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Effect of Hydrophobicity and Interfacial Activity of 2-Hydroxy-5-alkylbenzophenone Oximes upon the Rate of Copper Extraction from Acidic Sulfate Solution

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ABSTRACT

The rates of copper extraction from acidic sulfate solutions with 2-hydroxy-5-alkylbenzophenone oximes of various hydrophobicities were measured by means of the drop ascending method, and they are discussed from the view of hydroxyoxime partition between both extraction phases and hydroxyoxime interfacial activity. The measured extraction rates are compared with those predicted from partition and interfacial activity data for various versions of the extraction mechanism. The ratios of specific extraction constants for oximes of various hydrophobicities are estimated for the interfacial mechanism with the preadsorption of hydroxyoximes at the hydrocarbon/water interface. The order of the specific rate constants determined for the interfacial reaction is in agreement with the order of the free energy of hydroxyoxime adsorption at the hydrocarbon/water interface.

INTRODUCTION

After more than 20 years of industrial application of hydroxyoximes for copper extraction and intensive scientific study, (1) several problems are still not solved.

In our opinion the most important unsolved problem, reviewed recently by Harada and Miyake (2) and us (3), concerns the mechanism of metal extraction with hydrophobic chelating compounds used alone or in mixtures with other chelating and nonchelating extractants.

The usual published works concern commercial extractants, without or after some kind of purification (1–10). As a result, the extraction properties of commercial hydroxyoxime extractants have been well described. However, from the data obtained it is impossible to discuss the effect of hydroxyoxime hydrophobicity upon the extraction rate and mechanism.

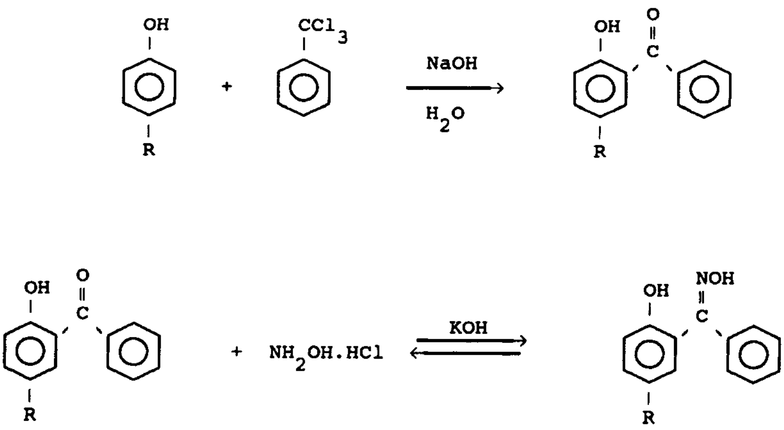
Individual model compounds have been used in only a few studies by Preston, Cox, van der Zeeuw, and our group. Thus, because we had various sets of homologous series, we decided to study the kinetics of metal extraction with homologues of different hydrophobicities by looking for relationships among extraction rates, interfacial activities, and the partition of hydroxyoximes in model extraction systems. Some such studies have been published by us (11–13).

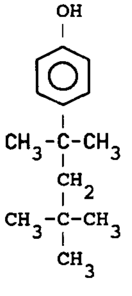
This article presents our study on the rate of copper extraction from acidic sulfate solution with 2-hydroxy-5-alkylbenzophenone oximes of various hydrophobicities. The aim of this work was to obtain kinetic data that can be used for further investigations of copper extraction, both with individual extractants and with mixtures containing extractants of another type. The effect of the hydrophobicity of α-acyloin oximes (analogs of LIX 63) upon the rate of copper extraction with 2-hydroxy-5-alkylbenzophenone oximes of various hydrophobicities will be presented in the second part of this work.

MATERIALS AND METHODS

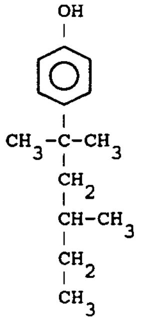
Hydroxyoximes

2-Hydroxy-5-alkylbenzophenone oximes were obtained according to the following reaction scheme (14, 15):

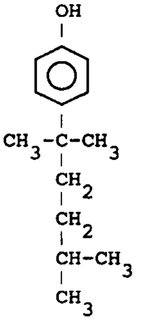




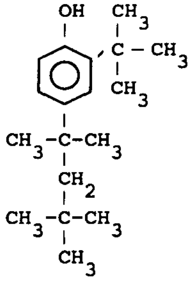
$I_R = 1697$



$I_R = 1610$



$I_R = 1769$



$I_R = 2008$

Commercial alkylphenols, 4-methylphenol (BHD, Great Britain) and 4-*t*-butylphenol (Merck Schuchardt, Germany) were used without further purification, while 4-*t*-octylphenol (Merck Schuchardt, Germany) was further crystallized. We previously demonstrated that both 4-methylphenol and 4-*t*-butylphenol contain only one compound, and their purity was estimated to be 100% (16). The purity of 4-*t*-octylphenol was estimated to be 96%. Chromatographic separation of the trimethylsilyl derivative by means of a packed column showed the presence of four components with retention indices (I_R) of 1610, 1697, 1769, and 2008. The main component of $I_R = 1697$ was identified as 4-(1,1,3,3-tetramethylbutyl)phenol. The components of $I_R = 1769$ and 2008 were identified as 4-(1,1,4-trimethylpentyl)phenol and 2-(*t*-butyl)-4-(1,1,3,3-tetramethylbutyl)phenol, respectively. The component of $I_R = 1610$ is probably 4-(1,1,3-trimethylpentyl)phenol.

(E)-Isomers of oximes of 2-hydroxy-5-alkylbenzophenone derivatives were obtained by reaction of appropriate ketones with hydroxylamine hydrochloride in the presence of KOH at room temperature. Following oximation, isomers (E) were purified by complexing them with copper and by releasing purified isomers (E) with hydrogen sulfide. Melting points and spectral data of the studied hydroxyoximes are presented below.

(E)-Oxime 2-hydroxy-5-methylbenzophenone (I): mp, 133–135°C; IR(KBr) (cm^{-1}) 3345 (OH), 1615 (C=N); ^{1}H-NMR (DMSO-d_6), (δ ppm) 11.05, 11.52 (OH), 6.54–7.57 (ArH), 2.08 (s, 3H, CH_3); ^{13}C-NMR (DMSO-d_6) (δ ppm) 155.28, 119.20, 158.91, 116.43, 129.76, 130.85, 127.05, 132.04, 128.46, 128.19, 128.57, 20.05.

(E)-Oxime 2-hydroxy-5-*t*-butylbenzophenone (II): mp 120–121°C; IR 3390, 3195 (OH), 1615 (C=N); ^{1}H-NMR 11.01, 11.50 (OH), 6.78–7.51 (ArH), 1.09 (s, 9H, CH_3); ^{13}C-NMR 155.11, 118.77, 159.02, 116.06, 126.24, 127.10, 140.55, 132.04, 128.46, 128.03, 128.46, 30.99, 33.48.

(E)-Oxime 2-hydroxy-5-*t*-octylbenzophenone (III): mp 110–111.5°C; IR 3400, 3180 (OH), 1620 (C=N); ^{1}H-NMR 11.03, 11.54 (OH), 6.77–7.52 (ArH), 0.62 (*s*, 9H, CH_3), 1.12 (s, 6H, CH_3), 1.51 (s, 2H, CH_2); ^{13}C-NMR 154.89, 118.60, 158.96, 115.78, 127.43, 127.87, 139.14, 132.15, 128.41, 127.98, 128.57, 31.15, 31.42, 31.75, 37.28, 56.08.

Extraction Rate Determination

The drop ascending method was used. Glass columns with inner diameters of 25 mm and of various lengths were used. The heights of the continuous aqueous phase in the corresponding columns were 0.085, 0.565, 0.98, and 1.6 m. The shortest column was used as the reference. The organic phase was dosed by means of a continuously working dosing pump.

The measurements were carried out at 21°C. Aqueous phases of pH 2, 3, and 4.2 adjusted with sulfuric acid contained 0.1 M $CuSO_4$. The hydroxyoxime concentration in the organic phase was in the 0.001 to 0.005 M range. Toluene was used as a diluent. In each case, 5 or 6 measurements were carried out by collecting about 10 cm^3 of the organic phase. The copper content in the organic phase before and after it was stripped with sulfuric acid was determined spectrophotometrically by using sodium diethyldithiocarbaminiane.

RESULTS AND DISCUSSION

The contact times between moving drops and the continuous aqueous phase were 16.1, 10.1, 5.9, and 1.1 seconds for column lengths of 1.6, 0.98, 0.565, and 0.085 m, respectively. The differences in this time as estimated in various experiments were usually significantly below 0.3 second. During 1 minute, 60–80 drops were formed with surface areas of 0.33–0.43 cm^2. The spherical shape of the drops was confirmed.

The linear velocity of drops in the column and their diameters were 0.096–0.1 m·s^{-1} and 0.0032–0.0037 m, respectively, which correspond to a Re number of about 330. These experimental values are in good agreement with the values predicted from Eqs. (1) and (2) (17).

$$w = \frac{d^2 g(\rho_c - \rho_d)}{18\eta_c} \frac{3\eta_c + 3\eta_d}{3\eta_d - 2\eta_c} \tag{1}$$

$$d = \left[\frac{6D_k\gamma}{(\rho_c - \rho_d)g}\right]^{0.33} \tag{2}$$

The values calculated from Eqs. (1) and (2) are 0.11 $m \cdot s^{-1}$ and 0.0034 m, respectively.

The effect of column length upon the amount of copper extracted is presented in Figs. 1 and 2. The vertical lines denote the confidence limits at a significance level of 0.05. As one can see, the relative errors are high, which is characteristic for this type of measurement. The average values, especially for 2-hydroxy-5-methylbenzophenone oxime, deviate significantly from a linear relationship.

As a result, a parabolic relationship usually approximates the experimental results better than does a linear equation. The atypical shape of the relationship obtained for 2-hydroxy-5-methylbenzophenone oxime can

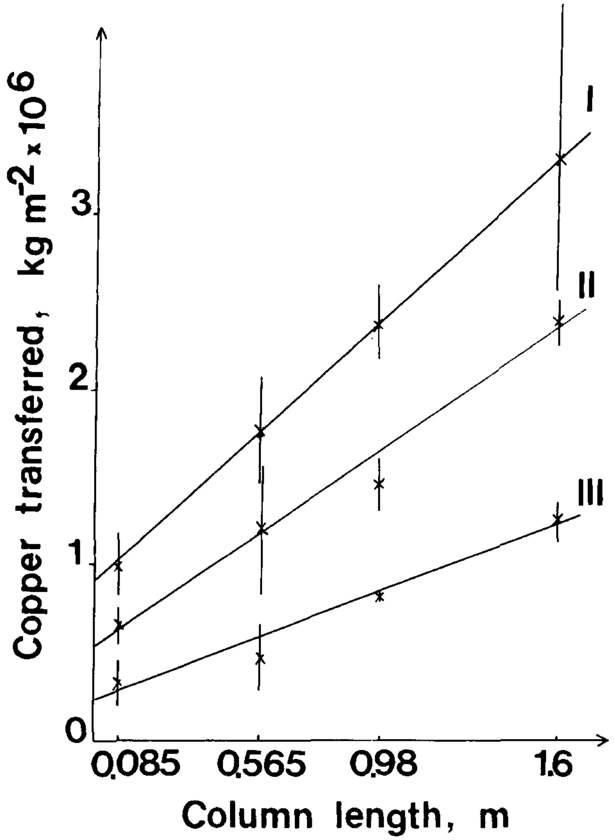


FIG. 1 Effect of column length upon copper extracted: $c_{\text{oxime}} = 0.003$ M, $c_{\text{CuSO}_4} = 0.1$ M, pH 2.

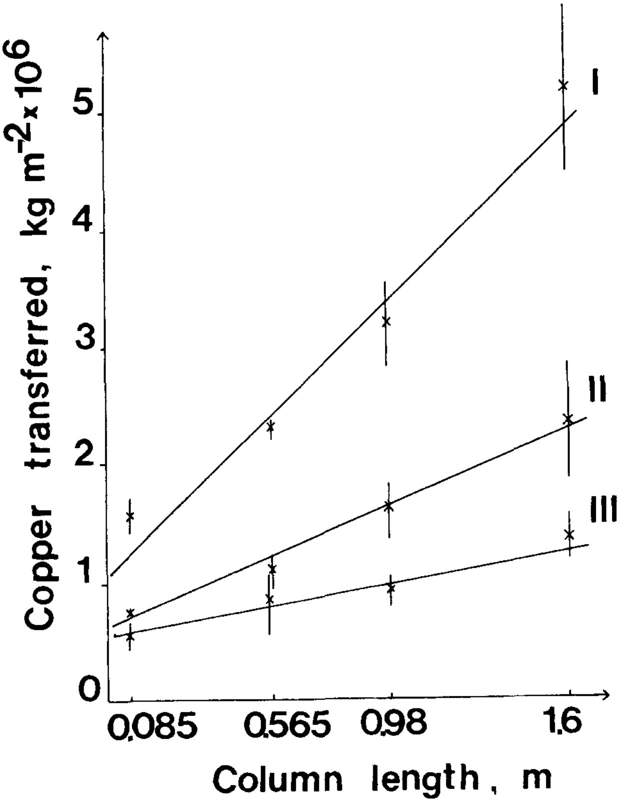


FIG. 2 Effect of column length upon copper extracted: $c_{\text{oxime}} = 0.001$ M, $c_{\text{CuSO}_4} = 0.1$ M, pH 3.

only be explained by the dissolution of this oxime in the continuous aqueous phase. This is especially important in short columns.

At pH 3, extraction occurs very quickly (the oxime concentration is three times lower than at pH 2), and after 1 second, i.e., in a column of 0.085 m length, the copper concentration in the organic phase is 4.7% above the equilibrium value, while after 16 seconds, i.e., in a column of 1.6 m length, it is equal to 9.2, 15.3, and 30.8% of equilibrium value for oximes III, II, and I, respectively.

Smaller amounts of copper were extracted at pH 2, but they were still high in comparison to the equilibrium values.

Mass transfer can occur in extraction columns: 1) during drop formation and their coalescence, 2) during a very short period of unsteady drop movement, 3) during drop movement with a steady velocity, and 4) at the interface of phase separation at the column top.

The most intensive extraction occurs during drop formation, and it is at least 2–4 times more intensive than what occurs during drop movement in the column. The percentage of copper transferred into drops during their formation is very high, especially in the two shortest columns. Even in the column 1.6 m long, the percentage is high (25–46%) (Table 1).

As a result, the shortest column was used as the reference column. Its choice significantly eliminates the effects of copper transfer during the formation of drops, their unsteady movement, and the phase separation interface at the column top.

By subtracting the amounts of copper extracted in the shortest column from those extracted in the other three columns, the amounts of copper extracted during drop movement at a constant velocity were obtained. Linear relationships (Figs. 3 and 4) were obtained with high values of regression coefficients, i.e., above 0.99. They still do not start from the zero point, but deviations are significantly lower than in the crude results presented in Figs. 1 and 2.

Experimental values of the mass transfer coefficient are given in Table 2. The mass transfer coefficients depend both upon hydroxyoxime hydrophobicity and pH, and the first effect is dominant. The highest mass transfer coefficients were obtained for copper extraction with the most hydrophilic 2-hydroxy-5-methylbenzophenone oxime at pH 3. At this pH the effect of the column length is also clearly demonstrated for the most hydrophilic 2-hydroxy-5-methylbenzophenone oxime. This effect can only be explained by some dissolution of 2-hydroxy-5-methylbenzophenone oxime, whose hydrophobicity is too small.

The rate of copper extraction can be limited by chemical or diffusion steps. The ratios of extraction rates (Table 3) are 2–4 times higher than

TABLE 1
Percentage of Copper Transferred into Drops during Their Formation

		Column length (m)		
Oxime	pH	0.565	0.98	1.6
I	2	57.7	42.6	30.6
II		54.7	44.5	28.6
III		81.1	40.6	25.6
I	3	79.6	55.6	30.6
II		70.6	47.0	33.4
III		72.5	68.4	46.6

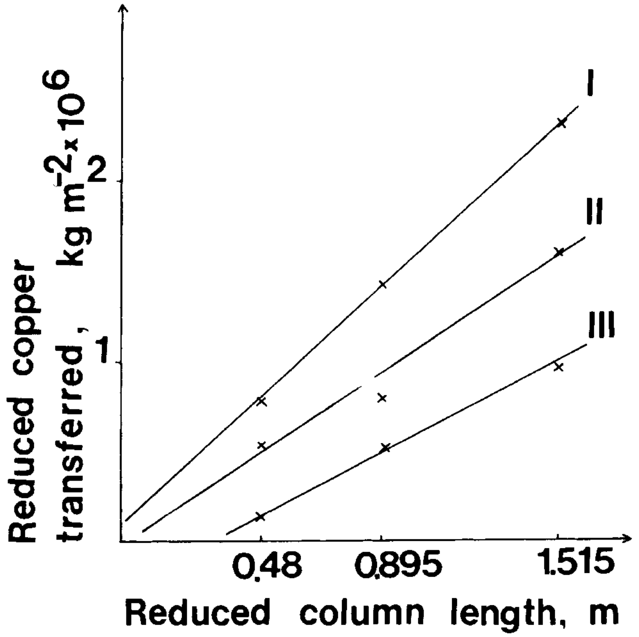


FIG. 3 Copper extracted during the movement of drops in columns: $c_{\text{oxime}} = 0.003$ M, $c_{\text{CuSO}_4} = 0.1$ M, pH 2.

TABLE 2
Experimental Values of the Mass Transfer Coefficients
k_t (m·s^{-1} × 10^6), where $k_t = \dfrac{m}{s(c_o^* - c_o)t}$

Oxime	Column (m)	pH 2	pH 3
I	1.6	6.76	9.11
	0.96	6.68	5.15
	0.565	5.65	2.95
II	1.6	3.70	4.41
	0.96	2.20	4.04
	0.565	2.60	3.75
III	1.6	1.82	2.03
	0.96	1.36	1.93
	0.565	1.43	2.04

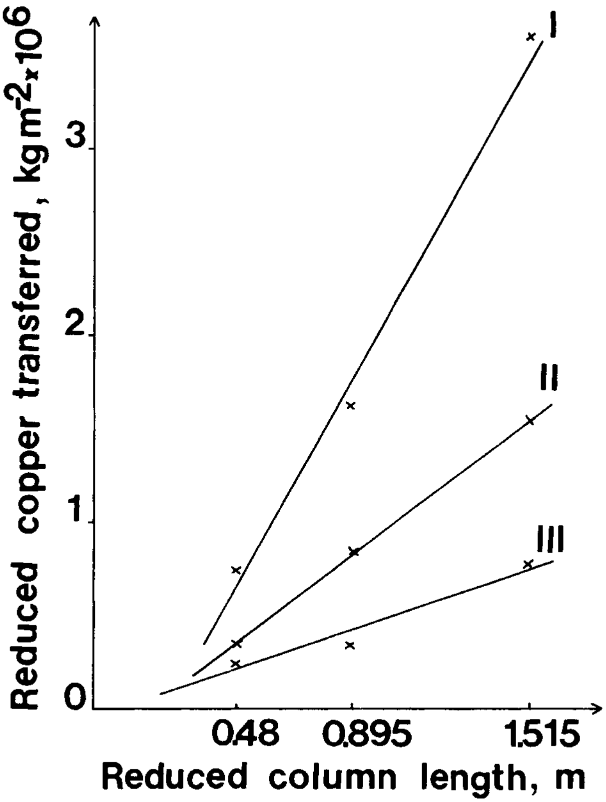


FIG. 4 Copper extracted during the movement of drops in columns: $c_{\mathrm{oxime}} = 0.001$ M, $c_{\mathrm{CuSO_4}} = 0.1$ M, pH 3.

TABLE 3
Ratios of Diffusivities (D_i/D_j) and Extraction Rates (r_i/r_j) (j = III)

		r_i/r_j	
Oxime	D_i/D_j	pH 2	pH 3
I	1.34	2.38	5.39
II	1.17	1.60	2.34
III	1.00	1.00	1.00

the ratios of the appropriate diffusivities given in the literature (20, 21) and/or calculated according to the Wilke–Chang method (20). The ratios of hydroxyoxime diffusivities change from 1 to 1.3, while the ratios of extraction rates change from 1 to 2.4 and from 1 to 5.4 at pH 2 and 3, respectively.

The importance of chemical kinetics is clearly demonstrated by the pH effect which could be neglected if extraction were limited to the mass transfer. The decrease of the extraction rate in short columns for the most hydrophilic 2-hydroxy-5-methylbenzophenone oxime is probably caused by the dissolution of the oxime in the continuous aqueous phase. This is in agreement with previous results of Hughes et al. (19) who obtained very high values of activation energy, ΔH = 40–50 kJ·mol^{-1}, which are typical for chemical processes. The values typical for diffusion processes are significantly lower, below 20 kJ·mol^{-1}.

If we consider only the chemical resistance and neglect the mass transfer processes, then two different reaction mechanism options can be discussed. In the first one, the traditional mechanism in the aqueous phase with the transfer of extractant molecules into the aqueous phase, there is a complexation reaction, and the transfer of complex molecules into the organic phase must be considered. By taking into account the low acidity constants and kinetic calculations of Flett (24), it is possible to neglect the dissociation of the phenolic group of hydroxyoximes. The dehydration reaction can also be neglected for copper extraction. In toluene, the association of hydroxyoximes can also be neglected. Thus

$$\mathrm{HL}_o = \mathrm{HL}_w \tag{3}$$

$$\mathrm{Cu}_w^{2+} + \mathrm{HL}_w = \mathrm{CuL}_w^+ + \mathrm{H}_w^+ \tag{4}$$

$$\mathrm{CuL}_w^+ + \mathrm{HL}_w = \mathrm{CuL}_{2w} + \mathrm{H}_w^+ \tag{5}$$

$$\mathrm{CuL}_{2w} = \mathrm{CuL}_{2o} \tag{6}$$

Assuming Eq. (5) is the limiting reaction, the following kinetic equation is obtained:

$$r = \frac{k[\mathrm{Cu}^{2+}]_w[\mathrm{HL}]_w^2}{[\mathrm{H}^+]_w} \tag{7}$$

which is in agreement with some kinetic data (5, 6, 10, 14).

For reactions in the aqueous phase, it is possible to assume that the effect of the alkyl group upon the specific rate constant may be neglected. The alkyl group is far from the chemically active groups, and it does not affect their activities. Thus, for two different hydroxyoximes, and at the same extraction conditions, i.e., the same reagent concentrations, the

TABLE 4
Experimental Relative Rates of Copper Extraction and Those Predicted by Assuming Complexation in the Aqueous Phase

Oxime		r_i/r_j		
$(HL)_i$	$(HL)_j$	pH 2	pH 3	$[(HL)_i/(HL)_j]^2$
I	II	1.5	2.3	13.8
I	III	2.4	5.4	191
II	III	1.6	2.3	13.8

ratio of extraction rates should be proportional to the square of the hydroxyoxime concentrations in the aqueous phase:

$$\frac{r_i}{r_j} = \frac{[(HL)_i]_w^2}{[(HL)_j]_w^2} \tag{8}$$

This means that the reaction rate should significantly depend upon hydroxyoxime hydrophobicity, and according to the data given in Table 4, 2-hydroxy-5-methylbenzophenone oxime should extract copper about 200 times quicker than 2-hydroxy-5-*t*-octylbenzophenone oxime. The following partition coefficient values were used for calculations: $\log P_{\mathrm{I}} = 3.44$, $\log P_{\mathrm{II}} = 4.01$, and $\log P_{\mathrm{III}} = 4.58$ (25). In reality, the effect of hydroxyoxime hydrophobicity upon the extraction rate is small, and depending upon the acidity of the aqueous phase, oxime I extracts copper only 3–5 times quicker than oxime III.

As the second option, the reaction at the interface or at the aqueous film near the interface can be considered. The experimental techniques now attainable do not allow these two versions to be differentiated. According to the literature data (1–10), the following reaction scheme can be considered.

$$Cu_w^{2+} + HL_{ad} = CuL_{ad}^+ + H_w^+ \tag{9}$$

$$CuL_{ad}^+ + HL_w = CuL_{2ad} + H_w^+ \tag{10}$$

$$CuL_{2ad} + 2HL_o = CuL_{2o} + HL_{ad} + HL_w \tag{11}$$

Agreement with the kinetic data is obtained when Eq. (10) is considered as limiting the reaction rate. In this case, the following kinetic equation is obtained:

$$r_s = k_s A_s \frac{[Cu^{2+}]_w [HL]_{ad} [HL]_w}{[H]_w^+} \tag{12}$$

where A_s is the interfacial surface area.

Hydroxyoxime concentration at the interface can be estimated by using the Gibbs and Szyszkowski isotherms:

$$\Gamma = -\frac{1}{RT}\frac{d\gamma}{d\ \ln[\mathrm{HL}]_o} \tag{13}$$

$$\gamma = \gamma_0\left[1 - B\ln\left(\frac{[\mathrm{HL}]_o}{A} + 1\right)\right] \tag{14}$$

Thus,

$$\Gamma = \frac{B\gamma_0}{RT}\frac{[\mathrm{HL}]_o}{[\mathrm{HL}]_o + A} \tag{15}$$

where A and B are the adsorption coefficients. The surface excess equals the interfacial concentration, $\Gamma = [\mathrm{HL}]_{ad}$.

The ratio of extraction rates of two different hydroxyoximes is given by

$$\frac{r_{si}}{r_{sj}} = \frac{k_{si}}{k_{sj}}\frac{P_j}{P_i}\frac{[\mathrm{HL}_i]_o^2}{[\mathrm{HL}_j]_o^2}\frac{([\mathrm{HL}_j]_o + A_j)}{([\mathrm{HL}_i]_o + A_i)} \tag{16}$$

By introducing the total concentration,

$$[\mathrm{HL}]_o = \frac{P}{P+1}[\mathrm{HL}]_{tot} \tag{17}$$

into Eq. (16), the following relation is obtained:

$$\frac{r_{si}}{r_{sj}} = \frac{k_{si}}{k_{sj}}\frac{P_i}{P_j}\frac{(P_j + 1)}{(P_i + 1)}\frac{B_i}{B_j}\frac{\{P_j[\mathrm{HL}]_{tot} + A_j(P_j + 1)\}}{\{P_i[\mathrm{HL}]_{tot} + A_i(P_i + 1)\}} \tag{18}$$

Thus, it is assumed that the extractant in partitioning is at equilibrium and that the volume of the initial organic phase does not change after mixing with the aqueous phase, i.e., the phases are totally immiscible.

Adsorption coefficients B and A can be calculated from the interfacial tension data, as described in our previous work (26–30). The values of these coefficients were also given in these works.

Thus, coefficient B_{ij}, defined by Eq. (19),

$$B_{ij} = \frac{P_i}{P_j}\frac{(P_j + 1)}{(P_i + 1)}\frac{B_i}{B_j}\frac{\{P_j[\mathrm{HL}]_{tot} + A_j(P_j + 1)\}}{\{P_i[\mathrm{HL}]_{tot} + A_i(P_i + 1)\}} \tag{19}$$

can be calculated for various combinations of hydroxyoximes. As a result, the ratio of the specific rate constants can be estimated:

$$\frac{k_{si}}{k_{sj}} = \frac{r_{si}}{r_{sj}}\frac{1}{B_{ij}} \tag{20}$$

TABLE 5

B_{ij} Coefficient and Relative Ratio of Specific Rate Constants for Interfacial Reaction Calculated from the Szyszkowski Isotherm

Oxime				
HL_i	HL_j	pH	B_{ij}	k_{si}/k_{sj}
I	II	3	5.34	0.43
		2	4.51	0.33
I	III	3	20.30	0.27
		2	19.92	0.12
II	III	3	4.40	0.53
		2	5.11	0.31

The values of B_{ij} and k_{si}/k_{sj} obtained are given in Table 5. The B_{ij} coefficient assumes positive values in the 4.4–5.3 range for both the set of oximes I and II and for the set of oximes II and III. B_{ij} is equal to about 20 for the set of I and III oximes. The effect of aqueous phase acidity is small and almost negligible. Thus, the B_{ij} coefficient assumes higher values than the ratio of appropriate extraction rates. As a result, the k_{si}/k_{sj} ratios are below unity and in the 0.12–0.53 range.

Similar values of B_{ij} and k_{si}/k_{sj} were estimated when other adsorption isotherms/equations (i.e., the Temkin isotherm, the spline function, and the polynomial) were used for computing (Tables 6–8).

This surprising result means that the specific rate constants so estimated for the interfacial process drop when hydroxyoxime hydrophobicity decreases, although the rate of extraction rises. Thus, the extraction rate increase is significantly lower than expected from the partition and interfacial activity data. However, these differences are much smaller than in the case of the bulk aqueous mechanism discussed previously.

TABLE 6

B_{ij} Coefficient and Relative Ratio of Specific Rate Constants for Interfacial Reaction Calculated from the Temkin Isotherm

Oxime				
HL_i	HL_j	pH	B_{ij}	k_{si}/k_{sj}
I	II	3	4.26	0.54
		2	4.10	0.37
I	III	3	20.10	0.27
		2	19.72	0.12
II	III	3	4.71	0.49
		2	4.81	0.33

TABLE 7

B_{ij} Coefficient and Relative Ratio of Specific Rate Constants for Interfacial Reaction Calculated from the Spline Functions

Oxime				
HL_i	HL_j	pH	B_{ij}	k_{si}/k_{sj}
I	II	3	4.93	0.47
		2	4.45	0.34
I	III	3	19.12	0.28
		2	20.24	0.12
II	III	3	3.88	0.59
		2	4.55	0.35

It is interesting that the order of the specific rate constants so estimated are in agreement with the values of the Gibbs free energy of adsorption, ΔG^{ad}, estimated from the Szyszkowski adsorption coefficient (31). Values of ΔG^{ad} equal to -19.03, -23.14, and -26.15 kJ·mol^{-1} were obtained for oximes I, II, and III, respectively. Thus, the hydroxyoxime adsorbs more strongly at the interface with an increase of alkyl chain length and adsorbed hydroxyoxime molecules, and the intermediate 1:1 complex molecules probably also have better orientation at the interface and are better prepared for the reaction to begin. As a result, higher values of the specific extraction rate are obtained for more hydrophobic compounds.

One can argue that the observed order of specific rate constants of the interfacial process is caused by the effect of the diffusion steps. However, we found that similar orders of specific rate constants are obtained when the kinetic results determined by other techniques, including the Lewis cell method, the AKUFVE method (32), and the short contact method (33), are taken into consideration.

TABLE 8

B_{ij} Coefficient and Relative Ratio of Specific Rate Constants for Interfacial Reaction Calculated from Polynomial of the Third Order

Oxime				
HL_i	HL_j	pH	B_{ij}	k_{si}/k_{sj}
I	II	3	3.83	0.60
		2	4.04	0.37
I	III	3	15.78	0.34
		2	19.37	0.12
II	III	3	4.12	0.56
		2	4.79	0.33

NOTATION

A, B	Szyszkowski adsorption constant
A_s	interfacial surface area
c	copper concentration
D	diffusivity
D_k	capillary diameter
d	drop diameter
γ	interfacial tension
γ_0	interfacial tension for oxime concentration equal zero
g	acceleration of gravity
HL	hydroxyoxime
Γ	surface excess
k_t	mass transfer coefficient
k_r	specific rate constant
m	mass of extracted copper
P	partition coefficient
r	extraction rate
ρ_c	density of continuous phase
ρ_d	density of drop
η_c	viscosity of continuous phase
η_d	drop viscosity
R	gas constant
S	interfacial surface area
T	absolute temperature
t	extraction time
w	linear velocity of drop

Subscripts and Superscripts

o	organic phase
w	water phase
i, j	compound number
tot	total
ad	adsorbed
s	interfacial process
v	volume process
d	drop
c	continuous phase
$*$	equilibrium value

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