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SULFONIC ACIDS: CATALYSTS FOR THE LIQUID-LIQUID EXTRACTION OF METALS

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ABSTRACT

Three sulfonic acid extractants, dinonylnaphthalene sulfonic acid (HDNNS), didodecylnaphthalene sulfonic acid (HDDNS) and di-(2-ethylhexyl) sodium sulfosuccinate (Aerosol OT, AOT) are compared as to their effects on the extraction of nickel with LIX63. The acidic extractants interact synergistically with the oxime. Interfacial tension results are presented which demonstrate that the sulfonates form reversed micelles in non-polar organic solvents. It is proposed that the reversed micelles catalyze the extraction by specific solubilization of both the metal and the extractant, resulting in an increase in the interfacial concentration of the reacting species. The ability of LIX63 to chelate with nickel without deprotonating permits the synergism to occur at low pH.

INTRODUCTION

Sulfonic acids have long been known to function as liquid ion exchange compounds (1-3). These reagents, the best known of which is dinonylnaphthalene sulfonic acid (HDNNS), have been proposed for a variety of applications including removal of cobalt and other metals from radioactive liquid wastes (4,5), separation of precious metals (6) and purification of wet phosphoric acid (7).

Recently, attention has been drawn to the use of sulfonic acids in combination with other extractants to achieve increased extraction rates and selectivities (8-14). Nyman and Hummelstedt (8) have demonstrated that the addition of small amounts of HDNNS (up to 0.01 mol dm^{-3}) increases the rate of nickel extraction with LIX70-Versatic acid mixtures. Similar results have been reported by Moore and Partridge (9) for copper extraction with LIX64N. Van Dalen and co-workers (10,11) have examined metal extraction with HDNNS-di-(2-ethylhexyl) phosphoric acid (D2EHPA) mixtures. The enhanced extraction of Ni(II) and Co(II) from acidic solutions with mixtures of HDNNS and LIX63 has been studied by several investigators (12-14).

On the basis of metal extraction and interfacial tension data, Osseo-Asare and Keeney (15) have recently proposed that the synergism observed in the LIX63-HDNNS system has an interfacial origin. The purpose of this paper is to extend this earlier discussion to mixtures of LIX63 with didodecylnaphthalene sulfonic acid (HDDNS) and with di-(2-ethylhexyl) sodium sulfosuccinate (Aerosol OT,AOT).

EXPERIMENTAL

Reagents

Commercial LIX63 was purchased from General Mills Chemicals, Inc. and was purified as described elsewhere (16,17) to give anti-5,8 diethyl-7-hydroxy-6-dodecanone oxime (HOx). HDNNS and HDDNS were supplied by King Industries, Inc. as SYNEX 1040 and 2040, respectively, and were purified according to the method of Danesi, et al. (18). AOT was obtained from Eastman Chemicals, Inc. and was used as received. All other chemicals were reagent grade and were used without further purification.

Interfacial Measurements

Interfacial tensions were measured using the du Nouy ring method. Details of the experimental procedure have been reported elsewhere (15,17).

Kinetic Measurements

Kinetic measurements were made using a stirred cell apparatus similar to the one described by Carter and Freiser (19). All measurements were made with the cell equilibrated at 25°C. Experimental determinations were made by contacting 250 ml volumes of a standardized hexane solution containing the extractants with 250 ml volumes of an aqueous nitrate solution (pH 2.5, $[Ni]=5.0\times10^{-3}$ mol dm^{-3}, 0.5 mol dm^{-3} KNO_3) and immediately dispersing the phases. Equal volumes (~2.5 ml) of the aqueous and organic phases were withdrawn at appropriate time intervals and allowed to separate. The aqueous phase was removed immediately and filtered. Nickel concentration in the aqueous phase was determined by atomic absorption spectroscopy.

Spectral Measurements

Electronic absorption spectra were recorded with a Cary 17 spectrophotometer and atomic absorption measurements were made on a Perkin Elmer 703 atomic absorption spectrophotometer.

RESULTS

Interfacial Tension Isotherms

Figures 1 and 2 show the interfacial tension behavior for the hexane/aqueous systems containing HDDNS and AOT, respectively. The isotherms are typical of surfactant species which form inverse micelles in the organic phase. The sharp change in linear behavior at low γ values marks the concentration at which the sulfonate molecules begin to aggregate into micelles (i.e., the critical micelle concentration, CMC). Sulfonate micelles have a polar core capable of solubilizing large quantities of aqueous solution. For example, an HDNNS micelle containing approximately 17 monomers/

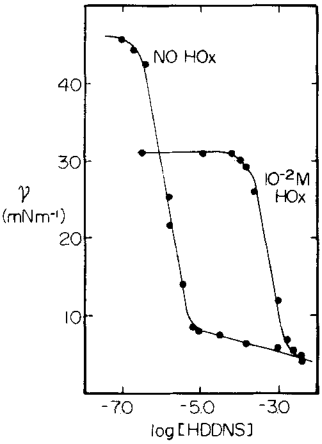

FIGURE 1. Hexane/water interfacial tension isotherms for HDDNS with and without 1.0 x 10^{-2} mol dm^{-3} HOx at 25°C. Aqueous phase at pH 2.5; ionic strength = 0.5 mol dm^{-3} (HNO_3); O/A = 1.

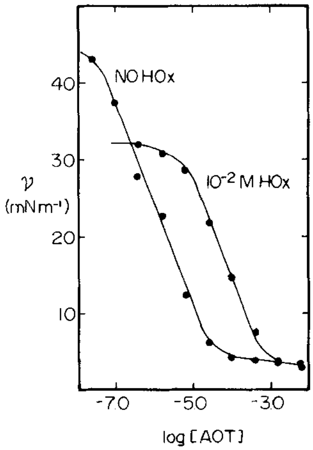

FIGURE 2. Hexane/water interfacial tension isotherms for AOT with and without 1.0 x 10^{-2} dm^{-3} HOx at 25°C. Aqueous phase at pH 2.5; ionic strength = 0.5 ml dm^{-3} (KNO_3); O/A = 1.

micelle, has a core volume of about 1650Å^3 (17). This is sufficiently large to contain about 50 water molecules. AOT micelles are known to be even larger (20).

Figures 1 and 2 also show the effect of 10^{-2}mol dm^{-3} HOx on the interfacial behavior of the sulfonates. The shifting of the CMC to higher sulfonate concentrations in the presence of HOx has also been observed in the case of the HOx-HDNNS system and has been shown to be due to preferential bulk association between the oxime and the sulfonate (15).

Extraction Behavior of HOx

The extraction characteristics of the aliphatic α-hydroxyoxime have been examined previously (21,22) and it has been reported that HOx does not extract Ni(II) appreciably at low pH values. This was confirmed in the present study by an experiment in which a 10^{-2}mol dm^{-3} HOx hexane solution was found to have a negligible effect on a 5.0 x 10^{-3}mol dm^{-3} Ni(II) aqueous solution at pH 2.5 after 1 hr contact time. Therefore, the nickel extraction due to the hydroxyoxime alone was considered to be insignificant under the experimental conditions of this work.

Effect of Sulfonate on Extraction with HOx

The extraction of Ni(II) from aqueous solution using hexane solutions of HDDNS and AOT at constant HOx concentration is presented in Figures 3-5. The results indicate that both the initial rate of extraction and the ultimate loading of the organic phase are increased dramatically in the region of the sulfonate critical micelle concentration. Similar results are obtained with HDNNS (15).

Extracted Complex Stoichiometry

Table 1 shows the [HOx]/[Ni(org)] ratios for the HOx extraction systems with HDDNS and AOT; the earlier results of the HOx-

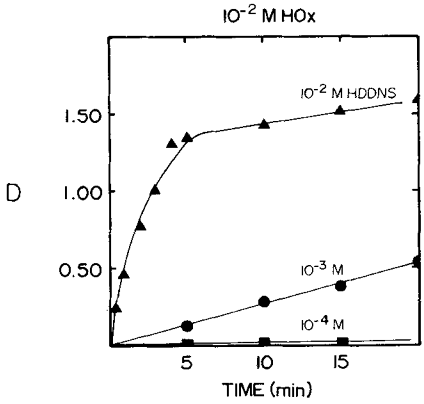

FIGURE 3. Extraction of aqueous Ni(II) (5×10^{-3} mol dm^{-3} initial) with HOx-HDDNS mixtures in hexane at 25°C. [HOx] = 1.0×10^{-2} mol dm^{-3}; initial aqueous phase at pH 2.5; ionic strength = 0.5 mol dm^{-3} (KNO_3); O/A = 1.

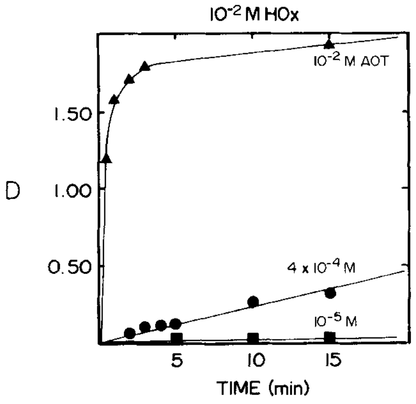

FIGURE 4. Extraction of aqueous Ni(II) (5×10^{-3} mol dm^{-3} initial) with HOx - AOT mixtures in hexane at 25°C. [HOx] = 1.0×10^{-2} mol dm^{-3}; initial aqueous phase at pH 2.5; ionic strength = 0.5 mol dm^{-3} (KNO_3); O/A = 1.

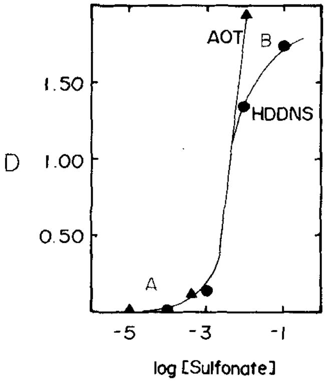

FIGURE 5. Effect of sulfonate concentration on the extraction of Ni(II) (5×10^{-3} mol dm^{-3} initial) in 5 min with HOx - sulfonate mixtures in hexane at 25°C. [HOx] = 1.0×10^{-2} mol dm^{-3}; initial aqueous phase at pH 2.5; ionic strength = 0.5 mol dm^{-3} (KNO_3); O/A = 1. A ≡ nonmicellar region; B ≡ micellar region.

HDNNS system (15) are also included for comparison. Under enhanced extraction conditions (i.e., the micellar region) in all three systems, extraction of Ni(II) occurs with a metal to oxime ratio of 1:3.

Figure 6 shows the electronic absorption spectra for the organic phases resulting from Ni(II) extractions performed under the conditions given by regions A and B of Figure 5. The spectra obtained in the HDDNS system are identical to those obtained using HDNNS. Figure 6 also shows the electronic absorption spectra for various Ni(II) complexes prepared according to procedures outlined elsewhere (17,23). These spectral results indicate that in the nonenhanced regimes (region A in Figure 5), HDNNS and HDDNS form nickel sulfonates. In the case of AOT, the similarity of the organic phase spectra with that of aqueous nickel sulfate solution suggests that nickel is extracted as solubilized ions in the micelle core. For all three mixed extractant systems, under enhanced extraction conditions (region B in Figure 5), Ni(II) appears to be extracted as the same oxime complex. Detailed

TABLE 1

Stoichiometry of the Ni(II) Complex Extracted with HOx-Sulfonate Mixtures

[Sulfonate] mol dm^{-3}	[HOx]/[Ni(org)] HDNNS[a]	AOT[b]	HDDNS[b]
1.0×10^{-1}	2.7	---	3.2
5.0×10^{-2}	2.8	3.0	---
1.0×10^{-2}	12.5	3.0	3.2
1.0×10^{-3}	50	---	4.7
4.0×10^{-4}	---	7.3	---

[a] Data from Ref. 15. [HOx] constant at 1.0×10^{-1} mol dm^{-3}; initial [Ni(aq)] = 1.0×10^{-1} mol dm^{-3}; O/A=1; ionic strength = 0.5 mol dm^{-3} (KNO_3).

[b] [HOx] constant at 1.0×10^{-2} mol dm^{-3}; initial [Ni(aq)] = 5.0×10^{-3} mol dm^{-3}; O/A = 1; ionic strength = 0.5 mol dm^{-3} (KNO_3).

investigation of the stoichiometry of the nickel oxime complex is currently in progress (23). Preliminary results indicate that it is a polymeric compound of the form $[Ni(HOx)_3](NO_3)_2 \cdot nH_2O$ in which the oxime appears to be complexed with the metal without deprotonation. This stoichiometry is in agreement with the nickel/oxime ratio of 1/3 presented in Table 1 and with an analysis reported by Tammi (24). Attempts to isolate or identify a mixed oxime-sulfonate complex have so far been unsuccessful.

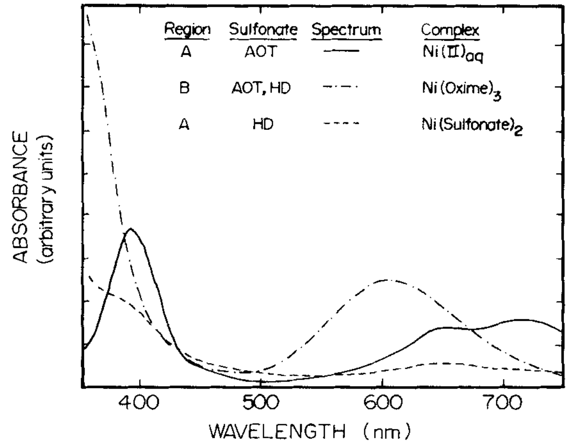

FIGURE 6. Electronic absorption spectra for (1) organic phases isolated from aqueous Ni(II) extraction using HO_x-sulfonate mixtures in hexane, and (2) Ni - oximate, Ni - sulfonate and Ni^{2+} (aq) complexes. A ≡ nonmicellar region; B ≡ micellar region.

DISCUSSION

In acidic solutions, nickel extraction with hydroxyoximes is very poor. The works of Flett, Cox and Heels (22) and Preston (25) indicate that significant nickel extraction (log D > 0) occurs only if the pH exceeds 5.5. However, as shown in the Results section above, mixtures of LIX63 (HOx) with sulfonic acids are capable of extracting nickel from pH 2.5 solutions. Even though sulfonic acids are known to be strong cation extractants in highly acidic solutions (2,3), the increased extractions reported in the present study cannot be attributed solely to nickel-sulfonate complexation. For an aqueous solution with initial pH = 2.5, the nickel distribution coefficient for an oxime-free system containing 1.0 x 10^{-1} mol dm^{-3} HDNNS has been found to be only 0.075 compared with 0.60 for a 1:1 oxime: sulfonate mixture containing 1.0 x 10^{-1} mol dm^{-3} of each extractant (15).

In the previous paper (15) it was postulated that metal extraction is enhanced as a result of the ability of sulfonate micelles to make Ni(II) more accessible for complexation by HOx. The additional experimental results presented here support this mechanism. Comparison of Figure 1 with Figure 3 and Figure 2 with Figure 4 shows that in the mixed extractant systems dramatic increases in extraction rates occur in the neighborhood of the sulfonate CMC.

Under enhanced extraction conditions the HOx-sulfonate systems are three phase consisting of an aqueous phase, an organic phase and a micellar phase. The micelles contain a large aqueous core with solubilized Ni(II). The fact that in the oxime-free AOT system the extracted nickel has been identified as residing within the micelle core suggests that Ni(II) can also be solubilized in the micelle cores of HDNNS and HDDNS. In view of the low aqueous solubility of HOx (26), it is unlikely that this extractant would be solubilized in the aqueous core. It is therefore, proposed that the oxime molecules are concentrated on the outer surface (i.e. the organic-side) of the sulfonate micelles. The reasonableness of such a location is supported by the oxime-sulfonate interaction demonstrated above in the Results section. The sulfonate micelles therefore appear to provide a concentrative effect; that is, in the micellar region, concentrations of both oxime molecules and aqueous (solubilized) nickel ions are high. Therefore, reaction rates would be expected to be also high.

For relatively high pH conditions, the complex extracted by HOx has been identified as $Ni(Ox)_2$ (22), whereas in the present study, the extracted complex appears to have the stoichiometry Ni:oxime = 1:3. A further role of the micelles might therefore be to provide conditions which lead to a preferred orientation for the complexation reaction

$$Ni(NO_3)_2\ (aq) + 3\ HOx\ (org) = Ni(HOx)_3\ (NO_3)_2\ (org)$$

Thus, in the micellar environment, the ability of the oxime to bind Ni(II) without deprotonating permits the synergistic extraction to occur at low pH.

The micellar catalyzed extraction mechanism may be summarized by the following steps (15):

1. Chelation reaction at the micellar interface:

$$Ni^{2+}(core) + 2\ NO_3^-(core) + 3\ HOx\ (int) = [Ni(HOx)_3(NO_3)_2](org)$$

2. Destruction of the micelle; loss of aqueous phase:

$$(HD)_m \cdot nH_2O(org) = nH_2O(aq) + mHD(org)$$

3. Creation of a new micelle with fresh aqueous core:

$$nH_2O(aq) + Ni^{2+}(aq) + 2NO_3^-\ (aq) + mHD(org)$$

$$= [(HD)_m \cdot Ni(NO_3)_2 \cdot nH_2O]\ (org)$$

This mechanism is oversimplified since the oxime is known to readily accept protons at low pH to give H_2Ox^+ in the organic phase (27). This charged complex would be expected to be interfacially active. In addition, the saturation of the bulk organic/aqueous interface by sulfonate molecules suggests the possibility of a competing phase transfer catalysis process. Furthermore, at very high sulfonate concentrations, it may be difficult to make a clear-cut distinction between the effects of micelles and microemulsions. Hence, additional steps in the mechanism, especially those involving diffusional and interfacial area considerations, need to be included. A more detailed analysis of the mechanistic extraction scheme requires kinetic data at constant interfacial area and information concerning the mass transport of all of the chemical species. Work is currently in progress to address these problems.

Although previous work has shown that the extraction of Ni(II) by HOx is enhanced by the presence of a sulfonic acid (12-15), these reports have made no direct attempt to identify the nature of the extracted Ni(II) complex. The ability of the aliphatic oxime to chelate with the nickel without deprotonating appears to be a significant factor in the observed synergism, since it permits extraction to occur at low pH. Preliminary work on the chemical behavior of the benzophenone oximes indicates that these extractants do not chelate unless a proton is lost from the oxime (23). It has already been shown that no enhanced extraction occurs with mixtures of the benzophenone oxime and the sulfonic acids (13).

It appears therefore that the sulfonic acids have tremendous potential as catalysts for the liquid-liquid extraction of metals if used in conjunction with the appropriate secondary extractant.

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