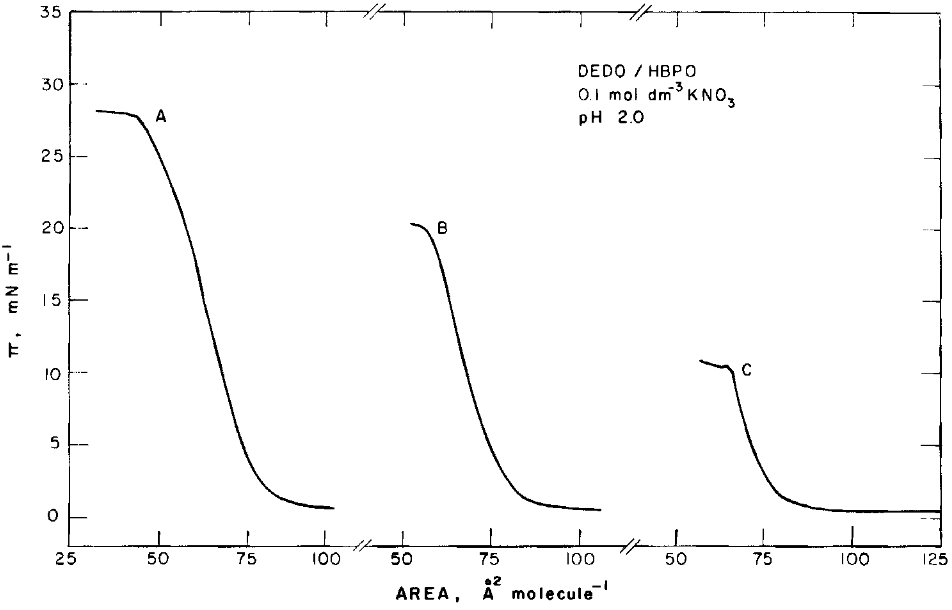

Figure 6. Influence of $Cu(NO_3)_2$ on the collapse pressure of equimolar DEDO/HBPO monolayers. The $Cu(NO_3)_2$ concentrations were: (A) No $Cu(NO_3)_2$ present, (B) 10 mmol $dm^{-3}$ and (C) 100 mmol $dm^{-3}$.

DEDO surface complex must await further studies involving a detailed chemical analysis of DEDO monolayers.

The presence of copper in the aqueous subphase had a dramatic influence on the collapse pressure ($\Pi_c$) of HBPO monolayers as shown in Figure 5; the collapse pressure decreased with increase in copper concentration in the aqueous phase. In the mixed monolayers, the collapse pressure will be a function of film composition if the film components are miscible; if they are not, the collapse pressure will be independent of composition and will be equal to that of the least stable compound present (16). The dependence of $\Pi_c$ on copper concentration therefore suggests that a mixed film is formed which contains the unreacted oxime and a copper oximate. The percent conversion of HBPO within the film is thus a function of the copper concentration in the aqueous subphase. It is interesting to note that in contrast to the condensation behavior observed with DEDO, copper had no detectable influence on the interfacial molecular area of HBPO.

The effect of copper on the Π-area isotherms of an equimolar mixture of DEDO and HBPO is shown in Figure 6. As with HBPO monolayers, copper had no significant effect on the average interfacial molecular area of the extractant

Table 1. Influence of copper on the collapse pressure ($\Pi_c$) of HBPO and DEDO/HBPO [1:1] mixed films[a].

| [Cu] (mmol $dm^{-3}$) | $\Pi_c$, HBPO (mN $m^{-1}$)[b] | $\Pi_c$, DEDO/HBPO (mN $m^{-1}$)[b] |
|---|---|---|
| 0 | 29.9 ± 0.3 | 27.4 ± 0.2 |
| 5 | 19.7 ± 0.3 | ND |
| 10 | 15.0 ± 0.1 | 20.5 ± 0.3 |
| 100 | ND | 10.5 ± 0.3 |

[a] Subphase contained 0.1 mol $dm^{-3}$ $KNO_3$, and specified $Cu(NO_3)$ concentration at pH 2.0 and 18°C.

[b] Values represent the mean from three monolayer films ± standard deviation.

ND: not determined

mixture and the collapse pressures were inversely proportional to copper concentration. The values of $\Pi_c$ in Figures 5 and 6 are summarized in Table 1.

## IMPLICATIONS OF MONOLAYER STUDIES

In regard to the mechanisms which have been proposed to explain the catalytic effect of LIX63 on metal extraction by LIX65N, some interesting conclusions can be drawn from the monolayer studies reported here.

Fleming (17) has presented interfacial tension measurements which were interpreted to suggest that DEDO prevents the formation of an interfacially-active adduct between HBPO and the $Cu(HBPO)_2$ complex, which is more surface active than HBPO and believed to inhibit interfacial mass transfer. If the formation of such an adduct occurred and, it acted as a mass transfer barrier, one would expect to observe a proportional relationship between the collapse pressure ($\Pi_c$) and copper concentration for HBPO films. However, as Figure 5 shows, $\Pi_c$ was inversely proportional to the aqueous $Cu^{2+}$ concentration.

When the values of $\Pi_c$ are compared at $[Cu^{2+}] = 10$ mmol $dm^{-3}$, it appears that the mixed film was more stable than that of pure HBPO. Chemical analysis of the monolayer films is required before this enhanced stability can be ascribed to either a shift in the extraction equilibrium and hence a lower film conversion, or to the formation of a mixed-ligand complex.

In the mechanism proposed by Atwood et al. (18,19) and Whewell et al. (20), a proton exchange reaction between the hydroxyoxime groups of DEDO and

HBPO was believed to lead to the formation of a catalytically active HBPO anion. One might expect that this would result in surface miscibility with negative deviations from ideal behavior (i.e., occurrence of specific interactions between DEDO and HBPO, such that $\Pi_v$ is less than that predicted by Raoult's law). The fact that large deviations from ideal mixing were not observed in the present monolayer study suggests that a proton exchange reaction between interfacially adsorbed DEDO and HBPO molecules does not occur. Furthermore, with a surface pKa of about 11.5 for HBPO (10,11), deprotonation would seem to be an extremely unlikely occurrence given the acidic conditions of a copper solvent extraction circuit (~ 4.5 g $dm^{-3}$ $H_2SO_4$) (1,2).

## ACKNOWLEDGMENTS

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