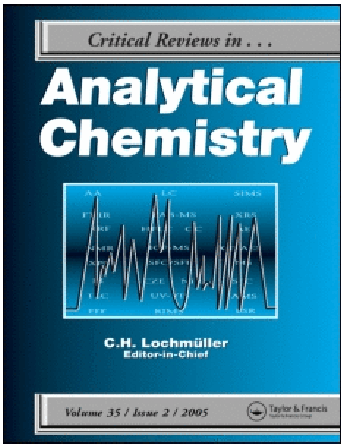

Critical Reviews in Analytical Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713400837

Physiochemical Modification of Extractants

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To cite this Article Szymanowski, Jan(1995) 'Physiochemical Modification of Extractants', Critical Reviews in Analytical Chemistry, 25: 3, 143 — 194
To link to this Article: DOI: 10.1080/10408349508050560
URL: http://dx.doi.org/10.1080/10408349508050560

Critical Reviews in Analytical Chemistry, 25(3):143–194 (1995)

Physicochemical Modification of Extractants

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ABSTRACT: The self-association of alcohols and alkylphenols in hydrocarbon solutions, their association with extractants, especially with hydroxyoximes, and adsorption of modifiers at hydrocarbon/water interfaces in systems containing only modifiers and mixtures of modifiers and extractants are reviewed. Considering these processes, it is possible to successfully model metal extraction and to explain the modifier effects on the equilibrium and kinetics of metal extraction. The models for association of extractants with modifiers, their coadsorption at the liquid/liquid interfaces, and metal extraction with extractant-modifier mixtures are presented. Modifiers affect metal extraction both thermodynamically and kinetically by changing the concentration of the extractant active species and by blocking the interface that can be completely occupied by modifier-adsorbed molecules.

KEY WORDS: metal extractants, modification, association, adsorption.

I. INTRODUCTION

Extraction properties of various extractants can be significantly changed by modifiers containing oxygen atoms in their structures. They are often used to prevent formation of a second organic phase; however, they also affect the equilibrium and kinetics of extraction. In some cases, the introduction of a modifier into an extraction system leads to suppression of extraction; in others, synergism takes place. Thus, they can be used to modify the extraction properties of extractants.

High molecular alcohols and alkylphenols, for example, tridecanol and/or nonylphenol, are often used, as in the case of commercial hydroxyoxime extractants, for example, **ACORGA P 5100, ACORGA P 5200, ACORGA P 5300, ACORGA PT 5050,** and **LIX 622.** Their introduction decreases the extraction capacity of hydroxyoximes but, at the same time, facilitates stripping.[1–7] Extraction isotherms become less steep and the equilibrium concentration of copper decreases in the organic phase, particularly in the region of low copper concentrations in the aqueous phase. In parallel, stripping isotherms, which are nearly straight lines, become shifted toward lower copper levels in the organic phase. Thus, in the presence of a modifier in appropriate amounts, higher quantities of copper may be transferred in the extraction-stripping cycle when compared with the system in which oximes of salicyl aldehyde-type extractants are used alone. Commercial **ACORGA P 5100, ACORGA PT 5050,** and **LIX 622** are appropriate examples.

Tridecanol affects copper extraction equilibrium with hydroxyoximes, **ACORGA P 5100** and **LIX 622,** more strongly than nonylphenol, **ACORGA PT 5050.** As a result, tridecanol can be applied in half the amount required for nonylphenol. In **ACORGA PT 5050,** the hydroxyoxime (**P 50**)/tridecanol ratio is 2:1 and the product exhibits extraction properties similar to those

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of **ACORGA P 5100,** in which the **P 50/** nonylphenol ratio is 1:1. Ester-type modifiers affect extraction properties of salicyl aldoxime extractants in a similar way. The presence of acidic alkylphenols is undesireable when extraction is carried out using ammonia solutions. The addition of nonylphenol to **P 50** extractant drastically augments ammonia transfer to the organic phase.[11]

Modifiers, negatively influence the rates of extraction and stripping.[1,5,8-10] As a result, copper extraction rates with the commercial extractants **ACORGA P 5100, ACORGA PT 5050,** and **LIX 64N** are fully comparable, even if higher than extractants containing only salicyl aldoxime derivatives.

Indium and ferric ions are strongly extracted with bis(2-ethylhexyl)phosphoric acid (HDEHP), and excessive quantities of strong mineral acids (e.g., 8 to 9 *M* HCl) are required for stripping.[12] Handling of such concentrated acids on an industrial scale poses difficult problems in terms of safety, waste disposal, corrosion, and cost. However, the addition of 5 to 10% v/o of trialkylphosphine oxides, **Cyanex 923** or **Cyanex 925,** depresses the indium extraction markedly at high acidities (>50 g/l sulfuric acid). The branched chain trialkylphosphine oxides, **Cyanex 925,** is more affective (at a lower concentration) than its straight chain homologs, **Cyanex 923.** As a result, stripping is possible with relatively weak acids (e.g., 2 *M* H_2SO_4). The presence of phosphine oxides also prevents the accumulation of a difficult-to-strip ferric ion complex in the solvent, which is observed when HDEHP is used alone or in a mixture with tributylphosphate (TBP).

Analogous results were reported for the extraction of other metals, e.g., cobalt using *bis*(2,4,4-trimethylpentyl) phosphinic acid and isodecanol,[13] uranium using triisooctylamine and trioctyl phosphine oxide,[14] and HDEHP combined with straight and branched chain phosphine oxides,[15] that is, trioctyl and tri(2-ethylhexyl)posphine oxides. This last system exhibits synergy and is exploited commercially in the extraction of U(VI) from wet-process phosphoric acid. Alcohols and ketones also affect the extraction of bismuth, indium, zinc, and cobalt with amine-type extractants and with TBP.[16-19] A decrease or an increase of the extraction can be observed in the presence of modifiers.

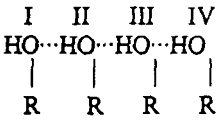
The following selected examples clearly demonstrate the importance of modifiers in formulating commercial extractants whose properties can be significantly changed, and improved, by appropriate selection of a modifier-type and its amount. The effect of modifiers on extraction properties of extractants may be connected with their abilities for self-association, association with extractant molecules, and adsorption at hydrocarbon/water interfaces; these phenomena are discussed in this review. However, in some cases, modifiers can also interact with extracted complexes and metal ions forming appropriate solvates/mixed complexes in the organic phase, as in the case of bismuth extraction from chloride media with trialkylbenzylamine in the presence of alcohol.[17] These problems are not discussed here.

II. SELF-ASSOCIATION OF MODIFIERS

Alcohol molecules that have hydroxyl groups can act both as an electron donor and electron acceptor. As a result, they can undergo self-association in nonpolar solvents, such as hydrocarbons used in solvent extraction. The literature on the self-association of alcohols in nonpolar solvents does not present a uniform picture.[7,20-40] This is connected to the uncertainty about the degree of polymerization and the importance of linear and cyclic structures. This causes confusion and controversy in the interpretation of experimental data for self-associated systems. Various models[20] can be well matched to the experimental data and the best fit does not prove the validity of the model. Depending upon the model considered, different conclusions may be drawn and various values of self-association constants determined.

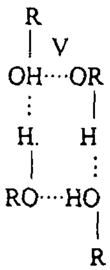
In general, alcohols are thought to associate into a series of n-mers. There have been several attempts at classifying the n-mers and at evaluating the equilibrium constants between the monomer and each n-mer. Both linear (acyclic) and cyclic n-mers have been postulated. Various methods, including ultrasonics,[23] dielectric,[24] spectrophotometric,[20-22,25,36-40] vapor pressure,[26] equation of state,[27] methyl radical abstraction,[28] NMR,[29,34,36,39,40] and calorimetry[30] have been used with ambiguous results.

Infrared (IR) spectra show a sharp monomer O–H stretch band at low alcohol concentrations in hydrocarbons and a broad band characteristic for associated species, whose intensity grows with concentration. These bands are at a higher energy than those observed for hydroxyoxime extractants[1,7,41] and are observed at 3650 and 3525 cm^{-1}, respectively.[7] The broad band is attributed in several papers to the presence of OH···OH dimers.[33-35,38] Freiser et al.[7] attribute it to the alcohol trimer. An opposing interpretation is given in the comprehensive studies of Fletcher and Heller[25] and Cáceres-Alonso et al.[30] They state that hydrocarbon solutions contain mainly alcohols in the form of monomer and tetramers. According to Fletcher and Heller,[25] tetramers can be linear and cyclic. Their relative ratio depends on the alcohol concentration, its structure, temperature, and type of solvent. The monomer-tetramer model is also proposed by Dixan[39] for methanol association.



1

Linear tetramer



2

Cyclic tetramer

Tetramer content increases with alcohol concentration and decreasing temperature. At 25°C in a system containing 1-decanol and *n*-decane, tetramers are the predominant species at an alcohol concentration >4%.[30] At an alcohol concentration near 4%, the contents of monomers and tetramers are each near 50% v/v. Dimers are essentially absent in over the entire range of alcohol concentration. The self-association of 1-octanol can be observed as soon as the total concentration becomes greater than about 0.01 *M*.

Fletcher and Heller[25,37] state that the band in IR spectra often attributed to the dimer species is unequivocally due not to an OH···OH dimer, but rather to some species whose concentration is proportional to the concentration of a monomer, possibly an alcohol-hydrocarbon complex. However, in systems containing branched alcohols (e.g., 4-propyl-4-heptanol) monomers are predominant even at high alcohol concentrations >10%. The content of tetramers falls, and dimers are present in solution.[25,30] At a 10% solution of 4-propyl-4-heptanol in *n*-decane at 25°C, the content of monomer, dimer, and tetramers can be estimated as equal to about 60, 20, and 15% v/v, respectively.[29] The dimer, trimer, and tetramer formation constants of 5-decanol in *n*-decane are equal to 0.3 M^{-1}, 6.0 M^{-2}, and 24 M^{-3}, respectively (in the original text, the constants are expressed as volumetric constants).[30]

For 0.05 *M* iso-octanol in dry heptane, no IR adsorption bands appear in the range 2500 to 3600 cm^{-1}. This proves that no associates of iso-octanol are formed up to that concentration. However, at higher concentrations (e.g., 0.157 *M*), two bands appear: one at 3500 cm^{-1} belonging to linear dimers and one at about 3280 to 3380 cm^{-1} belonging to higher aggregates. Thus, for branched alcohols, the concentration of tetramers is severely reduced and the lower species, i.e., trimers and dimers, are more important. Monomers are the predominant species for highly hindered alcohols, reflecting the decrease of self-association that steric hidrance of the hydroxyl group imposes on them. Secondary and tertiary alcohols form weaker H-bonds than primary alcohols. This is in agreement with data of Freiser et al.,[7] who observed a strong association of n-tridecanol but did not observe any aggregation of 2-(1,3-trimethylbutyl)-5,7,7-trimethyloctanol.

The linear tetramer contains three different hydrogen bonds and four different hydroxyl groups. HO(I) can be called a free hydroxyl group, whereas the others are associated but they are not identical as the H and the O are hydrogen bonded to slightly different species. The group I differs significantly from the others. For the cyclic tetramer, all four HO groups and hydrogen bonds are equivalent. The HO(V) group appears to adsorb at a slightly shorter wavelength and thus involves weaker hydrogen bonds. Tetramers can be the main species only when they are formed in reactions involving large-scale constants or alternatively disappear in slow reactions. Higher acidity of the terminal hydrogen on oligomers provides a strong driving force toward association. This would normally lead to pentamers and higher oligomers. However, if a pentamer can react to yield a cyclic tetramer and monomer, the proposed model can be explained by the assignment of reasonable rate constants. The reaction must be rapid for the linear pentamer to lose a monomer and form a cyclic tetramer.

$2ROH = (ROH)_2$ rapid (1)
$(ROH)_2 + ROH = (ROH)_3$ rapid (2)
$(ROH)_3 + ROH = (ROH)_4$ rapid (3)
$(ROH)_3 + ROH = (ROH)_4$ rapid (4)
$\text{Cyclic-}(ROH)_4 + ROH$
$= (ROH)_5$ slow (5)

Reactions 1 to 4 are shifted to the products, whereas Reaction 5 is shifted to the substrates.

The equilibrium constants for linear tetramer and cyclic tetramer formation of octanol in *n*-decane (Table 1) are comparable for both species and decrease when the temperature rises. The temperature increase diminishes alcohol association.

At 30°C, the equilibrium constants for total tetramer formation are given as equal to 490 and 430 M^{-3} for l-octanol and l-butanol, respectively, in *n*-decane[25] and 312 M^{-3} for the slightly hindered *t*-butanol in cyclohexane.[23] At 15°C, the value of the tetramer formation constant for l-octanol is near 2000 M^{-3}. In carbon tetrachloride, the self-association is found to be significantly lower than in *n*-decane, yet does not appear to change to any great extent for ethanol, 2-propanol, and phenol.[25]

TABLE 1
Equilibrium Constants for Linear and Cyclic Tetramers Formation (1-Octanol, *n*-Decane)

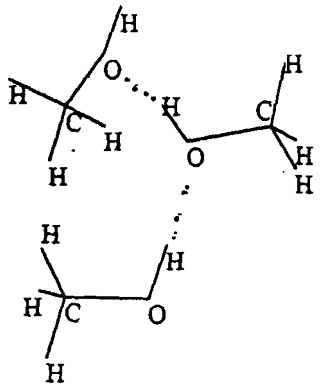
Temperature (°C)	Linear tetramer (M^{-3})	Cyclic tetramer (M^{-3})
5	1.73×10^2	5.98×10^2
15	6.41×10^2	1.75×10^2
30	1.63×10^2	3.24×10^2
45	4.72×10	7.02×10
75	5.46	4.89
100	1.17	7.36×10^{-1}

From Fletcher, A. N. and Heller, C. A., *J. Phys. Chem.*, 71, 3742, 1967. With permission. ©American Chemical Society.

The thermodynamic parameters given in Table 2 demonstrate the eager formation of 1-octanol tetramers and the shift of equilibrium toward a cyclic tetramer.[25]

Semiempirical molecular modeling carried out for isolated molecules in vacuum (Table 3) confirms the experimental results of Fletcher and Heller discussed above. The PM3 heat of formation per one alcohol molecule becomes more negative with an increase of association degree both for linear and cyclic associates. The heat is more negative for linear associates in comparison to cyclic associates for the first three species. However, the cyclic tetramer has the more negative heat of formation than the linear one. The optimized structures of these associates are as follows.

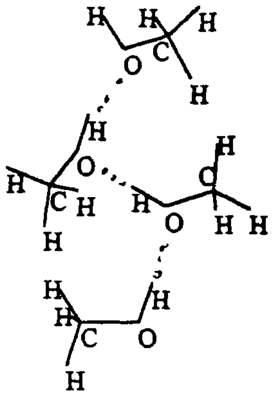
The association constants for phenols having various substituents are also reported in the literature.[25,42-48] The more acidic phenol shows a higher association number than ethanol, but according to Fletcher and Heller,[25] the equilibrium constants for tetramer formation change only by a factor of 2. They are equal to 70 and 45 M^{-1} at room temperature. The average association number λ of alkylphenols that have a short alkyl (ethyl-butyl) at 25°C in cyclohexane increases from about 1.2 to 3.2 when the true molar fraction of phenol [$(x = \sum {}_i n_i/(\sum {}_i n_i + n_s)$, where n_i and n_s denote numbers of moles of various mers of alkylphenol and of the solvent, respectively)] rises from 5×10^{-2} to 2.5×10^{-2} (Figure 1).[47] The polymerization constants (Table 4) are larger than the dimer-



3

Linear trimer

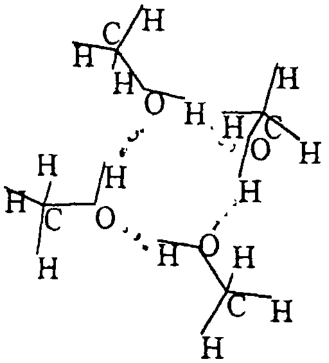
ΔH = -227.229kJ/mol



4

Linear tetramer

ΔH = -229.995 kJ/mol



5

Cyclic tetramer

ΔH = -231.277 kJ/mol

ization constants. This suggests the occurrence of chain-like associations with the absence of cyclic dimers at least, and is supported by the association studies of chlorophenols at various temperatures. The enthalpies of polymerization [(PhOH + (PhOH)$_i$ = (PhOH)$_{i+1}$, i $\geq$2)] are more negative than the enthalpies of dimerization [(PhOH + PhOH = (PhOH)$_2$)], for example, –13 and –19 kJ/mol^{-1} for 3-chlorophenol and –4 and –19 kJ mol^{-1} for 4-chlorophenol, respectively.[47] The effect of substituents on self-association of phenol derivatives is equivocal. Some authors[42–44,47,48] state that the self-association of phenols is lowered by substituents (Table 4), whereas others present the opposite data,[46] for example, the latter demonstrate that the association of 4-methylphenol is stronger than that of phenol.

The data presented relate to models of high chemical purity and anhydrous solvents; thus, the systems remote from the reality of extraction processes. Extractants are often complex mixtures containing an active substance and a modifier. The extractant molecules contain chemically active groups that can interact with modifier molecules. Moreover, in the extraction system, the hydrocarbon phase is saturated with water, whose molecules interact with both extractant and modifier molecules, forming various hydrates. Thus, competition is observed between various molecules forming self-associates, associates, and hydrates, and, as a result, the self-association of modifiers as well as extractants can be significantly diminished or even negated in actual extraction systems.

TABLE 2
Thermodynamic Parameters for Linear and Cyclic Tetramers Formation (1-Octanol, *n*-Decane)

Reaction	$-\Delta H^\circ_{298}$ (kJ/mol)	$-\Delta S^\circ_{298}$ (J/mol deg)	$-\Delta G^\circ$ (kJ/mol)
$4ROH=(ROH)_4$linear	68.97	148.8	24.70
$4ROH=(ROH)_4$cyclic	84.85	195.6	26.63
$(ROH)_4$linear$=(ROH)_4$cyclic	15.88	46.8	1.92

From Fletcher, A. N. and Heller, C. A., *J. Phys. Chem.*, 71, 3742, 1967. With permission. ©American Chemical Society.

TABLE 3
PM3 Heat of Formation of Methanol Associates (Calculated per One Alcohol Molecule)

Type of associate	Association degree	Relative heat of formation (kJ/mol)
Linear	Monomer	–217.2
Linear	Dimer	–222.6
Linear	Trimer	–227.2
Linear	Tetramer	–230.0
Cyclic	Dimer	–215.3
Cyclic	Trimer	–225.8
Cyclic	Tetramer	–231.3

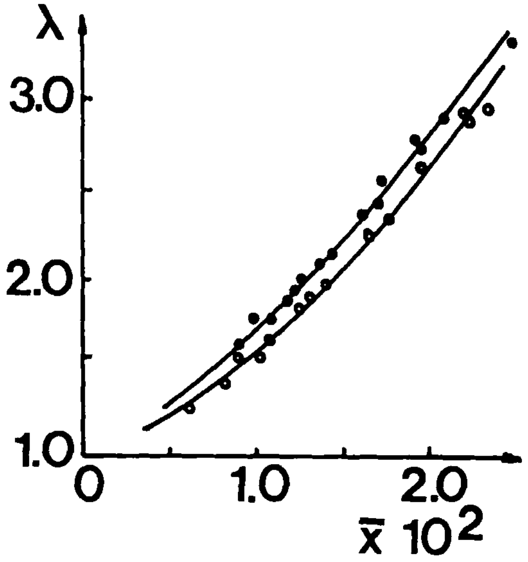


FIGURE 1. Mean association number of 4-*n*-propylphenol (○) and 4-ethylphenol (●) in cyclohexane at 298.15 K vs. true molar fraction of the phenol). (From Barela, R. and Buchowski, H., *Fluid Phase Equilibria,* 59, 99, 1990. With permission.)

TABLE 4
Association Constants of Some Substituted Phenols in Cyclohexane (25°C, molar fractions are used)

Phenol	Dimerization constant PhOH + PhOH = $(PhOH)_2$	Association constant PhOH + $(PhOH)_i$ = $(PhOH)_{i+1}$, $i \geq 2$
3-Ethylphenol	64	82
4-Ethylphenol	49	80
4-t-Butylphenol	35	48
4-n-Propylphenol	32	74
4-i-Propylphenol	20	72

From Barela, R. and Buchowski, H., *Fluid Phase Equilibria,* 39, 293, 1988.

III. SELF-ASSOCIATION OF EXTRACTANTS

This discussion is limited mainly to hydroxyoxime extractants, whose ability for self-association, contrary to various phosphoric and carboxylic acids, is of an order similar to that of modifiers. It is an interesting and most important case in that it allows strong modification of extraction properties in the presence of modifiers.

Chelating extractants often form dimers, but only in nonsolvating diluents. Higher associates are rarely found. They exist as monomers in solvating diluents, such as aromatic hydrocarbons and chloroalkanes. In organic diluents, hydroxyoximes undergo association (Table 5).[1] The mean associa-

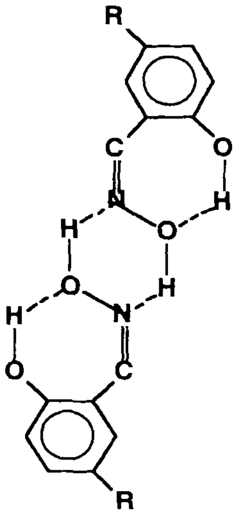
TABLE 5
Mean Association Numbers of Hydroxyoximes ($M_{exp}/M_{monomer}$) in Different Dilutes

Hydroxyoxime	Diluent	Oxime conc. (M)	Temp. (°C)	Association number	Ref.
Aromatic (with phenolic group)	Toluene	0.02	30	1.01–1.04	49
	Toluene	<0.1	37	1.0	50
	Toluene	<0.025	25	1.1	51, 52
	Toluene	0.01–0.04	—	1.09–1.14	53
	Toluene	0.05–0.3	25	1.2	51, 52
	Benzene	0.05–0.2	—*	1.0–1.17	54
	Benzene	<0.15	25	1.1	51, 52
	Cyclohexane	0.05–0.25	—*	1.0	55
	Chloroform	<0.1	25	1.1	51, 52
	Heptane	<0.01	37	1.0–1.07	50
	iso-Octane	0.01–0.04	—	1.29–1.41	53
	iso-Octane	0.025–0.2	25	1.6–2.8	51, 52
	Heptane	0.05–0.2	28	1.1–2.7	56, 57
Aliphatic (with aliphatic hydroxyl group)	Toluene	0.008	30	1.14	58
	Chloroform	0.05–0.4	25	1.1–1.4	51, 52
	Toluene	0.025–0.3	25	1.2–1.9	51, 52
	Benzene	0.05–0.3	25	1.4–1.8	51, 52
	Cyclohexane	0.05–0.2	—*	2–3	59
	iso-Octane	0.025–0.3	25	2.3–3.7	51, 52

From Szymanowski, J., *Hydroxyoximes and Copper Hydrometallurgy*, CRC Press, Boca Raton, FL, 1993. With permission.

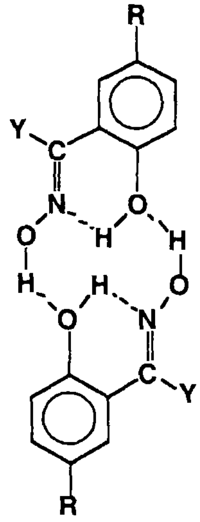
tion number depends mainly on the type of diluent and the type of hydroxyoxime. A significantly higher association is observed in nonsolvating diluents in comparison to solvating ones. Aliphatic hydroxyoximes (**LIX 63**) form linear associates containing a number of oxime molecules, whereas aromatic hydroxyoximes form cyclic dimers.

Depending on the configuration of the oximino group, the dimers of aromatic hydroxyoximes have different structures; greater association is observed for the noncomplexing *(Z)*-isomer in comparison to the *(E)*-isomer (Table 5). This may be due to the fact that the unshared electron pair on the nitrogen atom in *(Z)*-oximes is a stronger donor for hydrogen bond formation than the oxygen oximino group of the *(E)*-oxime.



6

(Z)-oxime dimer



7

(E)-oxime dimer

Dimerization constants increase when the length of the alkyl group increases (Table 6).

TABLE 6
Dimerization Constants From IR Measurements

Y	Alkyl, R	Heptane (Ref. 60)	Xylene (Ref. 60)	Carbon tetrachloride (Ref. 61)
H	H	17.1	—	3.3
H	C_2H_5	—	0.6	—
H	n-C_4H_9	25.7	—	—
		21.6*	—	—
H	n-$C_{12}H_{25}$	35.1	—	—
		31.0*	—	—
H	t-C_4H_9	27.0	1.3	—
		21.0*	—	—
CH_3	CH_3	—	—	8.9
C_6H_5	CH_3			
	(*E*)-Isomer	—	—	7.7
	(*Z*)-Isomer	—	—	38.5

Note: *From partition data.

From Szymanowski, J., *Surfactants in Solutions,* Mittal, B. K. L. and Lindman, B., Eds., Plenum Press, New York, 1989. With permission.

The effect of the alkyl chain branching on hydroxyoxime association cannot be unequivocally determined because it is impossible to compare results obtained at various laboratories where different methods and solvents of uncompared moisture contents are used.

IR spectra of 2-hydroxy-5-alkylbenzaldehyde oxime[60] and 2-hydroxy-5-alkylbenzophenone (*E*)-oxime[61] are similar, but the spectrum of 2-hydroxy-5-alkylbenzophenone (*Z*)-oxime[61] is significantly different (Figures 2 and 3). The spectra of 2-hydroxy-5-alkylbenzaldehyde oxime in heptane show a sharp band at 3580 cm^{-1} in the monomeric N–OH group and a band at 3420 cm^{-1} of the group in associated species. Somewhat different values for the wavelengths are given by independent authors for various oximes and solvents. In both monomeric and associated forms, the phenolic hydroxyl group is always strongly hydrogen bound to the oxime nitrogen atom (band at 3220 cm^{-1}).

The spectra in carbon tetrachloride are similar, but the appropriate bands are shifted by about 5 cm^{-1} toward a longer wavelength. The ratio of the integrated densities of monomer (D_M) to dimer (D_D) equal to $D_D D_M^{-2}$ is constant. This strongly supports the notion than only monomers and dimers are important species over the considered concentration range, that is, <0.012 *M*. The same conclusions can be drawn from the IR spectra of 2-hydroxy-5-alkylbenzophenone (E)-oxime.

The spectrum of solid 2-hydroxy-5-methylbenzophenone (*Z*)-oxime shows 3260, 3220, and 3180 cm^{-1} bands due to the intermolecular $\nu_{\text{oxime OH}}$ bond. In a carbon tetrachloride solution, the same bands are observed at 3267 and 3215 cm^{-1} (as a shoulder). This suggests that the band at the higher frequency is due to the dimer H-bond, whereas that at the lower frequency it is due to the trimer H-bond.[61] The formation of higher associates also can be deduced from the modeling of the extraction equilibria[63]

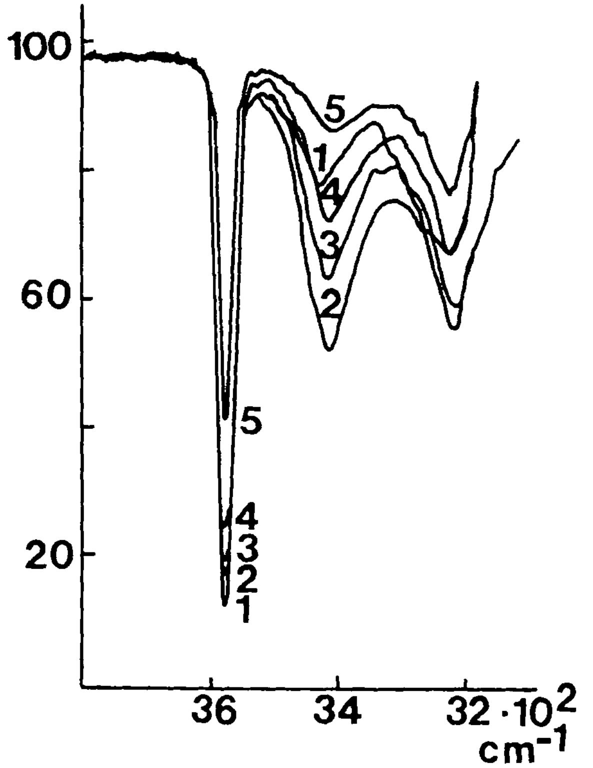


FIGURE 2. IR spectra of alkyl derivatives of salicylaldehyde oxime in heptane (0.292 cm; 1, 2-hydroxy-3,5-di(*t*-butyl)-benzaldehyde oxime, c = 0.012 *M*; 2, 3, and 4, 2-hydroxy-5-*t*-octylbenzaldehyde oxime, c = 0.012, 0.0096, and 0.0072, respectively; 5, 2-hydroxy-5-*n*-dodecylbenzaldehyde oxime, c = 0.0048 *M*). (From Stępniak-Biniakiewicz, D., *Polish J. Chem.*, 61, 433, 1987. With permission.)

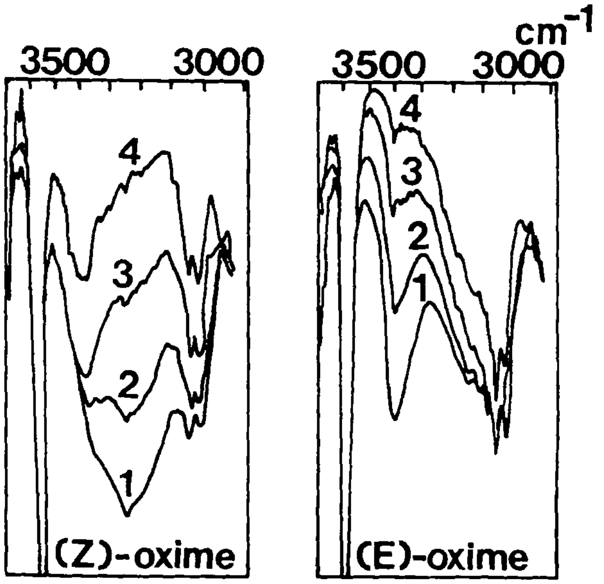


FIGURE 3. The hydroxyl stretching region of diluted solutions of 2-hydroxy-5-methylbenzophenone *(Z)*- and *(E)*-oximes in carbon tetrachloride (1, c = 0.01 *M*; 2, c = 0.005 *M*; 3, c = 0.002 *M*, and 4, c = 0.001 *M*). (From Rusińska-Roszak, D. and Łożyński, M., *Zesz. Nauk. Politech. Pozn., Chem. Inż. Chem.*, 16, 193, 1986. With permission.)

and adsorption data,[64] in which the association numbers of 2 to 4 and 1.5 to 3, respectively, were estimated for **LIX 65N**. Formation of dimers and trimers was also reported for cycloalkanone oximes.[65]

The degree of hydroxyoxime dimerization depends strongly upon the extractant concentration. Hydroxyoxime dimerization can be ignored in solutions of aliphatic or aromatic hydrocarbons up to a concentration of 0.01 and 0.1 *M*, respectively. Under such conditions, >90% of the hydroxyoxime molecules occurs in the monomeric form. However, dimerization mainly depends on the diluent and water content. Dimerization constants are in the order of a few units in aromatic hydrocarbons and change from 20 to 200 $dm^3\ mol^{-1}$ in aliphatic hydrocarbons. The following values for dimerization constants were reported for hydroxyoximes carrying a phenolic group: 80 to 120 $dm^3\ mol^{-1}$ in heptane;[66,67] 17 to 35 $dm^3\ mol^{-1}$, also in heptane;[60] 32 to 70 $dm^3\ mol^{-1}$ in *iso*-octane;[53] 117 $dm^3\ mol^{-1}$ in hexane;[68] 3 $dm^3\ mol^{-1}$ in xylene;[53] 5, 4 to 9, and 11.5 $dm^3\ mol^{-1}$ in toluene;[53,66,68] 2 $dm^3\ mol^{-1}$ in benzene;[66] and 31 to 210 $dm^3\ mol^{-1}$ in MSB diluent. The following values were reported for hydroxyoximes carrying an aliphatic hydroxyl group: 2.4 to 2.8 $dm^3\ mol^{-1}$ at 28°C and 7.8 to 81 $dm^3\ mol^{-1}$ at 50°C.[69]

This wide range of values of the dimerization constant in nonsolvating diluents is most likely due to the differing water content in the studied systems.

The association of various acidic and amine-type extractants in various solvents, usually anhydrous, was extensively studied 20 to 30 years ago[70-73] and several papers have been published, as in the case of dinonylnaphthalene sulfonic acid,[74-78] HDEHP and its salts,[79-91] etc. The formation of various linear and cyclic associates have been postulated and appropriate equilibrium constants estimated from the considered models. Organic acids, such as phosphoric, phosphonic, phosphinic and carboxylic acids, form dimers both in nonsolvating and solvating organic diluents.[70-72] Trialkylamines and their ammonium salts form dimers and trimers, but only in anhydrous diluents.[73]

The formation of reverse micelles has been considered rarely. Now, it is well known that reverse micelles of an aggregation number of about 10 are formed at relatively low concentrations in the presence of small amounts of water.[73,82-101] Dinonylnaphthalene sulfonic acid and HDEHP are good examples. These form reverse micelles at concentrations as low as 10^{-5} and 10^{-3} *M*, respectively. In the extraction system HDEHP/benzene/0.05 *M* $CaCl_2$ ^{1}H-NMR, spectroscopic investigation[89] has shown that the critical reversed micellar concentration is 6 to 11 × 10^{-3} *M;* the equilibrium constant for reverse micellization is $2.4 \times 10^{12}\ M^{-5}$;[6] and the reverse micelles consist of 6.6 HDEHP molecules on average.

The formation of aggregates of various types depends on the geometry of the surfactant/extractant molecules, described by the ratio $v/a_0\ell$, where v is the volume of hydrocarbon chain of the surfactant, a_0 is the optimal cross-sectional area per polar head in a planar interface, and ℓ is approximately 80 to 90% of the fully extended length of the surfactant chain (Figure 4).[102] The direction and degree of interfacial curvature are basically a result of this packing ratio and are influenced further by the differential tendency of water to swell the hydrophilic head area and of the hydrocarbon to swell the tail area. A smaller cross-sectional area of tail compared with head favors an aggregation in the aqueous phase. Spherical micelles, cylindrical micelles, and lamellars (or vesicles) are formed for $v/a_0\ell < 1/3$, $1/3 < v/a_0\ell < 1/2$, and $1/2 < v/a_0\ell < 1$, respectively. Reversed micelles in the organic phase are formed when the cross-sectional area of tail is greater than that of the head, $v/a_0\ell > 1$.

The formation of reverse micelles appears to be a general phenomenon operative in hydrometallurgical systems employing acidic organophosphorus extractants (**HDEHP, PC**

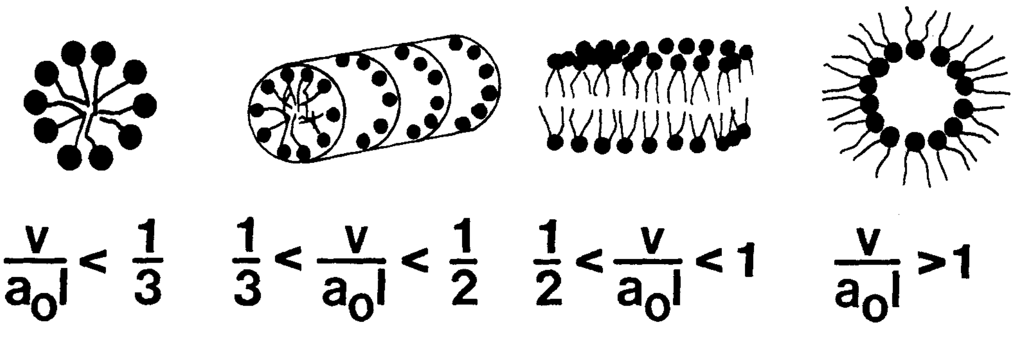


FIGURE 4. Effect of surfactant/extractant geometry on the structure of micelles.

88A, and **Cyanex 272**).[88-101] The aggregates that are formed in heptane during nickel extraction with **HDEHP** consist of nickel-HDEHP and NaDEHP species, which solubilize between five and six water molecules per HDEHP monomer.[95-98] It is postulated that about 3.0 to 3.4 water molecules are bound to the extractant head group and its associated metal ion, 0.4 water molecule is trapped and distributed among the hydrocarbon chains in the interfacial layer near the micellar core, and 1.9 to 2.0 free water molecules are present in the microenviroment in which the normal three-dimensional network of hydrogen bonds is disrupted by the reverse micellar structure.[96] Similar reverse micelles are formed in solvating and nonsolvating diluents, equilibrated with water, and their composition is stable over a wide range of concentrations. The diameter of the inner core of the water pools is estimated as 2.4 nm and the aggregation number as 50 for Ni-HDEHP sytems.[97,98] Smaller size reverse micelles are formed in Co-HDEHP systems.[98] Water content only slightly exceeds that required to fill the first coordination spheres of Na(I) and Co(II). The core of mixed micelles is built up of $Na(H_2O)_4^+$ and $Co(H_2O)_6^{2+}$ cations, and their hydrated shells are bound by a small number of bridging water molecules. The presence of TBP and an alcohol facilitates micelle formation and water uptake into the organic phase.[98] However, it seems logical that the composition and size of aggregates should depend on some experimental conditions.

Using photon correlation spectroscopy (PCS) in a study of the three extraction systems HDEHP/*n*-hexane/metal salt solutions of Ni(II), Zn(II), and Ca(II), it was found that the minimum mean effective hydrodynamic radius of metal-extractant aggregates is about 1 nm (Table 7).[88] An increase of HDEHP concentration causes only a small increase in the radius. In the nickel extraction system at pH 5, a tenfold increase in HDEHP concentration from 0.03 to 0.3 *M* leads to only a small increase in the radius from about 1.5 to 1.8 nm. Similarly, an increase of the metal concentration does not appear to have a major effect on the observed aggregation size. It is believed that an increase in HDEHP or metal ion concentration increases primarily the *number* rather than the *size* of the individual aggregates. On the other hand, changes in the hydrogen ion concentration can have a pronounced effect on the aggregate size. The higher the pH, the larger the metal-extractant aggregates. The effect of pH is evident in the case of nickel extraction, especially when the pH of the aqueous phase is >4.5. At pH 6, the radius of the Ni-HDEHP aggregates becomes as large as approximately 6 nm.

The parameter Q characterizes the polydispersity, and its lower limit for monodis-

TABLE 7
PCS Measurements of Organic Phase of Solvent Extraction System HDEHP/n-Hexane/Metal Chloride Solution at 293.15 K

Metal (conc., *M*)	HDEHP (conc., *M*)	pH	Radius (nm)	Polydispersity Q
Ca(II)	0.10	4.5	1.06	0.25
(0.50)	0.30	4.5	1.11	0.22
Zn(II)	0.10	2.5	1.32	0.21
(0.30)	0.30	2.5	1.39	0.21
Ni(II)	0.10	5.0	1.61	0.16
(0.05)	0.30	5.0	1.57*	0.14

Note: *Later values are of the order 1.8 nm.

From Neuman, R. D., Jones, M. A., and Zhou, N. F., *Colloids Surf.*, 46, 45, 1990. With permission.

perse aggregates is about 0.02; higher values indicate polydispersity.

Histograms of the size distribution of the metal-extractant aggregates are shown in Figure 5.[88] The size distributions are plotted using the scattered light intensity as a function of particle diameter and appear similar for the three solvent extraction systems. At lower pH values, the size distributions are very broad and generally appear somewhat bimodal. At higher pH, the size distribution shifts to larger particle sizes and the bimodal nature more or less disappears. Very narrow size distribution is then found for nickel extraction systems. Under some conditions, usually in the presence of high amounts of surfactant and cosurfactant, water solubilization in the hydrocarbon phase sharply increases and a microemulsion is formed. In some cases, especially in alkaline media, the extractants exhibit sufficiently strong interfacial activity, and the surfactant presence is not necessary. This was the case with **CYANEX** 272.[101] Alcohols generally act as cosurfactants.

Osseo-Asare[103] discussed the association of TBP and suggested that even in this case reversed micelles may be formed without presenting any strong evidence. The self-association of TBP is well known and is attributed to dipole-dipole interactions involving the P=O group. It is also well known that TBP forms various hydrates in two and three component systems containing water, i.e., TBP-water and TBP-diluent-water systems (see Reference 103). Osseo-Asare assumed that extractant molecules behave in line with current notions of surfactant aggregation. The first water molecules to enter the organic phase bind directly to the polar group of surfactant/extractant, in this case the P=O group of TBP. The resulting TBP*H_2O complex initially organizes as a linear aggregate. With increasing concentration, there is a structural reorganization into cyclic aggregates, i.e., reversed micelles. After all the available P=O sites are occupied by water molecules, additional water transferred into the organic phase is solubilized in the reversed micelle core, thus giving rise to a microemulsion. Such a model seems highly probable, especially for more surface-active acidic extractants, for example, dinonylnaphthalene sulfonic acid and HDEHP, and fits experimental association data.

The formation of reverse micelles or microemulsions in the organic phase can significantly change the extraction proper-

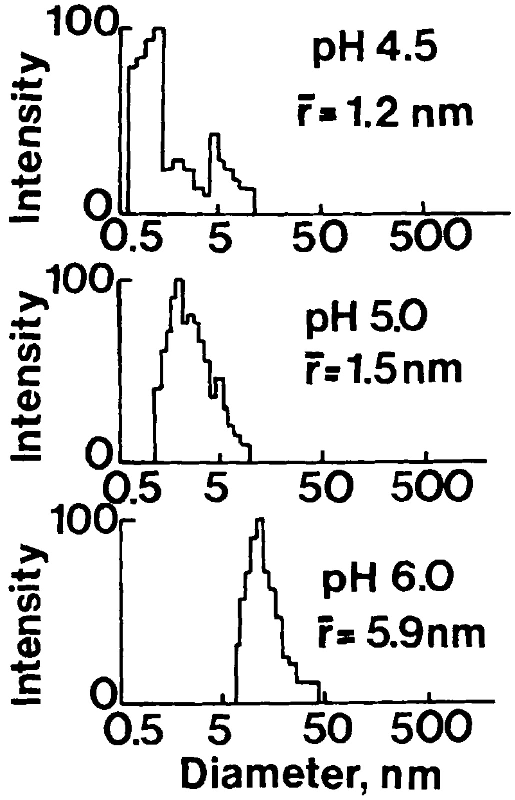


FIGURE 5. Effect of pH on size distribution of metal-extractant aggregates formed in the system 0.1 *M* HDEHP/*n*-hexane/0.05 *M* $NiCl_2$ at 293.15 K. (From Neuman, R. D., Jones, M. A., and Zhou, N. F., *Colloids Surf.*, 46, 45, 1990. With permission.)

ties of extractants. This problem has been discussed separately.[103]

IV. ASSOCIATION OF MODIFIERS WITH EXTRACTANTS AND EFFECT OF ASSOCIATION ON METAL EXTRACTION

There are few studies on the association of extractants with modifiers. Komasawa and Otake[4] studied the extraction of Cu(II) and Ni(II) with 2-hydroxy-5-alkylbenzophenone oxime in various diluents. They found that the extraction of copper falls in the following order of diluents: heptane > xylene ≫ nitrobenzene > butyl ether > methylheptyl ketone > 2-ethylhexanol > HDEHP (Table 8).

In nonsolvating diluents of the aliphatic hydrocarbon type, hydroxyoximes are present in marked proportion in the form of dimers, which decreases the concentration of the active monomer molecule. Carrying both hydroxy and oximino groups, the hydroxyoxime molecule can serve as a proton donor or electron acceptor. Molecules of aromatic hydrocarbons carrying Π electrons behave like electron donors. Therefore, in diluents of the aromatic hydrocarbon type, intermolecular Π complexes are present, whose decomposition constitutes an additional barrier that has to be overcome when hydroxyoxime complexes with metals are formed. The population fraction in dimer form is significantly depressed.[1] In the case of partially chlorinated diluents, solvates of various types may be formed: –OH(oxime)···X–C–H and Π(oxime)···H–C–X, where X denotes halogen in the diluent molecule, as aromatic rings

TABLE 8
Absorption Bands, Solvate Formation Constants, and Extraction Constants of 2-Hydroxy-5-Alkylbenzophenone Oxime

Parameter	Heptane	Xylene	Nitrobenzene	Butyl ether	Methylheptyl ketone	2-Ethylhexanol	HDEHP
Wave number, cm^{-1}							
Monomer = NOH	3595	3495	3465	3285	3310	3100–3300	—
Associated = NOH	3395	3395	—	—	—	—	—
Solvate formation constant, $dm^{-3}\ mol^{-1}$							
In heptane	—	5×10^{-6}	—	4.3×10^{-3}	9.0×10^{-3}	1.8×10^{-2}	2.0×10^{-2}
In xylene	—	—	—	2.1×10^{-3}	3.0×10^{-3}	5.2×10^{-3}	2.1×10^{-3}
Extraction constant							
Cu(II)	90	1.5	9.7×10^{-2}	3.0×10^{-3}	2.0×10^{-3}	1.3×10^{-3}	—
Ni(II)	1.2×10^{-4}	2.0×10^{-6}	—	—	—	1.2×10^{-9}	—

From Komasawa, I. and Otake, T., *J. Chem. Eng. Jpn.*, 16, 377, 1983. With permission.

of hydroxyoxime molecules also exhibit electron donor properties.

Hydroxyoximes form significantly strong complexes with n-donor substances containing an oxygen atom. This is well reflected in the values of the solvate formation constants given in Table 8 that show 5×10^{-6}, 4.3×10^{-3}, 9.0×10^{-3}, 1.8×10^{-2}, and 2.0×10^{-2} dm^{-3} mol^{-1} for 2-hydroxy-5-alkylbenzophenone oxime with xylene, butyl ether, methylheptyl ketone, 2-ethylhexanol and HDEHP, respectively, in heptane.[4] The band characteristic for the hydroxyoxime monomer rapidly disappears in the IR spectrum after introducing an n-donor substance to a hydroxyoxime solution in a hydrocarbon diluent, whereas a broad and intense band appears, typical of an hydroxyoxime complex, with n-donor compound.

Aliphatic alcohols, as well as ethers, exhibit greater electron density on the oxygen atom when compared with alkylphenols and, therefore, they more readily form strong complexes with hydroxyoxime molecules. Similar contents of the monomeric **P 50** extractant molecules, dimeric molecules, and hydroxyoxime complexes with the modifier are obtained using tridecanol in half the amount of nonylphenol.[5] Dalton et al.[5,6] estimated the contents of monomer of **P 50** extractant, its dimer, and its complex with nonylphenol in hexane as equal to 24, 76, and 0% and 8, 4, and 88% in systems containing 0 and 10% of nonylphenol, respectively (Figure 6). Structure 8 of the complex was suggested. This is in agreement with Freiser et al.,[8] who deduced the formation of 1:1 and 1:2 hydroxyoxime-alcohol complexes from the modeling of the copper extraction data.

The presence of modifiers decreases the extraction abilities of hydroxyoximes (Figure 7).[7] This effect can be well modeled when the following equilibria are considered:

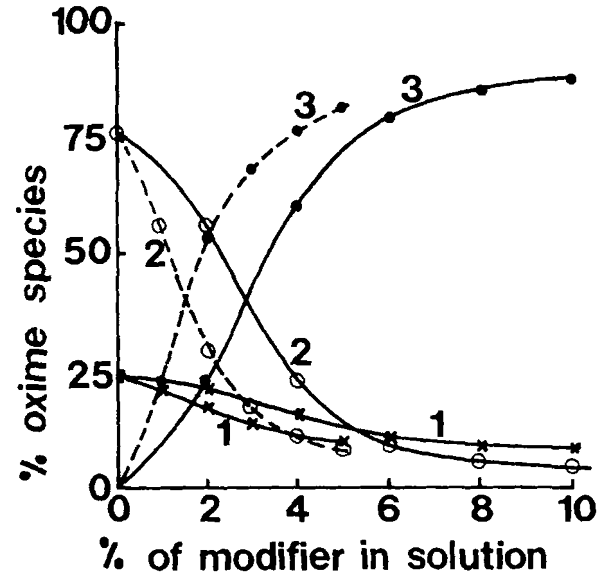


FIGURE 6. Effect of nonylphenol (solid line) and tridecanol (dashed line) on association of P 50 extractant in hexane (5% P 50). (From Dalton, R. F. and Severs, K. G., *Reagents in the Minerals Industry*, I.M.M., London, 1984, 107; a slide presented at the Conference and obtained from Dr. Dalton, R. F., ZENECA. With permission.)

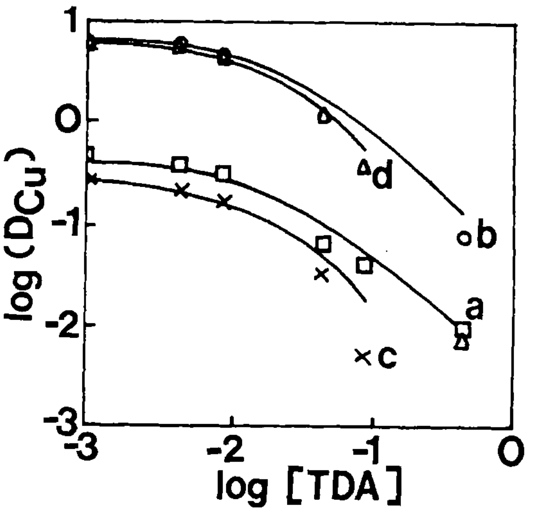


FIGURE 7. Effect of tridecanol (TDA) on copper extraction with 2-hydroxy-5-nonylbenzaldehyde oxime (NSA, curves a and b) and 2-hydroxy-5-dodecylbenzaldehyde oxime (DSA, curves c and d) (heptane/0.1 *M* $NaHSO_4$; pH 1.68; total copper, 8.98×10^{-5} *M;* extractant concentration; a, 0.00131 *M;* b, 0.00545 *M;* c, 0.00106 *M,* and d, 0.00528 *M*). (From Majdan, M., Sperline, R. P., Gu, W.-G., Yu, W.-H., and Freiser, H., *Solvent Extraction Ion Exchange,* 7, 987, 1989. With permission.)

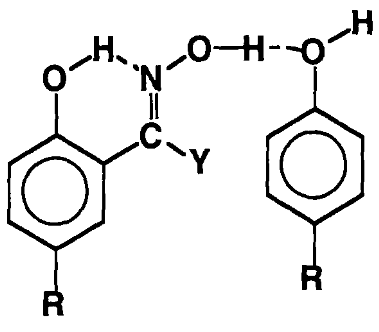
$$Cu_w^{2+} + 2HL_o = CuL_{2o} + 2H_w^+ \quad (6)$$

$$2HL_o = (HL)_{2o} \quad (7)$$

$$HL_o + nROH_o = HL{*}nROH_o \quad (8)$$

$$mROH_o = (ROH)_{mo} \quad (9)$$

where HL stands for hydroxyoxime and the subscripts w and o denote the aqueous and organic phases, respectively.



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The model takes into account the copper extraction equation in a simple but sufficient form (Reaction 6), dimerization of hydroxyoxime and modifier (Reactions 7 and 9, respectively), and coassociation of hydroxyoxime with alcohol (Reaction 8) and concentrations are considered.

The following relations for appropriate equilibrium constants are obtained.

$$K_{ex} = \frac{[CuL_2]_o[H]_w^2}{[Cu]_w[HL]_o^2} \quad (10)$$

$$K_{ass} = \frac{[HL * nROH]_o}{[HL]_o[ROH]_o^n} \quad n = 1 \text{ and } 2 \quad (11)$$

$$K_{ROH\,ass} = \frac{[(ROH)_m]_o}{[ROH]_o^m} \quad m = 3 \text{ and } 4 \quad (12)$$

$$K_{HL\,ass} = \frac{[(HL)_p]_o}{[HL]_o^p} \quad p = 2 \quad (13)$$

Equations 5 to 8, together with mass balance equations, allow us to model the extraction data.

$$[HL]_{tot} = 2[CuL_2]_o + [HL]_o + [HL * nROH]_o + n[(HL)_p]_o \quad (14)$$

$$[ROH]_{tot} = [ROH]_o + m[(ROH)_m]_o + n[HL * nROH]_o \quad (15)$$

$$[Cu]_{tot} = [Cu]_w + [CuL_2]_o \quad (16)$$

It can be assumed that the partition of alcohol, hydroxyoxime, and the complex can be neglected (they are slightly present only in the organic phase) and the volumes of the aqueous and organic phases are the same.

Each constant needed for modeling of the extraction data is determined with an error and introduces some uncertainty into the final conclusions. Figure 8[105] demon-

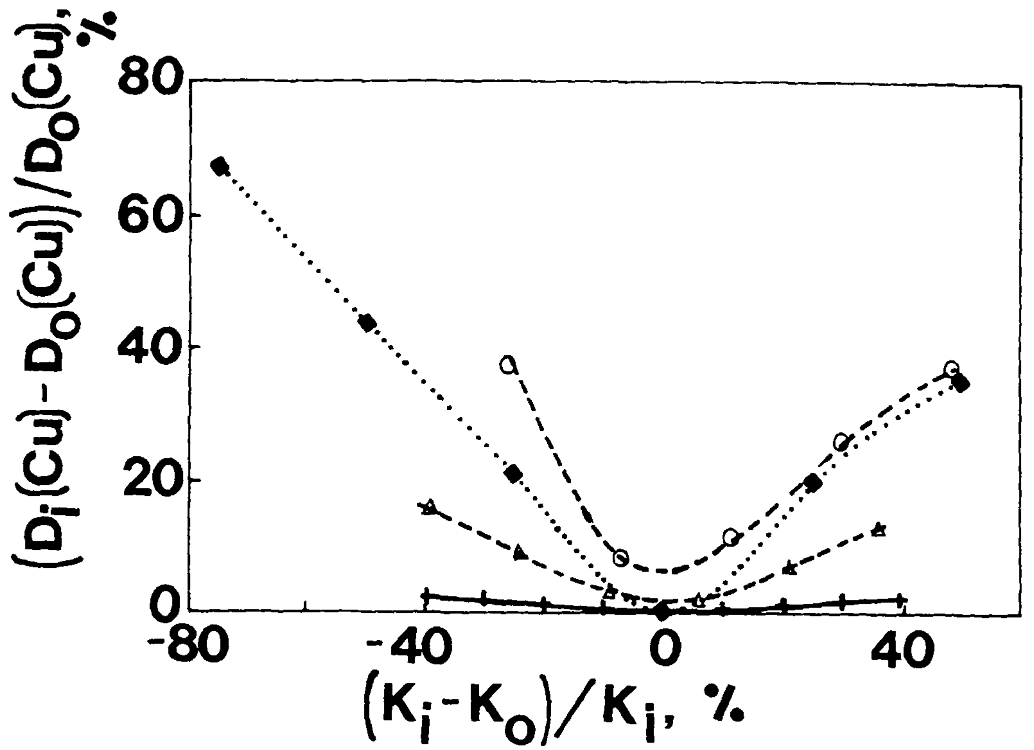


FIGURE 8. Effect of deviation of the equilibrium constants on the average relative error of copper distribution coefficient (K_{ex} = 135, K_{ass} = 33.1 M^{-1} for n = 1, and K_{ass} = 2690 M^{-2} for n = 2, $K_{ROH\ ass}$ = 1995 M^{-2} for n = 3, and $K_{HL\ ass}$ = 50.1 M^{-1}; ○, K_{ass}, n = 2; ◆, $K_{ROH\ ass}$, n = 3; △, K_{ass}, n = 1; +, $K_{HL\ ass}$). (From Bogacki, M., Łożyński, M., and Szymanowski, J., *Solvent Extraction Res. Dev. Jpn.*, 1, 108, 1994. With permission.)

strates the effect of the deviations of the constants on the average relative error of the copper distribution coefficient computed from the model. In each case considered, the minimum error is obtained for the best set of equilibrium constants. However, different equilibria affect, in various ways, the estimated errors. The effect of hydroxyoxime dimerization is almost negligible. This is in agreement with the data that demonstrate that although hydroxyoxime dimerization is easily detected in anhydrous solvents (see discussion in Reference 1), it can be neglected in actual extraction systems, even at hydroxyoxime concentrations of up to 10 to 15%.[106,107] The self-association of alcohol and its association with hydroxyoxime, especially for n = 2, strongly influence the error of the copper distribution coefficient determination.

Extraction data can be modeled quite well for various initial options, including the structure of alcohol associates and the values of Reactions 6 to 9 equilibrium constants. A good fit of the model to the experimental data of copper extraction is obtained when the formation of alcohol trimer or tetramer is assumed.[105] The relations similar to those given in Figure 14 can be obtained. Thus, although the model is very useful to describe experimental data, it cannot be used to predict the association and/or self-association equilibria from the extraction data, as is shown in Figure 9.[105] This figure demonstrates the effect of the number of alcohol molecules associated with one hydroxyoxime molecule on the association constant predicted from the extraction data assuming the formation of an alcohol trimer or tetramer.

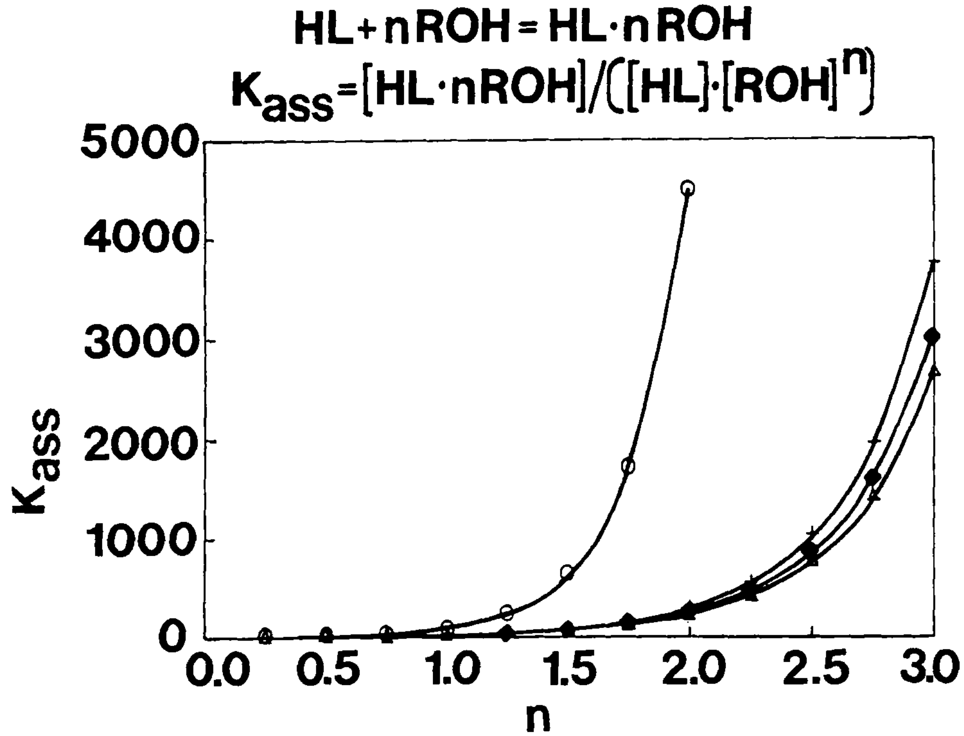


FIGURE 9. Association constant vs. number of alcohol molecules associated with 2-hydroxy-5-nonylbenzaldehyde oxime (○, n = 3, $K_{ROH\,ass}$ = 1995 M^{-2}; +, n = 3 $K_{ROH\,ass}$ = 10 M^{-2}; ◆, n = 4 $K_{ROH\,ass}$ = 50 M^{-3}; and Δ, n = 4, $K_{ROH\,ass}$ = 25 M^{-3}). (From Bogacki, M., Łożyński, M., and Szymanowski, J., *Solvent Extraction Res. Dev. Jpn.*, 1, 108, 1994. With permission.)

Quite different values of the association constant may be obtained by assuming the presence of alcohol trimers or tetramers in the organic phase. However, the formation of 1:1 and 1:2 hydroxyoxime-alcohol associates can be predicted, assuming the formation of both alcohol trimers or tetramers (Figure 10).

Ignoring the assumptions and association constants (trimer or tetramer formation and appropriate) the minimum of the mean square error of the computed copper distribution coefficient, MSE = $\Sigma(D_{exp} - D_{calc})^2/(k - 1)$, where k denotes the number of experimental data points, is obtained for n near 1 and 2 (0.8 to 1.6) in agreement with the Freiser et al.[8] results. Independent of them, the formation of significant amounts of higher associates containing three or more alcohol molecules associated with one hydroxyoxime molecule can be neglected in such calculations.

Semiempirical, self-consistent field theory calculations for hydrates of β-diketones,[108] alkanal oximes,[109] and associates of hydroxyoximes[105] and naphthalene sulfonic acids[110] with alcohols clearly indicate that the formation of various structures of associates must be considered. Hydroxyoxime molecule contains two free electron pairs on each oxygen atom that may act as electron donors, forming hydrogen bonds with modifier (alcohol and alkylphenol) molecules. The same concerns the free electron pair on the nitrogen atom of the oximino group, although in this case the formation of the intramolecular hydrogen bond seems more justified. A modifier molecule may approach a hydroxyoxime molecule from various sites, giving

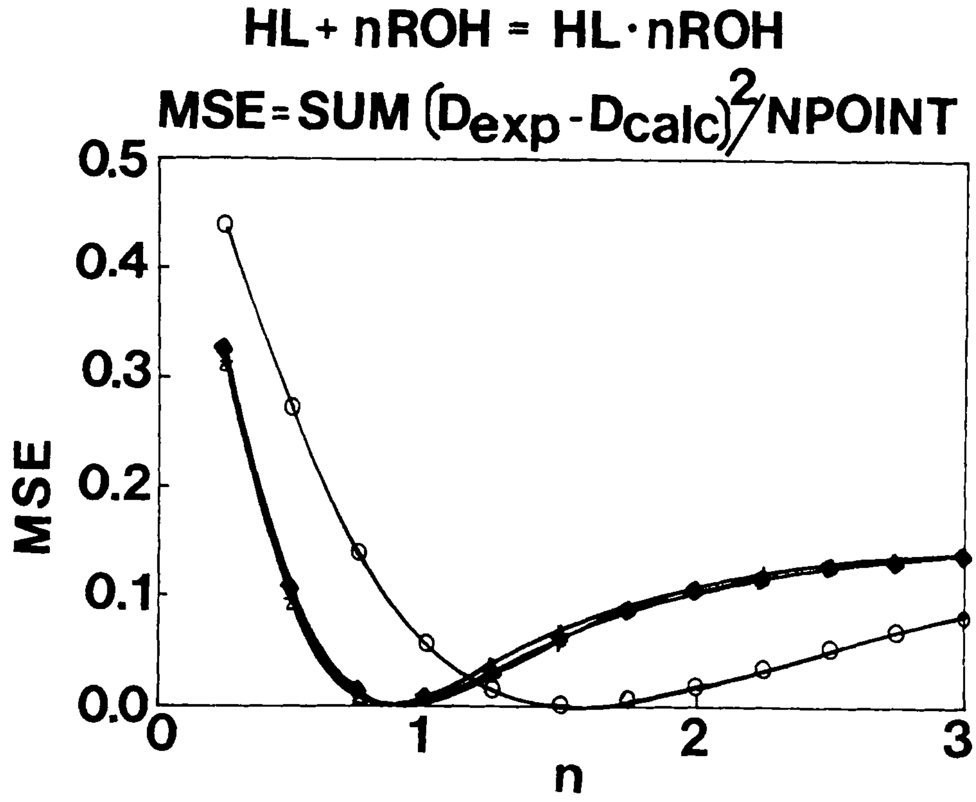


FIGURE 10. Effect of the number of alcohol molecules associated with 2-hydroxy-5-nonylbenzaldehyde oxime upon mean square error of copper distribution constant (○, n = 3, $K_{ROH\,ass} = 1995\ M^{-2}$; +, n = 3 $K_{ROH\,ass} = 10\ M^{-2}$; ◆, n = 4, $K_{ROH\,ass} = 50\ M^{-3}$; and Δ, n = 4, $K_{ROH\,ass} = 25\ M^{-3}$). (From Bogacki, M., Łożyński, M. and Szymanowski, J., *Solvent Extraction Res. Dev. Jpn.*, 1, 108, 1994. With permission.)

associates of somewhat different energies. Modifier molecules having an oxygen atom with two free electron pairs can also act as an electron donor and free hydroxyl groups of hydroxyoxime molecules as electron acceptors. Thus, the structure of the modifier-hydroxyoxime associate cannot be predicted *a priori*.

The PM3 heat of formation computed for various associates of salicylaldehyde oxime and methanol considered as the simplest models are given in Table 9. Column 4 gives PM3 heats of formation estimated for considered associates and column 5 presents the relative values of this heat calculated according to Equations 17 to 19, where n denotes the number of modifier molecules associated with a hydroxyoxime molecule. In this computation, the isolated molecules are considered but environmental effects, for example, of a hydrocarbon diluent, are neglected. This is an important simplification but it seems justified when a low aromatic content kerosene is used as the diluent.

$$\Delta H^{a}_{relative} = \left(\Delta H_{associate} - \left(\Delta H_{oxime} + n/4 * \Delta H_{cyclotetramer}\right)\right) \quad (17)$$

$$\Delta H^{b}_{relative} = \left(\Delta H_{associate} - \left(\Delta H_{oxime} + n\Delta H_{methylphenol}\right)\right) \quad (18)$$

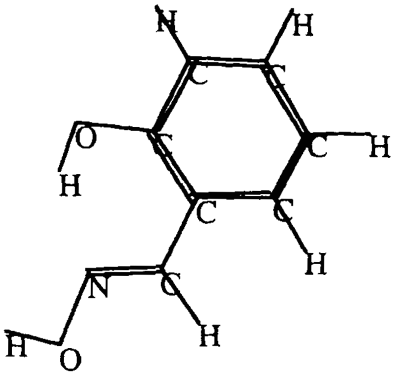
$$\Delta H^{c}_{relative} = \left(\Delta H_{associate} - n\Delta H_{monomer}\right)/n \quad (19)$$

TABLE 9
PM3 Heat of Formation (ΔH) and Dipole Moment (μ) for Various Associates of Salicylaldehyde Oxime and Methanol

No. of modifier molecules	Type of hydrogen bonds	Associate No.	$-\Delta H$ (kJ/mol)	$-\Delta H$ relative (kJ/mol)	μ (Debye)
Methanol					
0	None	9	64.493	—	1.130
1	Me(H)O...HON=	10	297.019	1.249[a]	0.998
	MeOH...OH	11	296.906	1.136[a]	2.753
	MeOH...O(H)N=	12	291.020	–4.750[a]	1.503
2	Me(H)O...HON= and MeOH...OH	13	529.955	2.908[a]	1.507
	Me(H)O...HON= and MeOH...O(H)N=	14	520.269	–6.778[a]	1.999
	MeOH...OH and MeOH...O(H)N=	15	517.691	–9.356[a]	3.338
3	Me(H)O...HON= MeOH...OH MeOH...O(H)N=	16	752.687	–5.637[a]	2.752
4-Methylphenol					
1	Ph(H)O...HON=	17	205.633	11.743[b]	1.656
	PhOH...OH	18	212.523	18.633[b]	2.670
	PhOH...O(H)N	19	205.556	11.666[b]	1.528
2	Ph(H)O...HON= and PhOH...OH	20	354.769	30.372[b]	1.589
	Ph(H)O...HON= and PhOH...O(H)N=	21	348.792	24.394[b]	1.043
	PhOH...OH and PhOH...O(H)N=	22	351.842	27.445[b]	2.975
3	Ph(H)O...HON= PhOH...OH PhOH...O(H)N=	23	497.423	43.574[b]	1.424
Methanol	Monomer		217.158	0.000[c]	1.487
	Dimer				
	Linear		445.117	5.400[c]	2.253
	Cyclic		430.514	–1.902[c]	1.961
	Trimer				
	Linear	3	681.686	10.070[c]	3.680
	Cyclic		677.400	9.641[c]	0.965
	Tetramer				
	Linear	4	919.979	12.836[c]	5.268
	Cyclic	5	925.109	14.118[c]	1.849
4-Methylphenol	PhOH		129.397		1.191

From Bogacki, M., Łożyński, M., and Szymanowski, J., *Solvent Extraction Res. Dev. Jpn.*, 1, 108, 1994. With permission.

Some ambiguity arises as a result modifier association. The heat of formation increases for higher self-associates and changes from –217.154 kJ/mol for monomeric methanol to –229.995 and –231.277 kJ/mol for linear and cyclic tetramers, respectively. This computation shows that the phenolic group of salicylaldehyde is intramolecularly bonded with the nitrogen atom of the oximino group (OH···NOH) (Structure 9).[105]



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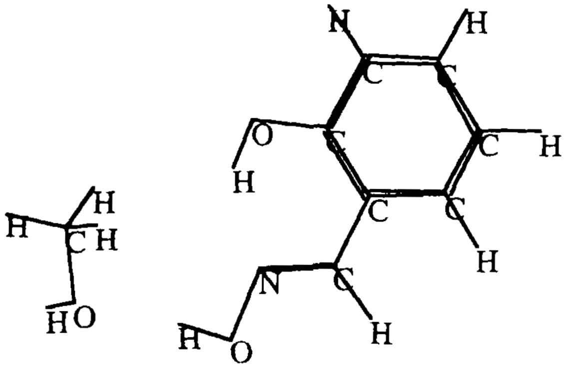
The heat of formation of hydroxyoxime-alcohol 1:1 associate is similar for the three structures considered, 10 ~ 11 > 12. In the most stable Structure 10, alcohol acts as the electron donor to the hydroxyimino group. When it acts as the electron acceptor, then the intramolecular bond with the oxygen atom of the phenolic group of salicylaldehyde oxime is favored (Structure 11). It is reflected both in the values of the heat of formation and the lengths of the intra- and intermolecular bonds (Table 10). However, the formation of the N···HOCH$_3$ associate is not observed. The intramolecular bond in salicylaldehyde oxime is significantly weakened by formation of Associate 12.



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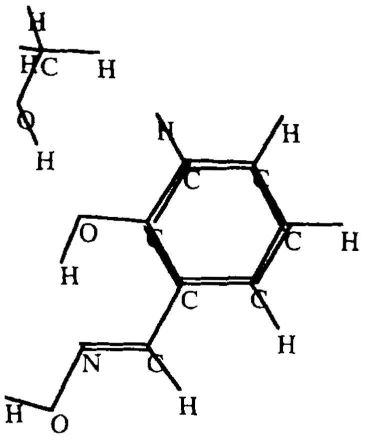

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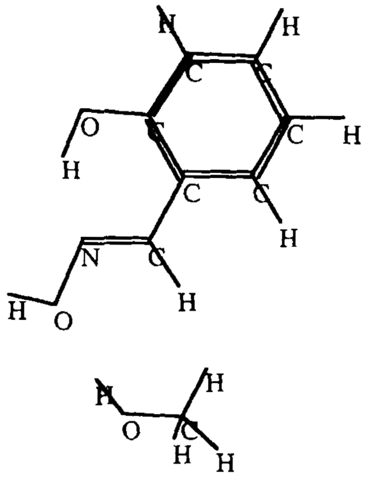

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TABLE 10
Length of Intra- and Intermolecular Bonds in Hydroxyoxime Modifier Associates

Associate No.	Intramolecular bond Length (A)	Intramolecular bond Angle (degree)	Intermolecular bond Type	Intermolecular bond Length (A)	Intermolecular bond Angle (degree)
Methanol					
10	1.836	143.5	Me(H)O...HON=	1.809	178.3
11	1.835	143.5	MeOH...OH	1.830	176.4
12	1.851	143.3	MeOH...O(H)N=	1.848	170.5
13	1.820	143.3	Me(H)O...HON=	1.808	179.4
			and MeOH...OH	1.823	178.1
14	1.840	143.3	Me(H)O...HON= and	1.800	178.1
			MeOH...O(H)N=	1.836	177.2
15	1.839	143.3	MeOH...OH and	1.831	176.8
			MeOH...O(H)N=	1.844	176.2
16	1.825	143.1	Me(H)O...HON=	1.799	179.8
			MeOH...OH	1.824	178.8
			MeOH...O(H)N=	1.839	175.3
4-Methylphenol					
17	1.838	143.8	Ph(H)O...HON=	1.815	175.6
18	1.833	143.5	PhOH...OH	1.832	153.6
19	1.853	143.3	PhOH...O(H)N	1.849	155.8
20	1.817	143.8	Ph(H)O...HON=	1.811	175.6
			and PhOH...OH	1.830	153.4
21	1.843	143.7	Ph(H)O...HON= and	1.807	175.6
			PhOH...O(H)N=	1.843	156.4
22	1.838	143.3	PhOH...OH and	1.833	153.5
			PhOH...O(H)N=	1.852	156.2
23	1.824	143.7	Ph(H)O...HON=	1.801	177.7
			PhOH...OH	1.831	154.3
			PhOH...O(H)N=	1.845	159.4

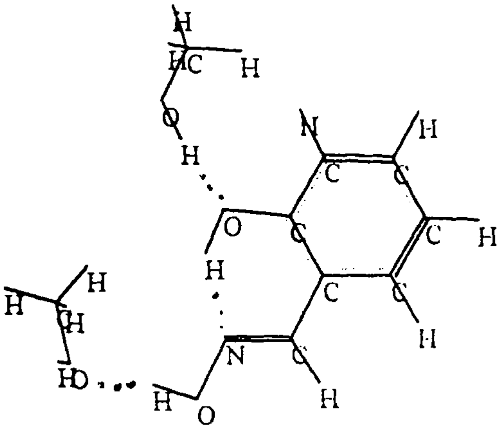
From Bogacki, M., Łożyński, M., and Szymanowski, J., *Solvent Extraction Res. Dev. Jpn.*, 1, 108, 1994. With permission.

If one assumes that the entropy of formation of Associates 10 to 12 are approximately the same, then it is possible to estimate the contents of these three associates in equilibrium. The following percentages are obtained: 48.9, 46.7, and 4.3% for Associates 10, 11, and 12, respectively. Thus, Associates 10 and 11 are dominant in the organic phase.

The differences in the heat of formation are more important for salicylaldehyde oxime-methanol 1:2 associates. In the most stable Structure 13, one methanol molecule acts as the electron donor and forms the hydrogen bond with the hydroxyimino group, whereas the second methanol molecule acts as the electron acceptor, forming the hydrogen bond with the phenolic group. The intramolecular hydrogen bond in salicylaldehyde is strengthen, as is reflected in the length of this bond (Table 10). The other two Structures 14 and 15 are less favorable.

Their relative contents can be estimated as equal to 97.4, 2.0, and 0.7%, for Associates 13, 14, and 15, respectively.[105]

The relative heats of formation (column 5 in Table 9) suggest that 1:2 and 1:1 associates coexist in equilibrium in comparable



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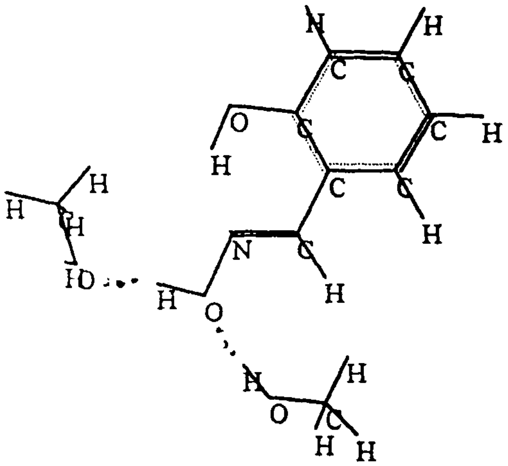

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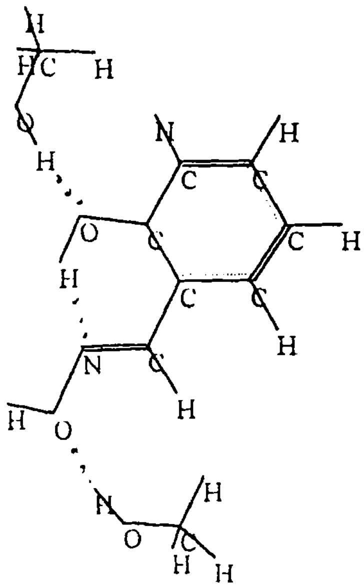

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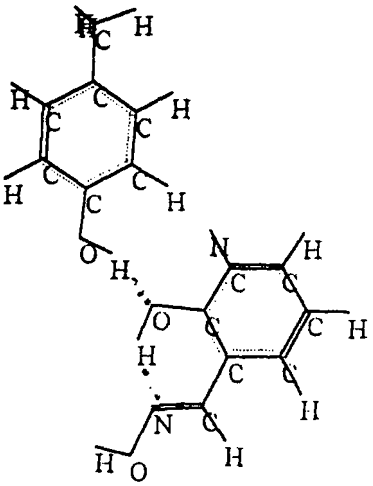
quantities because the values of $\Delta\ H_{\text{relative}}$ estimated for 2:1 associates are only somewhat less negative than those of 1:1 associates. However, the relative ratio of 1:2 and 1:1 associates cannot be estimated because it is impossible to assume similar entropies of formation for these species.

Thus, these results agree well with experimental data of Freiser et al.[7] and reveal the identity of the alcohol-oxime associates present in the organic phase.

4-Methylphenol yields similar associates as methanol with salicylaldehyde, but the associate structure affects the heat of formation in a somewhat different way than in the case of methanol. For 1:1 associates it falls in the order 18 ≫ 17 ~ 19, and the following relative concentrations of these species are estimated, 89.1, 5.5, and 5.4%, respectively. Thus, the effect of associate structure is stronger for 4-methylphenol than for methanol. In the most stable Structure 18, 4-methylphenol acts as the electron acceptor from the oxygen of salicylaldehyde oxime phenolic group.[105] It is obvious that the most stable 1:2 associate, Structure 20, must contain the MePhOH···OH bond. The second methylphenol molecule acts as electron donor, forming a hydrogen bond with the hydrogen of the oximino group. The relative content of 1:2 associates changes in the range of 20 > 22 > 21, and equals 71.6, 22.0, and 6.9%, respectively. These observations qualitatively explain the different abilities of alcohols and alkylphenols to modify the extraction properties of hydroxyoximes.

Molecular dipole moments significantly depend on the structure of the hydroxyoximes-modifier associates. The associate stability is not correlated with the dipole moment, e.g., the most stable 1:1 associates have the highest (Structures 11 and 18) and the lowest (Structure 10) dipole moments. Associates 11 and 18 have dipole moments similar to that of 16 (1:3 associate) and are higher than those of Structures 13 and 14 (1:2 associates). Only Structures 15 and 22 have a higher dipole moment.



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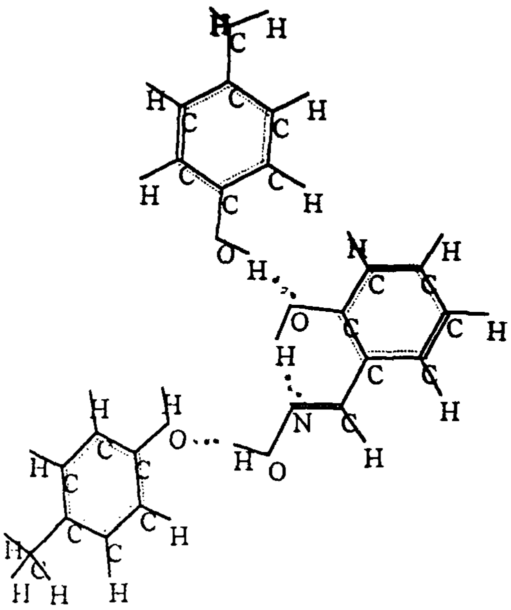

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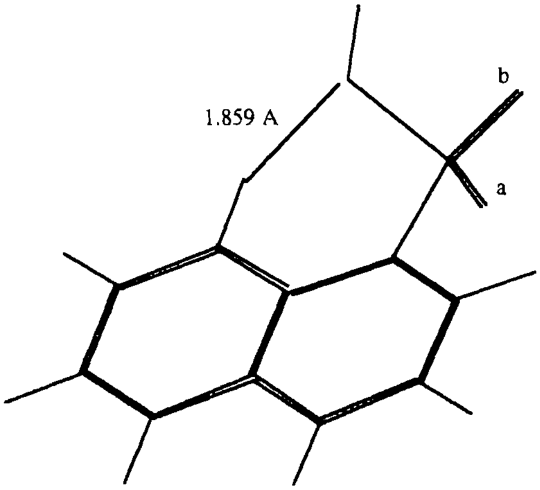
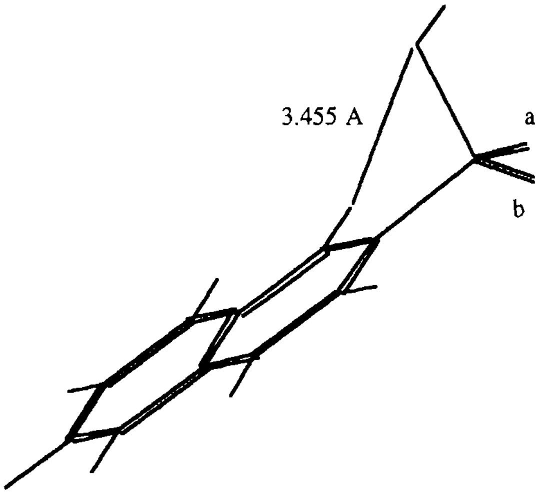
In recent years, ICI used some esters of unknown structure to modify the extraction behavior of salicylaldehyde oxime alkyl derivatives.[1,4,5,111] They can act only as electron donors, but it seems that the formation of the hydrogen bond with the hydrogen atom of the hydroxyamino group should be highly facilitated. The formation of modifier associates with other types of extractants also was reported,[112-114] and their probable average structures were evaluated by the modeling of the interfacial tension data. The formation of dinonylnaphthalene sulfonic acid and isodecanol 3:1 associate and of dinonylnaphthalene sulfonic acid and nonylphenol 3:3 associate in decane was deduced,[112] assuming the formation of tetramers by isodecanol and nonylphenol in decane. The formation constants were estimated as equal to 10^{13} mol^{-3} dm^{9} and 4.1×10^{13} mol^{-5} dm^{15}, respectively. Using the same method for modeling, the formation of **HOSTAREX A327** (tri-*n*-octyl/decylamine, octyl to decyl of about 1:1) and isodecanol 1:1 associate in aliphatic kerosene[113] and HDEHP and isodecanol 1:1 associate in decane[114] were assessed. The association of amine-type extractants with alcohol and its effect on metal extraction was discussed.[16-18]

1-Naphthalene sulfonic acid (1-HNS) and 2-naphthalene sulfonic acid (2-HNS) are considered as low molecular models of dinonylnaphthalene sulfonic acid, which is not well defined. In sulfonic acids, both oxygen atoms (a and b) bonded with sulfur seem to be equivalent. However, this is not the case of naphthalene sulfonic acids, and especially of 1-HNS, which is reflected in the heats of formation of their associates with methanol and 4-methylphenol.[110] The following values of the PM3 heat of formation are reported: –547.5 and –541.5 kJ/mol, and –570.9 and –570.5 kJ/mol for 1:1 associates, respectively, of 1-HNS and 2-HNS with methanol. The same is true for the association of these acids with 4-methylphenol. This is caused by the formation of a relatively strong hydrogen bond between the oxygen atom of the sulfonic group and the hydrogen atom at position 8 of the aromatic ring in 1-HNS. The hydrogen bond length is 1.859 Å for the optimized structure of 1-HNS, whereas the appropriate distance is equal to 3.455 Å for 2-HNS. Thus, one may expect significantly different properties and association behaviors of 1-HNS in comparison to 2-HNS. This is clearly demonstrated in



1-HNS
24



2-HNS
25

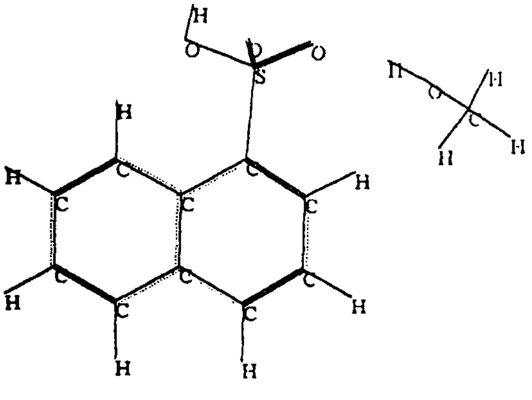
the optimized structures of 1-HNS and 2-HNS.

The weak hydrogen bonds C–H···O were considered in some papers for various compounds using independent methods.[118,119] In the group of 1:1 associates, the most stable structures are obtained as the modifier acts as the electron acceptor and forms the hydrogen bond with the oxygen (=O). The heats of formation for such 1:1 associates are more negative than the sum of formation heats of reagents. These differences are in the range of 7.6 to 9.1 and 26.6 to 28.9 kJ/mol for 1:1 associates with methanol and 4-methylphenol, respectively. Thus, the association with alkylphenol is favorable. Structures 26 and 27 are the optimized structures of such associates.

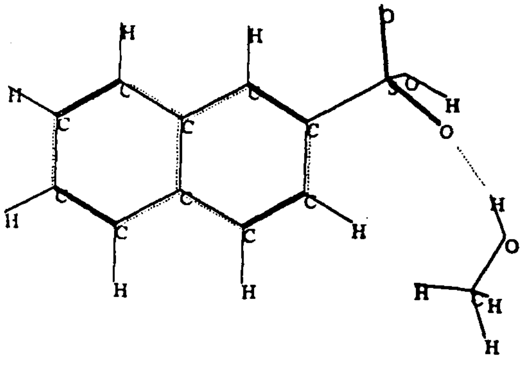
If the differences in the two oxygen O= are neglected and both associates MeOH···OS are treated as equivalent, then the following respective contents of these 1:1 associates are obtained: 68.7 and 91.1% for 1-HNS and 2-HNS with methanol and 98.5 and 99.6% for 1-HNS and 2-HNS with 4-methylphenol. The contents of other associates are negligible, with the exception of the 1-HNS:methanol 1:1 associate with the Me(H)O···HOS hydrogen bond.

The PM3 heats of formation of HNS: modifier 1:2 associates are more negative than of 1:1 associates. This means that 1:2 associates are easily formed. Again, more negative values are obtained for naphthalene sulfonic acid associates with alkylphenol. The following values of $\Delta H_{\mathrm{relative}}$ are reported: –15.1 and –28.6 kJ/mol for 1-HNS and 2-HNS associate with methanol and –46.7 and –54.3 kJ/mol for optimized formulas of these acids with 4-methylphenol, respectively.[110] In the most stable 1:2 associate, one methanol molecule acts as the electron acceptor and the second molecule as the electron donor, forming MeOH···OS and Me(H)O···HOS hydrogen bonds. The relative contents of these species are 84.7 and 99.0%. Thus, the content of other forms is negligible. The most stable 1-HNS: 4-methylphenol 1:2 associate has the same structure. However, its content falls to 74.2% and significant amounts (23.3%) of the 1:2 associate, with two molecules of 4-methylphenol acting as the electron acceptors, are observed. Such a structure becomes dominant for the 2-HNS:4-methylphenol 1:2 associate (89.9%).

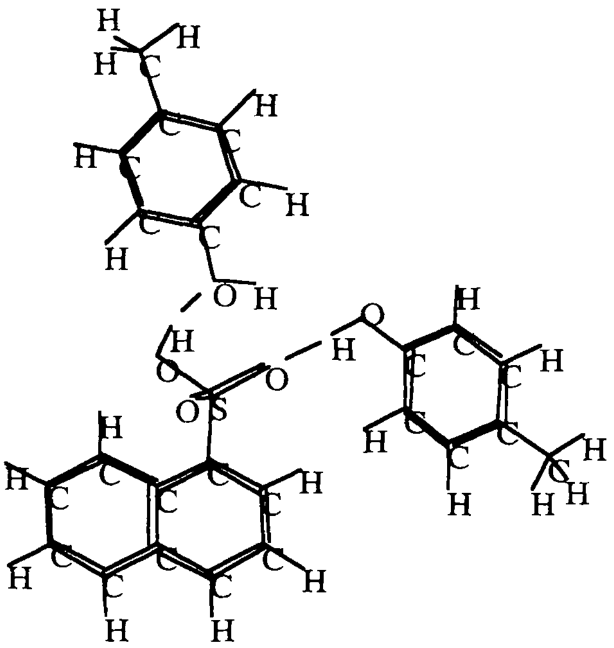
The presence of significant amounts of higher associates (1:3 and 1:4) of 1-HNS with methanol is not probable. The absolute



1-HNS:Methanol=1:1
26



2-HNS:Methanol=1:1
27



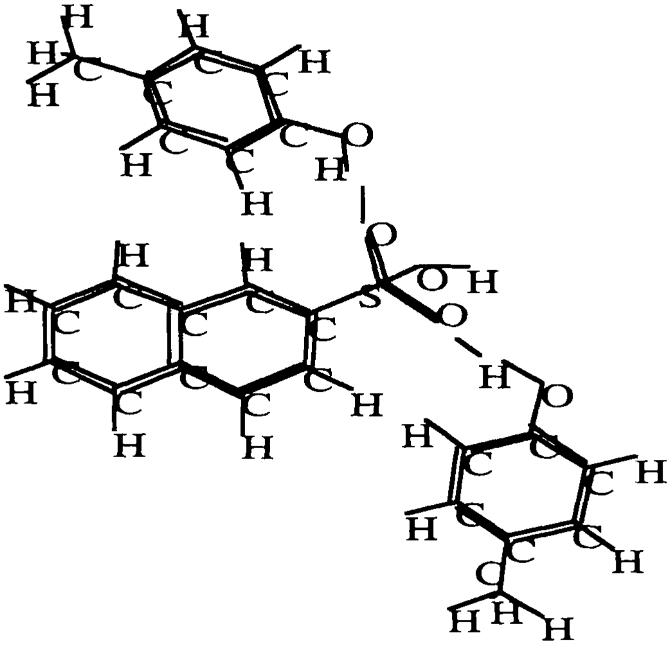
1-HNS:4-Methylphenol=1:2

28

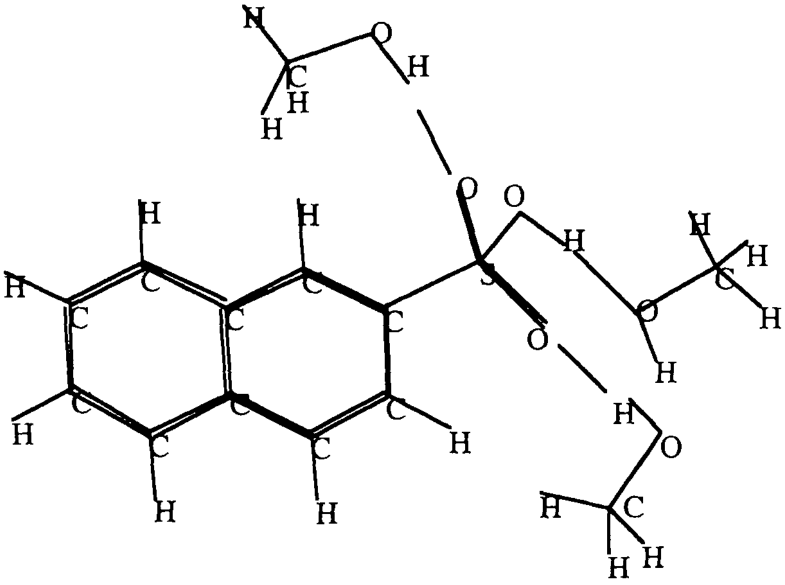
PM3 heats of formation become more negative in comparison to the 1:1 and 1:2 associates, but the relative values are of the same order, i. e., –(16.3 to 17.5) kJ/mol in respect to –15.1 kJ/mol. However, one must take into account that the entropy of the associate formation also should be negative because free molecules have a high degree of freedom in comparison to associates. This decrease probably compensates for the observe change of the heat of formation. The formation of 1:3 associate seems possible for 2-HNS, for which the relative heat of formation equals –36.7 kJ/mol. However, the formation of 1:4 associate has little probability ($\Delta H_{relative} = -33.1$ kJ/mol). In the dominant 1:3 associate (90.9%), two methanol molecules act as the electron acceptor and the third as the electron donor.

Both naphthalene sulfonic acids can form 1:3 and 1:4 associates with 4-methylphenol. The relative heats of formation estimated for these associates are significantly more negative in comparison to 1:1 and 1:2 associates. The most stable 1:3 associates are well defined and their contents are equal to 89.2 and 90.3% for 1-HNS and 2-HNS, respectively. As in the case of methanol, two 4-methylphenol molecules act as the electron acceptors and one molecule as the electron donor. In the 1:4 associate, three alkylphenol molecules act as the electron acceptor and one molecule as the electron donor, as in the case of 2-HNS.

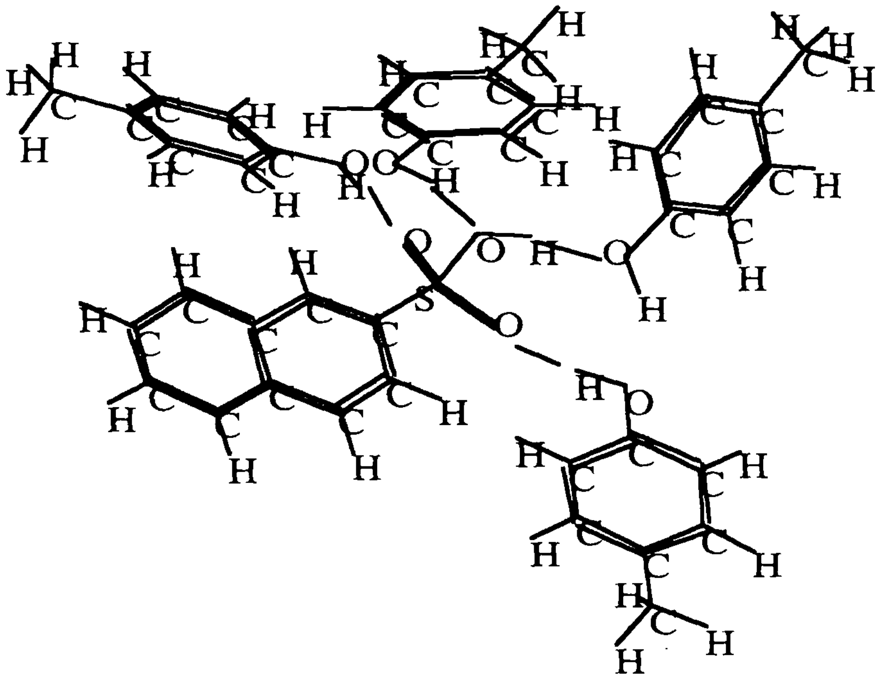
Extractants also can act as modifiers when used in a mixture with other types of extractants. **LIX 864, LIX 865,** and **LIX 984** are appropriate examples among the commercial extractants.[1,114] They are mixtures of a strong extractant with a weak extractant, that is, **LIX 860** and **LIX 64N** in **LIX 864; LIX 860** and **LIX 65N** in **LIX 658;** and **LIX 860** and **LIX 84** in **LIX 984,** where **LIX 860** and **LIX 84** contain 2-hydroxy-5-dodecylbenzaldehyde oxime and 2-hydroxy-5-nonylacetophenone oxime as the active substance, respectively. They contain no additional, nonchelating modifiers, but their extraction properties are better than expected from summing up the properties of



2-HNS:4-Methylphenol=1:2
29



2-HNS:Methanol=1:3
30



2-HNS:Methylphenol=1:4

31

the individual components (Figures 11 and 12). They maintain strong extraction abilities, but stripping is markedly facilitated, resembling that noted with weak extractants. 2-Hydroxy-5-nonylbenzophenone oxime, which is the active substance in **LIX 64N** and **LIX 65N**, must act as the modifier, forming hydrogen bonds with **LIX 860** and **LIX 84**. The formation of such mixed associates between two different extractants was confirmed by Osseo-Asare[116,117] and also deduced from the interfacial tension data. The formation of dinonylnaphthalene sulfonic acid and 5,8-diethyl-7-hydroxy-6-dodecanone oxime (**LIX 63**) 1:1 associate in hexane was presented. It also was suggested that mixed micelles are also formed with **LIX 63** molecules located probably in the palisade region of the micelles, that is, between the HDNNS molecules.

V. ADSORPTION OF MODIFIERS AT LIQUID/LIQUID INTERFACES

Modifier molecules, usually having a hydrophilic hydroxyl group and a hydrophobic hydrocarbon chain, exhibit an amphiphilic character and adsorb at water/hydrocarbon interfaces, decreasing the interfacial tension. Comprehensive studies of their adsorption, mainly with alcohols[120-136] and alkylphenols,[137,138] have been described.

There are important differences in interfacial tension data reported by various authors that is probably connected with inadequate purities of the studied alcohols and alkylphenols. It is now generally accepted that only well-defined substances of special purity can be used for surface and/or interfacial activity studies. Such purity can be obtained by using multiple compression and expansion at the air/water or hydrocarbon/water interface, followed by sucking off the interfacial layers after each step of expansion by means of automatic equipment.[139] Purification by fractional distillation, crystallization, column chromatography, and preparative gas chromatography may not be adequate.

The interfacial activity of alcohols and alkylphenols depends on the alcohol/alkylphenol chain length and its structure

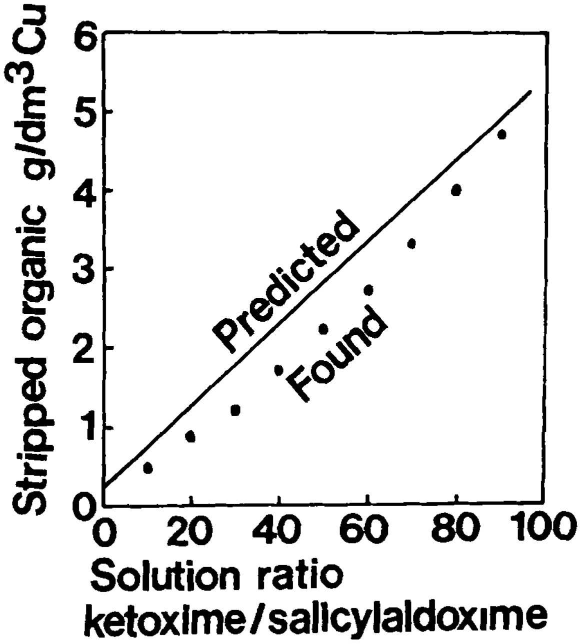


FIGURE 11. Copper content in organic phase after stripping as a function of LIX 65N/LIX 860 ratio (aqueous feed, 30 g dm^{-3} Cu(II) and 170 g dm^{-3} H_2SO_4; organic phase, 20% solutions in Kermac 500T; phase contact time, 3 min). (From Kordosky, G. A., Sierakoski, J. M., and House, J. E., *Proc. Int. Solvent Extract. Conf.*, Denver, 1983, 191. With permission.)

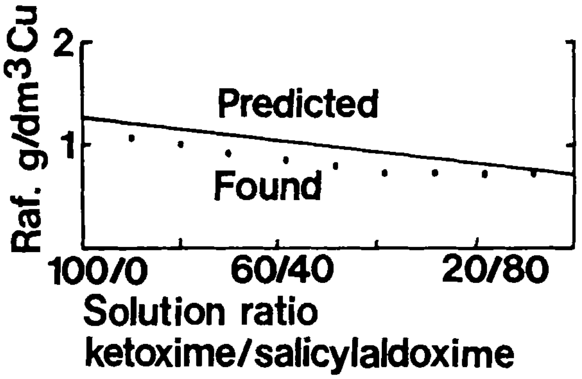


FIGURE 12. Copper content in aqueous phase after extraction as a function of LIX 65N/LIX 860 ratio (aqueous feed, 5.45 g dm^{-3} Cu(II), pH 1.9; organic phase, 20% solutions in Kermac 500T; phase contact time, 3 min). (From Kordosky, G. A., Sierakoski, J. M., and House, J. E., *Proc. Int. Solvent Extract. Conf.*, Denver, 1983, 191. With permission.)

(straight or branched), solvent structure, and the temperature. In systems containing alkanes as the organic phase, the surface pressure ($\Pi = \gamma^o - \gamma$, where γ^o denotes the interfacial tension in the system that does not contain an alcohol, c = 0) falls when the number of carbon atoms in the alkyl chain increases (Figure 13).[128] The same order is observed when the length of the hydrocarbon chain in alkanes is considered.[128] The surface pressure decreases when the temperature rises (Figure 14).[128]

The modifiers having a branched alkyl exhibit lower interfacial activity (lower values of the surface pressure and higher values of the interfacial tension are obtained) than their analogs with normal alkyls (Figures 15 and 16).[138] The effect of the alkyl chain length on alkylphenol interfacial activity seems to depend on the diluent. In systems containing a solvating diluent (e.g., toluene) the interfacial activity falls with both the increase of the alkyl chain length and its branching. In systems containing a nonsolvating diluent (e.g., octane) the interfacial activity rises with the increase of the alkyl chain length, but falls for the branched compounds. This latter parameter seems to be more important than the effect of the alkyl length. As a result, compounds having a long, strongly branched alkyl can exhibit weaker interfacial activity than their analogs with a short straight alkyl. Simultaneously, different orders of interfacial activity of alkylphenols having various length and structure of the alkyl group can be observed. Similar effects of alkyl chain structure and diluent type were observed for 2-hydroxy-5-alkylbenzophenone oximes and intermediates[138] and for 2-hydroxy-5-alkylbenzaldehyde oximes.[140]

The standard free energy of adsorption $\Delta\mu^o$ is given by Equation 20

$$\Delta\mu^o = -RT \ln (\Pi/x)_o \qquad (20)$$

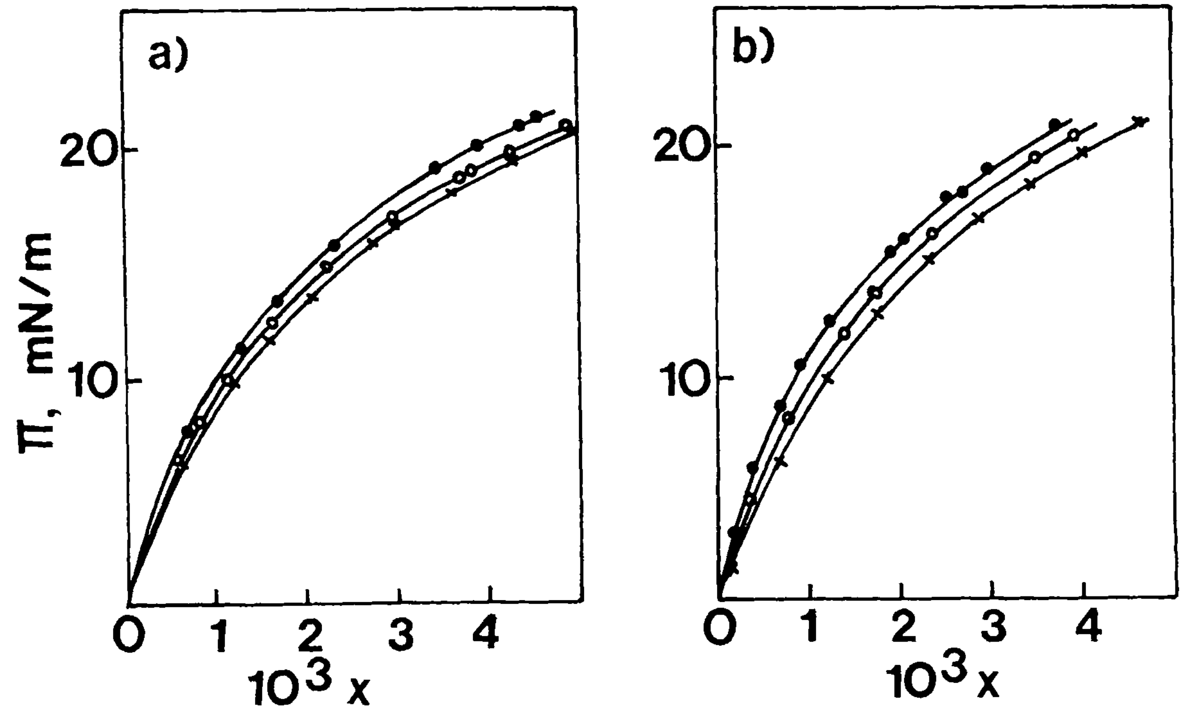


FIGURE 13. Surface pressure isotherms at 20°C (a) dodecane/water interface; ●, octanol; ○, decanol; ×, dodecanol; (b) ●, octane/water; ○, dodecane/water; ×, hexadecane/water). (From Aveyard, R. and Briscoe, B. J., *J. Chem. Soc. Faraday Trans.*, 1, 68, 478, 1972. With permission.)

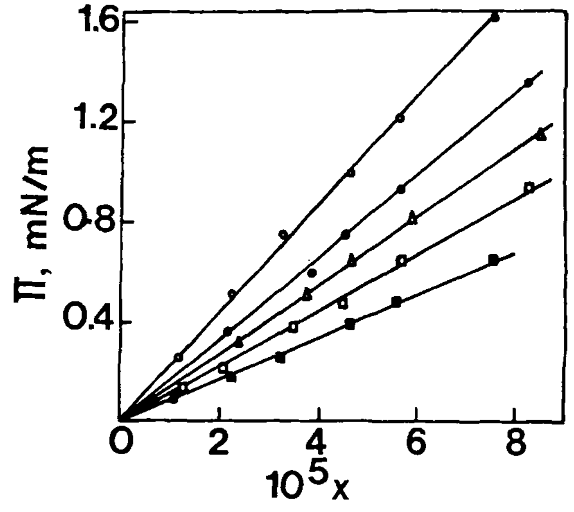


FIGURE 14. Surface pressure isotherms for dodecanol at octane/water interface at various temperatures (○, 15°C; •, 20°C; Δ, 25°C; □, 30°C; and ■, 35°C). (From Aveyard, R. and Briscoe, B. J., *J. Chem. Soc. Faraday Trans.*, 1, 68, 478, 1972. With permission.)

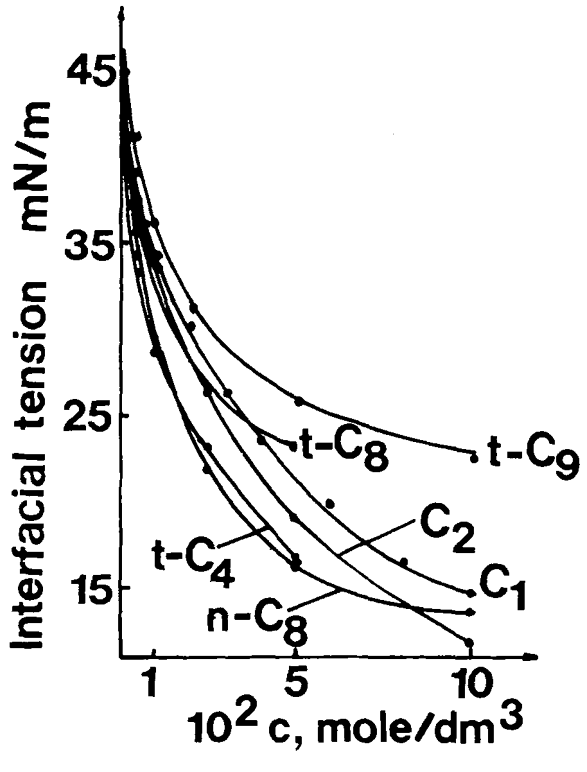


FIGURE 15. Interfacial tension at the octane/water interface for 4-alkylphenols at room temperature. (From Szymanowski, J. and Prochaska, K., *J. Colloid Interface Sci.*, 123, 456, 1988. With permission.)

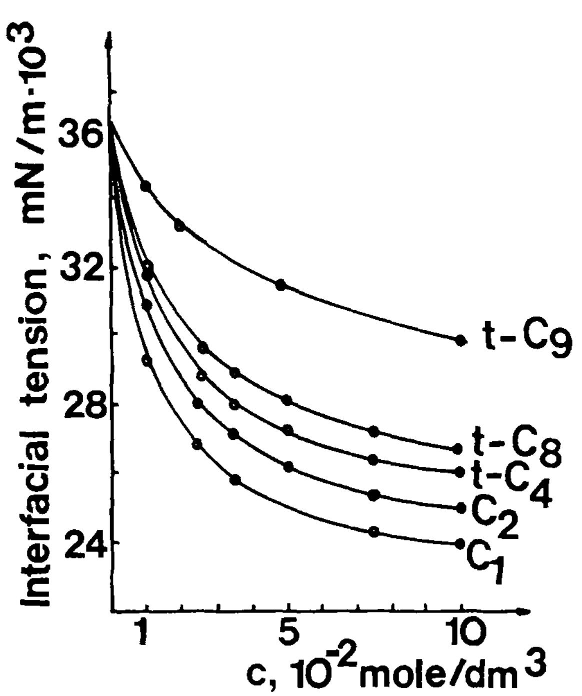


FIGURE 16. Interfacial tension at the toluene/water interface for 4-alkylphenols at room temperature. (From Szymanowski, J. and Prochaska, K., *J. Colloid Interface Sci.*, 123, 456, 1988. With permission.)

where x is the molar fraction of alcohol in the hydrocarbon phase and $(\Pi/x)_0$ is the slope of the (Π,x) plot in the linear, low Π region. The standard states are, for the surface $\Pi = 1$ mN m^{-1}, and for the bulk a hypothetical state in which the product of the molar fraction and activity coefficient is unity, are slightly, but significantly, dependent on the alkane and alcohol chain lengths.[128] The minimum of $-\Delta\mu^o$ is obtained for dodecanol when dodecane is used as the organic phase. No such minimum is found with the alkane chain length for the adsorption of a fixed alcohol, and $-\Delta\mu^o$ falls when the length of the alkane chain increases.

The free energy of adsorption per methylene group from water is approximately equal to the free energy of the transfer of the methylene group from water to alkane. The effect of the alcohol chain length on $\Delta\mu^o$ is very small. From this it might be supposed that the methylene groups in the absorbed solute molecules reside entirely in the alkane and therefore are not in contact with the interfacial water. However, the molar free energy of adsorption of the CH_2 group from vapor to the alkane/vapor surface ($\Delta\mu^o = -2.05$ kJ mol^{-1}) is close to the value for adsorption from vapor to the water/vapor interface ($\Delta\mu^o = -1.76$ kJ mol^{-1}).[128] Therefore, it is impossible to preclude some solute configurations in which methylene groups are in contact with water at the hydrocarbon/water interface. It seems obvious that the final conclusion depends upon the length of the alcohol alkyl chain, and for alcohols used as modifiers in solvent extraction the interactions of methylene groups with water molecules can be neglected with a high probability.

The standard heat of adsorption ΔH^o may be obtained from the standard free energy of adsorption $\Delta\mu^o$ determined at various temperatures according to this equation.

$$\Delta H^o = \frac{d(\Delta\mu^o/T)}{d(1/T)} \qquad (21)$$

A plot $\Delta\mu^o/T$ against $1/T$ obtained for adsorption of n-octanol dodecane/water interface at 15 to 35°C is linear (Figure 17), and ΔH^o is estimated as –31.4 kJ/mol.[127] The heat of the transfer of the *n*-alcohols (butanol to hexanol) from dilute solution in alkanes to dilute solutions in water was determined colorimetrically as about –30 kJ/mol.[130] This means that the greater part of this heat is supposed to result from the transfer of the –OH group. The adsorption process also involves the transfer of the –OH group from alkane to water at the interface and so ΔH^o is of the expected magnitude.

The partition coefficients were determined for some alcohol/alkane/water systems (Table 11).[130] K_c and K_x denote the ratios of molar concentrations and molar fractions in aqueous and alkane phase, respectively. K_c is constant for alcohol concentration in octane up to 0.02 to 0.06 *M* and then falls as a result of alcohol self-association, which should be taken into account at higher alcohol concentrations.

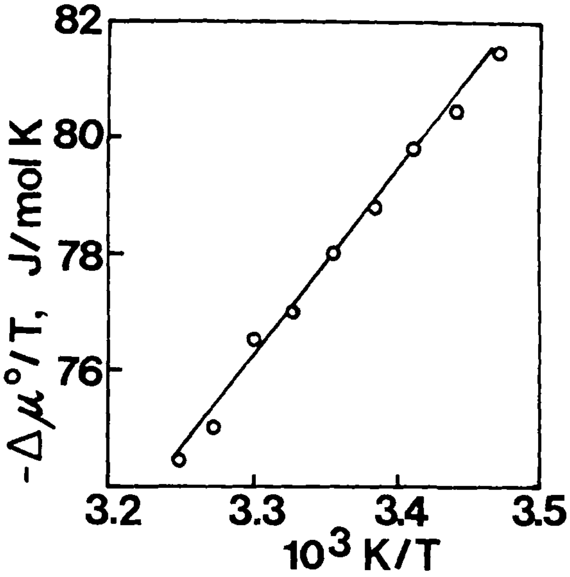


FIGURE 17. The plot $\Delta\mu^o/T$ against $1/T$ obtained for adsorption of n-octanol at dodecane/water interface at 15 to 35°C. (From Aveyard, R. and Briscoe, B. J., *Trans. Faraday Soc.*, 66, 2911, 1970. With permission.)

The partition coefficient may be used to determine the standard free energy of the transfer of the monomeric solute from water to alkane phase, $\Delta G^o_{w/alk}$

$$\Delta\mu^o_{alk} - \Delta\mu^o_w = \Delta G^o_{w/alk} = RT \ln K_x \qquad (22)$$

where R is the gas constant, T is the temperature in absolute scale, and K_x is the partition constant defined by the ratio of molar fractions.

One linear relationship is observed for the standard free energy of the transfer vs. solute chain length for all three alkanes (octane, dodecane, and hexadecane), which allows us to determine the increment for one methylene group as equal to $\Delta G^o_{w/alk}(CH_2) = -3.3$kJ/mol. The molecular area of adsorbed alcohol molecules at the saturated hydrocarbon/water interfaces, calculated from the Gibbs equation

TABLE 11
Partition of Alcohols in Alkane/Water Systems at 20°C (at High Dilution)

n-Alkane	*n*-Alcohol	K_c	K_x
C_8	C_4	6.5±0.4	0.72±0.04
	C_5	1.56±0.04	0.173±0.004
	C_6	0.53±0.02	0.059±0.002
	C_7	0.117±0.007	0.0130±0.0008
C_{12}	C_4	9.1±0.6	0.72±0.05
	C_5	2.04±0.08	0.162±0.006
	C_6	0.60±0.02	0.048±0.001
	C_7	0.137±0.006	0.0109±0.0005
C_{16}	C_4	11.9±0.5	0.733±0.03
	C_5	2.46±0.06	0.152±0.004
	C_6	0.78±0.02	0.048±0.001
	C_7	0.170±0.007	0.0105±0.0005

From Aveyard, R. and Mitchell, R. W., *Trans. Faraday Soc.*, 65, 2645, 1969. With permission.

$$a = -(kT/x)(\partial x/\partial \gamma) \qquad (23)$$

where k stands for the Boltzman constant and γ denotes the interfacial tension, changes from 0.185 to 0.313 nm^2 $molecule^{-1}$. These values are near to the close-packed area (0.22 nm^2 $molecule^{-1}$) observed for insoluble monolayers of alcohols at the air/water interface, where the alkyl chains are aligned approximately normal to the surface.

The (Π,a) data can be described successfully by two-dimensional gas equations of state, including the Schofield-Rideal equation

$$\Pi(a - a_0) = ikT \qquad (24)$$

where a_0 denotes the molecular area at the saturated interface and i is the constant. The a_0 and i values are almost constant and only slightly dependent on the length of the hydrocarbon chains of alcohol and alkane (Table 12).[128] The effect of temperature on these parameters determined for the adsorp-

TABLE 12
Values of a_0 and i for Alcohol Adsorption at Alkane/Water Interface (25°C, Calculated by Fitting Equation 24)

Alcohol	Alkane	a_0 (nm^2 $molecule^{-1}$)	i
Dodecanol	Decane	0.25	0.99
Dodecanol	Dodecane	0.30	0.90
Octanol	Octane	0.24	1.04
Octanol	Dodecane	0.26	1.01

From Aveyard, R. and Briscoe, B. J., *J. Chem. Soc. Faraday Trans.*, 1, 68, 478, 1972. With permission.

tion of *n*-octanol at the water/octane interface also is negligible (Table 13).[130] Different values of a_0 and i also can be found in the literature, for example, 0.313 nm^2/molecule and 0.712 given by Ross and Chen,[131] who did not take into account the self-association of *n*-octanol in *n*-octane. There are considerable deviations from the ideal solution behavior in the region of the molar fraction of alcohol equal to 1×10^{-2}, which must be taken into consideration when the interfacial tension data are interpreted.

The effect of solvent structure and temperature on interfacial activity of 1-octadecanol was very well demonstrated by Motomura et al.[135] The following hydrocarbons were used as the model solvents: hexane, cyclohexane, cyclohexene, mesitylene, toluene, and benzene. The surface tension isotherms in systems containing hexane and cyclohexane are significantly different from systems containing benzene, toluene, and mesitylene (Figure 18). The isotherms have a typical character in the latter system and the interfacial tension monotonically decreases with concentration. The interfacial activity of alcohol is not great, and the variation of γ both with alcohol concentration and temperature is small.

Break points are observed on interfacial tension isotherms determined for systems containing hexane and cyclohexane, and the interfacial tension drops suddenly. This is caused by the transition from the expanded to the condensed film. As a result, a sharp increase of the surface excess (Figure 19) and a sharp decrease of the molecular area ($\Gamma = 1/a$) is observed. This phenomenon depends on temperature and is usually neglected in solvent extraction studies. The surface excess becomes smaller and the molecular area larger with a rise in temperature. The surface excess is remarkably large for the systems containing hexane and cyclohexane, whereas it is low for systems containing aromatic hydrocarbons. Intermediate values are obtained for the system containing cyclohexene. The affinity of aromatic solvent molecules to water molecules is strong enough to reduce the adsorption of alcohol. Similar relations were observed for hydroxyoxime extractants.[1,138]

The surface excess isotherms in nonsolvating hydrocarbons (hexane, cyclohexane) seem to have maximum caused by their strong self-association. Thus, the monomer concentration in the hydrocarbon phase instead of the total concentration should be

TABLE 13
Values of a_0 and i for *n*-Octanol Adsorption at *n*-Octane/Water Interface (25°C, Calculated by Fitting Equation 24)

Temperature (K)	a_0 (nm^2 $molecule^{-1}$)	i
288.15	0.25	0.94
290.65	0.23	0.98
293.15	0.25	0.97
295.65	0.23	1.00
298.15	0.24	1.00
300.65	0.25	0.99
303.15	0.24	1.00
305.65	0.23	0.99
308.15	0.26	1.02

From Aveyard, R. and Briscoe, B. J., *Trans. Faraday Soc.*, 66, 2911, 1970. With permission.

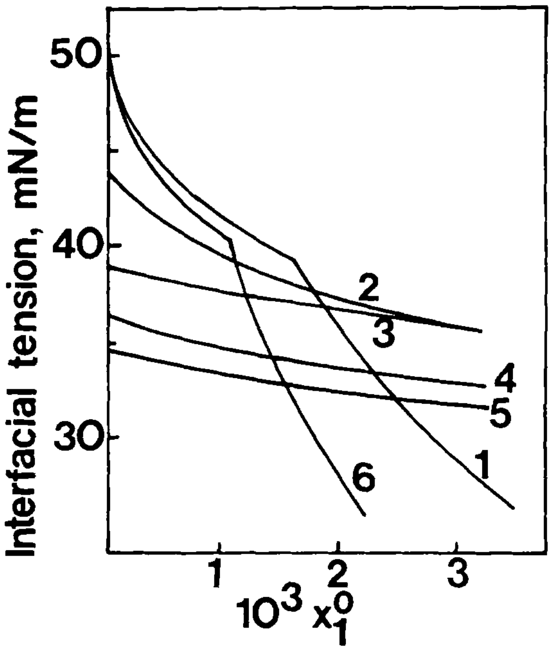


FIGURE 18. Interfacial tension isotherms for 1-octadecanol at 293.15 K (triple distilled water; 1, cyclohexane; 2, cyclohexene; 3, mesitylene; 4, toluene; 5, benzene; and 6, hexane). (From Ikenaga, T., Matubayasi, N., Aratono, M., Motomura, K., and Matuura, R., *Bull. Chem. Soc. Jpn.*, 53, 653, 1980. With permission.)

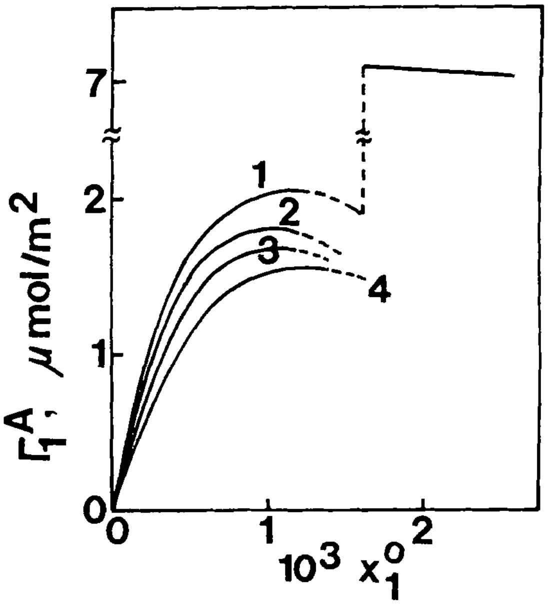


FIGURE 19. Surface excess isotherms for 1-octadecanol at cyclohexane/water interface (1, 293.15 K; 2, 298.15 K; 3, 303.15 K; and 4, 308.15 K). (From Ikenaga, T., Matubayasi, N., Aratono, M., Motomura, K., and Matuura, R., *Bull. Chem. Soc. Jpn.*, 53, 653, 1980. With permission.)

considered, as in the case of hydroxyoxime extractants.[140-145] Break points are also observed on plots γ vs. temperature in systems containing aliphatic (hexane) and cyclic (cyclohexane and cyclohexene) hydrocarbons (Figure 20), but they were not observed in other systems considered.[135] The temperature at which the condensed film is formed becomes lower in the order: hexane, cyclohexane, and cyclohexene, whereas the concentration rises in the same order. The interfacial tension changes very strongly both with temperature and alcohol concentration in the region where the condensed film is formed.

The different adsorption properties of octadecanol in solvating and nonsolvating diluents also are reflected in the values of

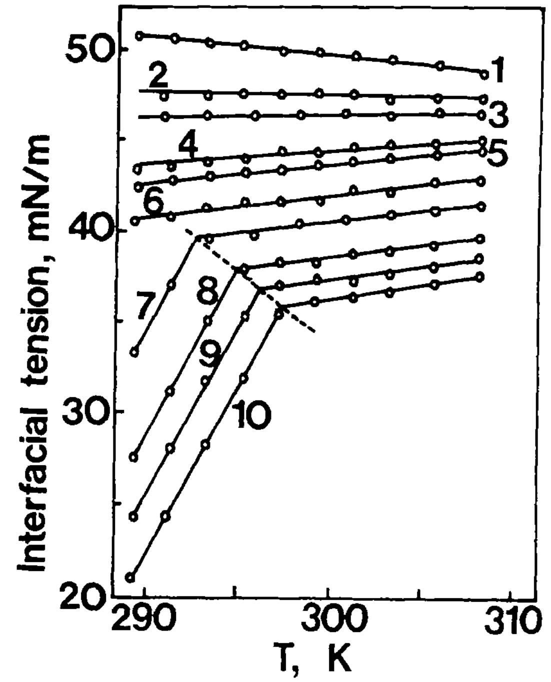


FIGURE 20. Interfacial tension vs. temperature curves of 1-octadecanol at the cyclohexane/water interface at a constant molar fraction (1, 0; 2, 0.138×10^{-3}; 3, 0.241×10^{-3}; 4, 0.522×10^{-3}; 5, 0.734×10^{-3}; 6, 1.012×10^{-3}; 7, 1.556×10^{-3}; 8, 2.065×10^{-3}; 9, 2.542×10^{-3}; and 10, 3.049×10^{-3}). (From Ikenaga, T., Matubayasi, N., Aratono, M., Motomura, K., and Matuura, R., *Bull. Chem. Soc. Jpn.*, 53, 653, 1980. With permission.)

entropy and energy of interface formation defined by relations:

$$\Delta S = -(\partial\gamma/\partial T)_{p,x} \tag{25}$$

$$\Delta u = \gamma + T\Delta S - p\Delta v \tag{26}$$

where Δv is the volume of interface formation. The term $p\Delta v$ is negligibly small and can be neglected. In systems containing hexane and cyclohexane, ΔS decreases rapidly with increasing alcohol concentration from the positive value of pure interface to a negative value in a low concentration region (Figure 21). The transition from expanded to condensed film is also observed. The transition is reflected in the abrupt fall of the entropy of interface formation as the freedom of motion of octadecanol molecules is restrained in the condensed state. In systems containing benzene, toluene, and mesitylene, the extent of variation of ΔS is very small, and ΔS values become smaller in the order: mesitylene, toluene, and benzene. The formation of pure interface causes an increase in the entropy of the whole system, but the adsorption of alcohol diminishes it. The energy of interface formation changes in the same way as that of the entropy (Figure 22).

The interfacial tension between organic liquid and water is related to their mutual solubility. The small value of the interfacial tension between water and benzene is accounted for by the large affinity of the benzene ring for water caused by its Π electrons. Hydrophobic alkyl side chains decrease this affinity. As a result, the interfacial tension increases and the entropy and energy of interface formation decrease, although the differences between benzene, toluene, and mezitylene are not great. The affinity of these solvents for water disturbs the adsorption of alcohol at the interface as reflected in the

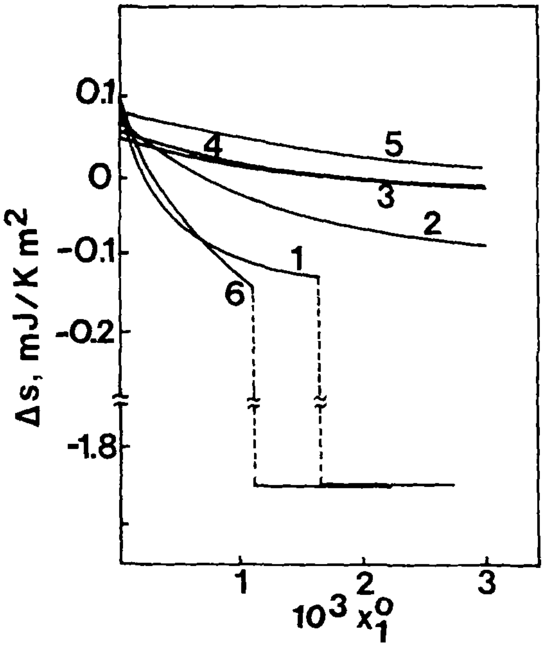


FIGURE 21. Entropy of interface formation vs. molar fraction curves at 293.15 K (triple distilled water; 1, cyclohexane; 2, cyclohexene; 3, mesitylene; 4, toluene; 5, benzene; and 6, hexane). (From Ikenaga, T., Matubayasi, N., Aratono, M., Motomura, K., and Matuura, R., *Bull. Chem. Soc. Jpn.*, 53, 653, 1980. With permission.)

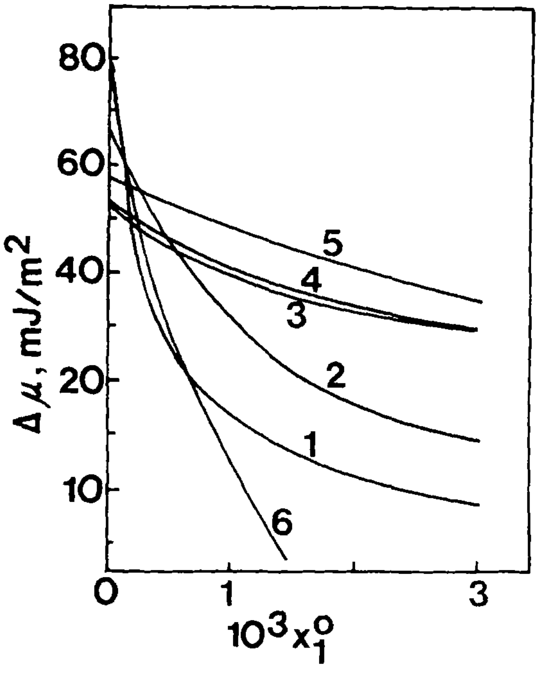


FIGURE 22. Energy of interface formation vs. molar fraction curves at 293.15 K (triple distilled water; 1, cyclohexane; 2, cyclohexene; 3, mesitylene; 4, toluene; 5, benzene; and 6, hexane). (From Ikenaga, T., Matubayasi, N., Aratono, M., Motomura, K., and Matuura, R., *Bull. Chem. Soc. Jpn.*, 53, 653, 1980. With permission.)

small values of surface pressure and surface excess. Alcohol adsorption from hexane and cyclohexane is characterized by a large value of the surface excess, the significant dependence of entropy and energy of interface formation on the concentration, and the phase transition from expanded to condensed film. Such behavior is understandable on the basis of the low mutual solubility of saturated hydrocarbon and water, the high affinity of the hydroxyl group of alcohol for water, and the strong lateral force between alcohol molecules.

In view of discussed results, it is obvious that alcohols present in the solvent extraction systems must retard the extraction. However, this effect depends significantly upon the type of solvent, alcohol concentration, and temperature. Results obtained in model, diluted and well-defined, systems cannot be extrapolated to actual, concentrated and not well-defined, extraction systems.

VI. COADSORPTION OF MODIFIERS WITH EXTRACTANTS AT HYDROCARBON/WATER INTERFACES IN EXTRACTION SYSTEMS

Coadsorption of modifiers with extractants at hydrocarbon/water interfaces has been discussed in only a few papers.[112-114,135] Two cases were considered: (1) the adsorption of modifiers (isodecanol and nonylphenol) in systems containing strongly interfacial active extractants such as dinonylnaphthalene sulfonic acid (**HDNNS**),[112] **HDEHP**,[114] and tri-*n*-octyl/decylamine (**HOSTAREX A327**),[113] and (2) the adsorption of the modifier (isodecanol) and extractants (decyl pyridinemonocarboxylates) that exhibit interfacial activity similar to isodecanol.[135]

The addition of an excess of modifier (alcohol or alkylphenol) to a solution containing a strongly interfacial active extractant (e.g., **HDNNS**) shifts the interfacial tension isotherm toward higher concentrations of extractant and disturbs the micelle formation (Figures 23 and 24). A nonsurface active modifier-extractant complex is formed, which diminishes the surface active species. Such a phenomenon also was reported in a system containing HDNNS and 5,8-diethyl-7-hydroxy-6-dodecanone oxime (**LIX 63**).[116,117] The formation of 1:1 complex was postulated.

The modifiers are less surface active than **HDNNS, HDEHP,** and **HOSTAREX A327**. However, when used in excess, they adsorb at the interface and saturate it. The extractant molecules are not present at the interface. As a result, the interfacial tension falls to the value corresponding to the modifier content in the organic phase. At an appropriate extractant concentration, its adsorption is observed and the interfacial tension begins to decrease, but with a lower gradient. The linear parts of the interfacial tension isotherm (γ vs. log $c_{extractant}$) are less steep than in the systems that do not contain modifiers. Thus, the interfacial concentration of extractant is lower than in the absence of

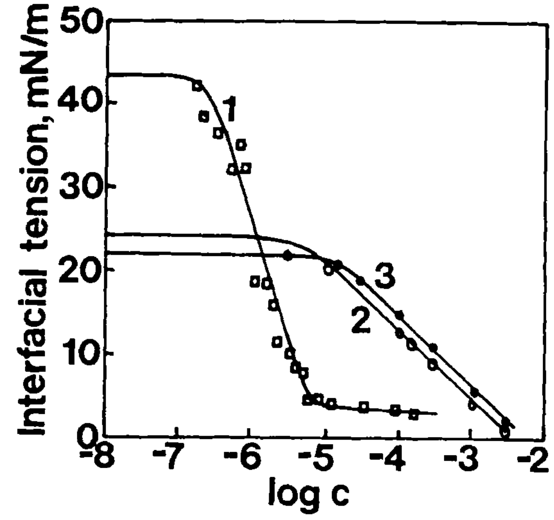


FIGURE 23. Interfacial tension vs. log $[HDNNS]_{total}$ (*M*) relationships (25°C) at n-decane/0.1 HCl interface, in the presence or absence of isodecanol (1, without modifier; 2, 0.105 *M* (2% v/v isodecanol; 3, 0.21 *M* (4% v/v) isodecanol). (From Szymanowski, J., Blondet, I., Cote, G., Bauer, D., and Sabot, J.-L., *Hydrometallurgy*, 28, 277, 1992. With permission.)

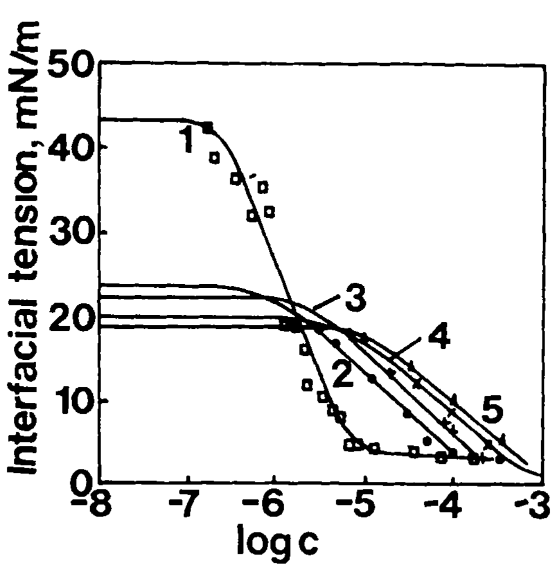


FIGURE 24. Interfacial tension vs. log $[HDNNS]_{total}$ (*M*) relationships (25°C) at *n*-decane/0.1 HCl interface, in the presence or absence of *p*-nonylphenol (1, without modifier); 2, 0.04 *M* (1% v/v p-nonylphenol); 3, 0.07 *M* (2% v/v *p*-nonylphenol); and 4, 0.015 *M* (4% v/v) *p*-nonylphenol). (From Szymanowski, J., Blondet, I., Cote, G., Bauer, D., and Sabot, J.-L., *Hydrometallurgy,* 28, 277, 1992. With permission.)

modifier. In this region, the coadsorption of the extractant and modifier is observed, with the mutual ratio changing with an increase of the extractant concentration. At an appropriately high extractant concentration, its molecules fully displace the modifier molecules at the interface.

The considered phenomenon can be described by the following model that takes into account:

Self-association of modifier (Equation 9 given previously); it can be neglected up to about 0.05 or even 0.1 *M*.

Association of extractant with modifier

$$pHL_o + nROH_o = (HL)_p{*}nROH_o \quad (27)$$

Coadsorption of extractant and modifier at the interface

The Gibbs adsorption equation for two solutes in diluted solutions can be written as

$$d\gamma = -RT(\Gamma_1 d(\ln a_1 + \Gamma_2 d(\ln a_2) \quad (28)$$

where Γ_1 and Γ_2 are the excess surface concentrations of solutes 1 and 2 at the interface, and a_1 and a_2 are their respective activities in the solution phase.

If activities are replaced by concentrations, if there is no interaction between adsorbed solutes at the interface, and if the Langmuir isotherm is valid, then the surface excess is given by Equations 29 and 30

$$\Gamma_1 = \Gamma_1^{max}\alpha_1 c_1 / (1 + \alpha_1 c_1 + \alpha_2 c_2) \quad (29)$$

$$\Gamma_2 = \Gamma_2^{max}\alpha_2 c_2 / (1 + \alpha_1 c_1 + \alpha_2 c_2) \quad (30)$$

where α_1 and α_2 are the adsorption coefficients.

If $\Gamma_1^{max} = \Gamma_2^{max}$, then Equation 28 can be integrated, giving Relation 31

$$\gamma = \gamma^o - RT\Gamma^{max} \ln(1 + \alpha_1 c_1 + \alpha_2 c_2) \quad (31)$$

Equations 9, 27, and 31, together with the mass balance equations, describe the process and model the interfacial tension isotherm presented as the plot of the interfacial tension and extractant monomer concentration.[112,114] Figure 25 confirms the validity of the model and indicates the importance of the coassociation and self-association, which significantly change the concentrations of individual species, that is, the extractant and the modifier in bulk of the organic phase. All the curves coincide when the actual extractant monomer concentration is considered. The model allows us to obtain the following associate structures and equilibrium constants: $(\mathbf{HDNNS})_3(\text{isodecanol})_1$ and $(\mathbf{HDNNS})_3(\text{p-nonylphenol})_3$ with the formation constants 1.2×10^{13} mol^{-3} dm^{9} and 4×10^{14} mol^{-5} dm^{15}, respectively, for Reaction 27 and $(\text{isodecanol})_4$ and $(p\text{-nonylphenol})_3$ with the formation constants of 50 mol^{-3} dm^{9} and 10 mol^{-2} dm^{6}, respectively, for modifier association.

The model also allows us to estimate the interface coverage by the two competing

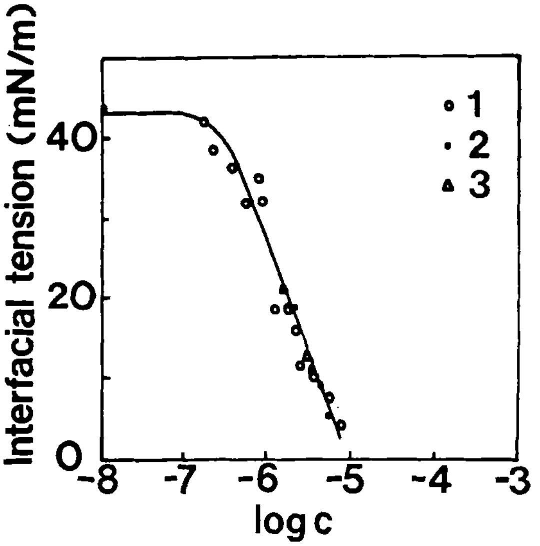


FIGURE 25. Interfacial tension vs. log $[\mathbf{HDNNS}]_{\text{monomer}}$ (*M*) relationships (25°C) at *n*-decane/0.1 HCl interface, in the presence or absence of isodecanol (1, without modifier; 2, 0.105 *M* (2% v/v isodecanol); and 3, 0.21 *M* (4% v/v isodecanol); $(\mathbf{HDNNS})_3(\text{isodecanol})_1$ and $(\text{isodecanol})_4$ with the formation constants of 1.2×10^{13} mol^{-3} dm^9 and 50 mol^{-3} dm^9, respectively). (From Szymanowski, J., Blondet, I., Cote, G., Bauer, D., and Sabot, J.-L., *Hydrometallurgy*, 28, 277, 1992. With permission.)

components, that is, extractant and modifier molecules. However, it is not possible to assume in each case that the values of the surface excess at saturation are approximately the same for both competing components (assumption needed to integrate Equation 28 into Equation 31), as in the case of **HDEHP** and isodecanol.[114]

However, it is not a typical case that $\Gamma_1^{\max} = \Gamma_2^{\max}$ is needed to integrate Relation 28.

The surface excess concentration of each of two amphiphilic substances can be calculated from the Gibbs adsorption equations.[146]

$$\Gamma_1 = -1/(RT)\left(\partial\gamma/\partial c_1\right)_{c_2} \qquad (32)$$

$$\Gamma_2 = -1/(RT)\left(\partial\gamma/\partial c_2\right)_{c_1} \qquad (33)$$

The molar fraction of component 1 at the surface is then given by the relationship

$$x_1 = \frac{\Gamma_1}{\Gamma_1 + \Gamma_2} \qquad (34)$$

These equations are valid for diluted systems containing either a mixture of two nonionic amphiphilic substances below their critical micelle concentration (CMC) or a mixture of a nonionic substance and an ionic one, also below their cmc, in the presence of a swamping excess of electrolyte with a common ion.

Thus, one can consequently determine the excess surface concentration and molar fraction at the interface from two series of the interfacial tension-concentration curves in which the concentration of the second amphiphilic component is kept constant, that is, γ vs. c_1 for c_2 = constant and γ vs. c_2 for c_1 = constant.

A convenient system for studies is that in which the interfacial tension isotherms γ vs. extractant concentration are determined for the constant ratios of extractant-to-modifier concentration.[147-152] In such a case of a mixture of two amphiphilic substances, it is possible to use the non-ideal solution theory to estimate the relative effectiveness of adsorption defined by the molar fractions of these substances at the interface. The approach was initially derived for air/aqueous solutions and then broaden to liquid/liquid systems.

The molar concentrations of two amphiphilic substances (extractant and modifier) in the solution (c_1 and c_2) are given by the equations:

$$c_1 = \alpha_1 c_{1,2} = c_1^{o} f_1 x_1 \qquad (35)$$

$$c_2 = \alpha_2 c_{1,2} = c_2^{o} f_2 x_2 \qquad (36)$$

where α_1 and α_2 are molar fractions of extractant 1 and modifier 2 in the total concentration $c_{1,2}$ in the solution phase, $\alpha_1 = 1 - \alpha_2$; c_1^o, c_2^o and $c_{1,2}$ are solution-phase molar concentrations of extractant, modifier, and their mixture, respectively, required to produce a given interfacial tension value; f_1 and f_2 are activity coefficients of extractant and modifier, respectively, in the mixed adsorption monolayer; x_1 and x_2 are their molar fractions in the adsorption monolayer, $x_1 = 1 - x_2$. It is assumed that the solubilities of the extractant and modifier are negligible in the aqueous phase and that the total concentrations can be considered. From non-ideal solution theory, the activity coefficients at the interface can be approximated by the relationships:

$$\ln f_1 = \beta^{\sigma}(1 - x_1)^2 \tag{37}$$

$$\ln f_2 = \beta^{\sigma}(1 - x_2)^2 \tag{38}$$

where $\beta\sigma$ is the molecular interaction parameter for mixed monolayer formation.

Equations 35 to 38 give relationships valid for nonionic amphiphilic substances:

$$\frac{x_1^2 \ln\left(c_1 / c_1^o x_1\right)}{\left(1 - x_1\right)^2 \ln\left[c_2 / c_2^o\left(1 - x_1\right)\right]} = 1 \tag{39}$$

$$\beta^{\sigma} = \frac{\ln\left(\alpha_1 c_{1,2} / c_1^o x_1\right)}{\left(1 - x_1\right)^2} \tag{40}$$

from which the relative effectiveness of adsorption at the interface and the molecular interaction parameter can be determined. These equations are also valid for mixtures containing nonionic and ionic amphiphilic substances when a swamping constant concentration of electrolyte is present. In another case, the activity coefficients of both solutes at the interface (f_1 and f_2) and in solutions containing only one amphiphilic substance (f^o_1 and f^o_2) must be known. Equation 41 must be used.

$$\frac{x_1^2 \ln\left(c_1 f_1 / c_1^o f_1^o x_1\right)}{\left(1 - x_1\right)^2 \ln\left[c_2 f_2 / c_2^o f_2^o\left(1 - x_1\right)\right]} = 1 \tag{41}$$

For a given ratio of two species and imposed interfacial concentration, their bulk concentrations c_1 and c_2 can be easily determined if they do not associate together. In the opposite case, the association constant must be known. Furthermore, the bulk concentrations c^o_1 and c^o_2 can be easily derived from the plots γ vs. c_1 and γ vs. c_2 obtained from solutions containing only one type of species (extractant or modifier). By introducing the values c^o_1, c^o_2, c_1, and c_2 into Equation 41, one can iteratively derive the values of x_1 and $x_2 = (1 - x_1)$. Thus, the relations γ vs. c for individual reagents and their fixed mixture must be known, as is presented in Figures 26 and 27. They consider two different cases of various interfacial activities of extractant and modifier.

Figure 26 demonstrates that **HOSTAREX A327** is more surface active than isodecanol, and the isotherm determined for the mixture of these two reagents lies between isotherms of individual components. Moreover, the isotherm of the mixture lies near the iso-

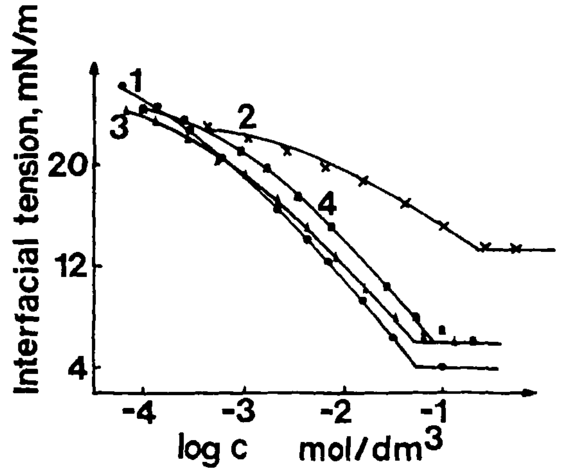


FIGURE 26. Interfacial tension isotherms at 6% lactic acid aqueous solution/kerosene interface at room temperature (1, **HOSTAREX A327**; 2, isodecanol; 3 and 4, **HOSTAREX A327** to isodecanol = 0.72:1 mol/mol, 3, interfacial tension vs. **HOSTAREX A327** concentration; 4, interfacial tension vs. sum of **HOSTAREX A327** and isodecanol concentrations). (From Szymanowski, J., Miesiac, I., Schügerl, K., and Sobczyńska, A., *Solvent Extraction Ion Exchange*, 10, 509, 1992. With permission.)

therm of the **HOSTAREX A327**, which suggests that the interface is almost completely occupied by extractant molecules. This is confirmed by the computed values of the molar fractions of **HOSTAREX A327** at the interface, $x_1 > 0.72$.[113]

Decyl picoliniate used as a model for **ACORGA CLX 50** is less surface active than decanol (Figure 27), and the latter is a dominant species at the interface, $0.40 < x_1 < 0.42$.[153] Moreover, the isotherms of the mixtures are shifted to the lower concentration region in comparison to the isotherms of the individual components. Thus, a synergism in the interfacial tension reduction efficiency is observed.

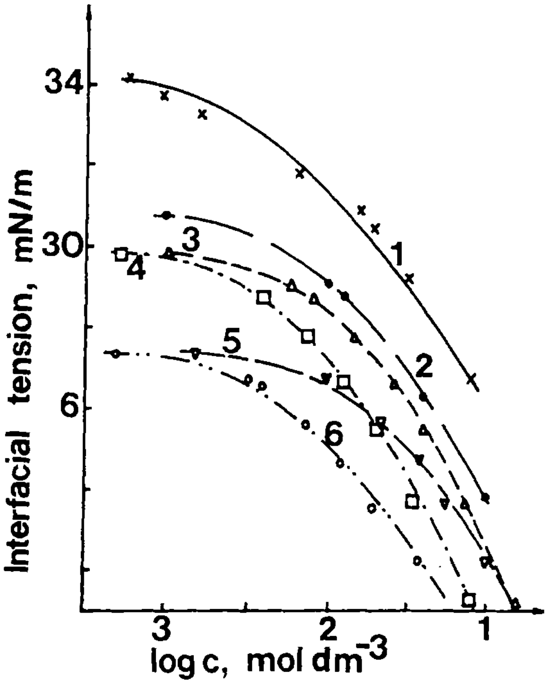


FIGURE 27. Interfacial tension isotherms at 0.1 *M* HCl/toluene interface at 25°C (1, decyl picoliniate; 2, decanol; 3 and 4, decyl picoliniate to decanol = 1:1 mol/mol; and 5 and 6, decyl picoliniate to decanol = 1:2 mol/mol; curves 3 and 5 correspond to the interfacial tension vs. decyl picoliniate concentration and curves 4 and 6, interfacial tension vs. sum of decyl picoliniate and decanol concentrations). (From Szymanowski, J., Cote, G., Sobczyńska, A., Firgolski, K., and Jakubiak, A., *Solvent Extraction Ion Exchange*, 12, 69, 1994. With permission.)

The synergism can be characterized by the efficiency and the effectiveness in surface/interfacial tension reduction.[154] The first parameter is defined as the solution-phase concentration required to produce a given surface/interfacial tension (reduction). Synergism in this respect is present in a binary mixture of amphiphilic substances when a given surface tension (reduction) can be attained at a total mixed surfactant concentration lower than that required of either component by itself. The conditions for synergism in this respect are the same for air/liquid and liquid/liquid interfaces. They are as follows[147]

$$\beta^\sigma < 0 \tag{42}$$

$$|\beta^\sigma| > \left|\ln \frac{c_1^o t}{c_{2,t}^o}\right| \tag{43}$$

where $c_{1,t}^o$ and $c_{2,t}^o$ are the total system concentrations of individual amphiphilic substances required to produce a given interfacial tension in the two-phase systems containing only the individual components and all systems (containing individual components and their mixtures) are compared at the same phase volume ratio.

When synergism exists, a minimum exists in the $c_{1,2}$ vs. α curve, which allows us to obtain the maximum synergism parameters. At this point of maximum synergism, the molar fraction α_1^* of extractant 1 in the total concentration $c_{1,2}$ in the solution phase is equal to the molar fraction at the interface and is given by the expression:

$$\alpha_1^* = x_1 = \frac{\ln\left(c_{1t}^o / c_{2,t}^o\right) + \beta^\sigma}{2\beta^\sigma} \tag{44}$$

The minimum total concentration of mixed amphiphilic substances in the system $c_{1,2,t}^{\min}$ to produce a given interfacial tension is given by the relationship:

$$c_{1,2,t}\min = c_{1t\,\exp}^o\left[\beta^\sigma\left(\frac{\beta^\sigma - \ln c_{1t}^o / c_{2,t}^o}{2\beta^\sigma}\right)^2\right] \tag{45}$$

Synergism in surface/interfacial tension reduction exists when the CMC of the mixture of amphiphilic substances reaches a lower surface/interfacial tension than that obtained at the cmc of either component of the mixture by itself. However, this is not a case encountered in solvent extraction because the modifiers are not surface active strong enough and they do not form micelles.

Recently, Prochaska[159] studied the interfacial activity of various types of hydroxyoximes and hydrophobicity (2-hydroxy-5-alkylbenzophenone and α-acyloin oximes having various lengths and structures of the alkyl group) and did not observe any synergism in the interfacial tension reduction.

The approach discussed above is very useful, but its application is limited to a narrow range of concentrations in which the three interfacial tension values can be read from the graphs. Therefore, the coadsorption can be determined only for a small range of the interfacial tension.

In all the considered extraction sytems, one can expect retardation of extraction caused by interface blocking by the adsorbed modifier molecules. However, this effect should be especially strong in the case when a mixture of an extractant of low interfacial activity (e.g., decyl picoliniate) and an alcohol (decanol) are used for extraction.

VII. CONCLUSIONS

The effect of modifiers on the equilibrium and kinetics of metal extraction can be explained by their association with extractant molecules and coadsorption at the hydrocarbon/water interface. Both extraction and adsorption data can be modeled when self-association and adsorption of extractant and modifier molecules and their mutual association and coadsorption are taken into consideration. Appropriate procedures were given.

ACKNOWLEDGMENT

The work was supported by Polish KBN Research Donation for Institute Activity DS PP No 32/221.

APPENDIX

Commercial Extractants Mentioned in the Paper

Extractant	Manufacturer	Components
ACORGA P 50	ICI	2-Hydroxy-5-nonylbenzaldehyde oxime
ACORGA P5100	ICI	P 50 + nonylphenol, 1:1
ACORGA P 5200	ICI	P 50 + nonylphenol, 1:2
ACORGA P 5300	ICI	P 50 + nonylphenol, 1:3
ACORGA PT 5050	ICI	P 50 + tridecanol, 2:1
LIX 860	Henkel	2-Hydroxy-5-dodecylbenzaldehyde oxime
LIX 622	Henkel	LIX 860 + tridecanol
LIX 65N	Henkel	2-Hydroxy-5-nonylbenzophenone oxime
LIX 63	Henkel	5.8-Diethyl-7-hydroxy-6-dodecanone oxime
LIX 64N	Henkel	LIX 65N + LIX 63, 44:1
LIX 864	Henkel	LIX 860 + LIX 64N
LIX 865	Henkel	LIX 860 + LIX 65N
LIX 84	Henkel	2-Hydroxy-5-nonylacetophenone oxime
LIX 984	Henkel	LIX 860 + LIX 84
ACORGA CLX-50	ICI	Pyridine-3,5-dicarboxylic acid esters
TBP	Various	Tributylphosphate
PC 88A	Daihachi	2-Ethylhexyl 2-ethylhexylphosphonate
CYANEX 272	Cyanamid	*Bis*(2,4,4-trimethylpentyl)phosphinic acid
CYANEX 923	Cyanamid	Straight-chain trialkyl phosphine oxides
CYANEX 925	Cyanamid	Branched-chain trialkyl phosphine oxides
HDEHP	Various	*Bis*(2-ethylhexyl)phosphoric acid
HOSTAREX A327	Hoechst	Tri-*n*-octyl/decylamine

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