

COPPER(II) EXTRACTION BY, ALKYL- AND ALKENYL-SUBSTITUTED 8-QUINOLINOLS

Mírko ČERNÝ, Jan VILÍMEC, Jitka ŠTASTOVÁ, Vladimír ROD and Miloš KRAUS

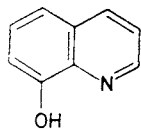
*Institute of Chemical Process Fundamentals,
Czechoslovak Academy of Sciences, 165 02 Prague 6-Suchbát*

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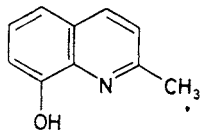
The equilibrium and kinetics of copper extraction from water solutions of copper(II) perchlorate into chloroform by 8-quinolinol, 2-methyl-8-quinolinol, six 7-alkenyl-8-quinolinols (with C₃ to C₁₂ side chains) and by 7-(*p*-tert.butylbenzyl)-8-quinolinol were measured. The data were treated by previously derived models which take into account the complex nature of the extraction process. The equilibrium data were expressed as extraction constants K_{ex} , the rate data as the rate parameter Θ and initial extraction rates J^0 , respectively. The influence of the position, size and structure of the substituents on these parameters is discussed. A strong effect of the position of the double bond C=C in the side chain was found.

A number of complexing agents were recommended for the hydrometallurgical extraction of copper from its solutions, among them derivatives of 8-quinolinol (8-hydroxyquinoline)^{1,2}. For commercial applications, the 8-quinolinol based agent Kelex 100 was offered and eventually, it was studied repeatedly (e.g.³⁻⁸) with favourable results. The analysis of its composition revealed as its main constituent 7-(1-ethenyl-3,3,5,5-tetramethylhexyl)-8-quinolinol (*IIIc*)⁹⁻¹².

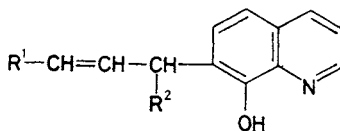
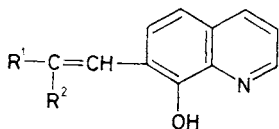
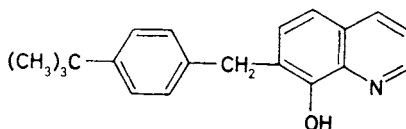
As a continuation of our interest in the influence of extractant structure on the equilibrium and kinetics of metal extraction¹³, we have studied 8-quinolinol (*I*) and its derivatives 2-methyl-8-quinolinol (*II*), 7-(2-propenyl)-8-quinolinol (*IIIa*), 7-(1-ethenyl-3,3-dimethylbutyl)-8-quinolinol (*IIIb*), the above mentioned compound *IIIc*, 7-(5,5,7,7-tetramethyl-2-octenyl)-8-quinolinol (*III d*), 7-(1-propenyl)-8-quinolinol (*IVa*), 7-(2-ethyl-1-hexenyl)-8-quinolinol (*IVb*) and 7-(*p*-tert.butylbenzyl)-8-quinolinol (*V*), respectively, for extraction of copper(II) from perchlorate water solutions into chloroform in the pH range 1.5 to 12.0. The treatment of data was based on previously developed model of the extraction process¹⁴.



I



II

III a, $R^1 = R^2 = H$ III b, $R^1 = H$, $R^2 = CH_2C(CH_3)_3$ III c, $R^1 = H$, $R^2 = CH_2C(CH_3)_2CH_2C(CH_3)_3$ III d, $R^1 = CH_2C(CH_3)_2CH_2C(CH_3)_3$, $R^2 = H$ IV a, $R^1 = H$, $R^2 = CH_3$ IV b, $R^1 = C_2H_5$, $R^2 = C_4H_9$ 

V

EXPERIMENTAL

Materials

8-Quinolinol (I) and 2-methyl-8-quinolinol (II) were commercial reagents (both p.a. grade, Lachema or Fluka, resp.) and were used after recrystallization from ethanol.

7-(2-Propenyl)-8-quinolinol (IIIa) (ref.¹⁵). Potassium (16.5 g) was dissolved in 350 ml of dry methanol and 60 g of 8-quinolinol with 50 g of allyl bromide were added. The mixture was refluxed under nitrogen for 5 h, methanol was distilled off and 20 g of NaOH in 200 ml water was added. The product was extracted with diethyl ether and yielded by distillation 52.5 g of 8-allyloxyquinoline, b.p. 95–100°C/6.6 Pa. Heating of it at normal pressure in nitrogen atmosphere to 200°C resulted in violent reaction, accompanied by a temperature rise to 290°C. Distillation of the reaction mixture yielded 45.0 g of IIIa, b.p. 95–96°C/6.6 Pa, m.p. 42.0°C (the literature reports m.p. 42–43°C (ref.¹⁶) and 46°C (ref.¹⁷)).

7-(1-Ethenyl)-3,3-dimethylbutyl)-8-quinolinol (IIIb). 8-Quinolinol (14.8 g) was dissolved in 50 ml of dimethylformamide, 6.6 g of KOH in 15 ml of methanol and 14.6 g of 1-chloro-5,5-dimethyl-2-hexene¹⁸ were added; the mixture was heated to 37°C for 20 h. Water was added and the product extracted with diethyl ether. Distillation yielded 18.95 g of the corresponding O-alkenyl-8-quinolinol, m.p. 115–122°C/106–133 Pa. It was heated under reduced pressure in a distillation flask and when the temperature of the oil bath reached 260°C, an exothermic reaction started and 11.4 g of a material distilled, b.p. 222–230°C/9.1 kPa, m.p. 47.5–48.5°C. NMR analysis confirmed the structure IIIb ($\delta(CH_3) = 30.1$, $\delta(CH_2) = 113.3$). For $C_{17}H_{21}ON$ (255.4) calculated: 79.96% C, 8.29% H; found: 79.77% C, 8.22% H.

7-(1-Propenyl)-8-quinolinol (IVa) (ref.¹⁹). The mixture of 24.7 g of 7-(2-propenyl)-8-quinolinol, 40.5 g of KOH and 260 ml of 1-butanol was refluxed for 7 h. 1-Butanol was removed by steam distillation, the residue was neutralized by HCl and extracted with diethyl ether. Compound IVa

was isolated by distillation (12.5 g), b.p. 96–98°C/13.3 kPa, and by recrystallization from ethanol (9.7 g). M.p. 85.5–86.0°C, ref.¹⁹ reports 86.5–87.0°C.

7-(2-Ethyl-1-hexenyl)-8-quinolinol (IVb) (ref.²⁰). From 24.65 g of 8-quinolinol, 17.0 g of 2-ethylhexanal, 22 ml of toluene and 0.3 g of powdered KOH, after 24 h of azeotropic distillation of the water formed and removal of the solvent, unreacted aldehyde and quinolinol by vacuum distillation a fraction boiling at 196–200°C/1.8 kPa was obtained (4.75 g). Redistillation yielded 1.3 g of IVb, b.p. 125–127°C/27 Pa; ref.²⁰ reports 179–180°C/666 Pa. The purity of the product was confirmed by gas chromatography and NMR.

7-(5,5,7,7-Tetramethyl-2-octenyl)-8-quinolinol (IIIId). All operations were made in a stream of nitrogen. To a mixture of 5.8 g of sodium hydride and 25 ml of dry toluene a solution of 28.0 g of 8-quinolinol in 170 ml of dry toluene was added slowly with stirring. A yellow-green precipitate of the sodium salt was formed and the mixture was then refluxed for 1 h. A total of 39.2 g of 1-chloro-5,5,7,7-tetramethyl-2-octene²¹ was added and the mixture was refluxed for 6 h. Water was added, the organic layer was taken into diethyl ether, the extracts were washed with 5% sulfuric acid and with water and distilled. Unreacted starting compounds were recovered by distillation (16 g) and then a mixture of isomeric O-dodeceny-8-quinolinols, boiling 150 to 160°C/26.6 Pa, was obtained (6.15 g). Its rearrangement at 270°C and 17 kPa gave a product distilling at 220–240°C (4.5 g). NMR analysis showed that the product is a mixture of IIIc and IIIId in the ratio 1 : 1, according to the intensity of the signals at $\delta = 49.2$. The patent²⁰ claims preparation of pure IIIId by this procedure. For C₂₁H₂₉ON (311.5) calculated: 80.98% C, 9.38% H; found: 80.86% C, 9.32% H.

7-(*p*-Tert-butylbenzyl)-8-quinolinol (V). To a mixture of 12.7 g of NaOH and 530 ml of dry toluene a hot solution of 69.3 g of 8-quinolinol in 180 ml of dry toluene was added in a flask protected by a continuous stream of nitrogen. After 1 h of refluxing, 87 g of *p*-tert-butylbenzylchloride²² was added and the mixture refluxed for 6 h. The slurry was allowed to stand for 2 days and then it was decomposed by 250 g of crushed ice with 65 ml of concentrated hydrochloric acid. Water (250 ml) was added and the organic compounds were extracted with 420 ml of chloroform. Chloroform was evaporated from the extract under reduced pressure and the residue was crystallized from ethanol. The product (24.2 g) was transformed into the copper salt by shaking its solution in 500 ml of toluene with a water solution of 8 g of cupric acetate. The formed precipitate was filtered off, dried (24.0 g) and mixed with 115 ml of sulfuric acid (4 mol l⁻¹) and 135 ml of chloroform. The aqueous layer was extracted with chloroform and after removal of the solvent, the residue was crystallized from ethanol. Compound V (16.5 g) had m.p. 110.0°C; ref.²³ reports 108–109°C. NMR analysis confirmed the structure V (signals $\delta(\text{CH}_3) = 31.4$, $\delta(\text{C quart.}) = 34.3$, $\delta(\text{CH}_2) = 35.1$).

Stock solutions of copper(II) perchlorate were prepared by dissolving copper sheet (Merck) in perchloric acid (UCB, p.a.). Sodium perchlorate (Lachema, p.a.) was used for adjusting the ionic strength. Chloroform (Lachema, p.a.) was purified using the recommended procedure²⁴ and stabilized by addition of 0.5% ethanol.

Analysis

Concentration of copper in the aqueous phase for equilibrium and kinetic measurements was determined chelatometrically, using glycinethymol blue as indicator in the solutions buffered with urotropine to pH 5.0–5.5. For low concentrations, photometry was used with morpholinium dithiocarbamate as the reagent in the presence of polyvinylalcohol ($\lambda = 430$ nm). For the organic phase, either direct spectrometry ($\lambda = 435$ nm) or analysis of the aqueous phase after stripping into water served for the determination of copper.

Equilibrium Measurements

Two types of equilibria were measured. One series concerned the distribution of the extractants between water and chloroform stabilized with 0.5% of ethanol. The distribution ratio of each extractant which depends on its distribution constant and dissociation constants was determined by measuring the concentration of the extractant in the aqueous phase spectrometrically ($\lambda = 250-255$ nm, 278 for compound *IIIa*) at 8 to 12 different pH values in the range 1.5 to 12.0. The total concentration of extractant c_L was known from its amount taken into the experiment. By repeated experiments, the relative standard deviation of extractant concentration was found to be $s_r \approx 2\%$.

For the determination of the extraction constant K_{ex} , the aqueous phase consisted of a solution of copper(II) perchlorate with ionic strength adjusted to $I = 0.1 \text{ mol l}^{-1}$ by addition of sodium perchlorate. The starting concentrations of copper were in the range $5 \cdot 10^{-4} - 3 \cdot 10^{-2} \text{ mol l}^{-1}$. The pH value (range 2.0-3.0) was adjusted by perchloric acid. With each extractant, 5 to 8 measurements were made at different pH values in order to cover the range of distribution ratios D_{Cu} from 0.2 to 5.0. The relative standard deviations were $s_r(\text{Cu})_w \approx 1\%$ and $s_r(\text{Cu})_{org} \approx 0.3\%$.

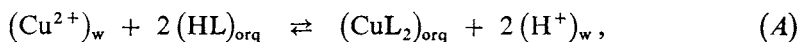
Kinetic Measurement

The used equipment was the diffusion cell with mixing of both phases by vibrating perforated plates¹⁴. The pH value (mostly 4.5) was kept constant by a pH-stat which actuated an automatic burette feeding $2.0 \cdot 10^{-5} \text{ mol l}^{-1}$ sodium hydroxide into the aqueous phase. In ten-minute intervals the consumption of the hydroxide solution was recorded and from it, the amount of copper transferred into the chloroform phase was determined. The conditions and treatment of data are described in the section Results and Discussion.

RESULTS AND DISCUSSION

Extraction Equilibria

The extraction of copper by 8-quinolinols is described by the over-all stoichiometric equation



where the ligand L denotes the deprotonized anion the extractant $\text{R}-\text{C}_9\text{H}_5\text{N}-\text{OH}$, the subscripts w and org the aqueous and chloroform phase, respectively, of the system. Its equilibrium extraction constant K_{ex} is defined by

$$K_{ex} = [\text{CuL}_2]_{org} [\text{H}^+]_w^2 / [\text{Cu}^{2+}]_w [\text{HL}]_{org}^2. \quad (1)$$

However, a series of parallel reactions proceed in the system which are described by the appropriate equilibrium constants K_{a1} , K_{a2} for the deprotonization of the quinolinol, $K_D(\text{HL})$ and $K_D(\text{CuCl}_2)$ for the distribution of the reactants between the organic phase and water and β_1 and β_2 for the formation of the CuL^+ and CuL_2 complexes in water, respectively. Because it was not possible to find directly the

concentrations $[\text{HL}]_w$, $[\text{HL}]_{\text{org}}$ and $[\text{Cu}^{2+}]_w$ from experimental data on extraction, $K_D(\text{HL})$, K_{a1} and K_{a2} were determined independently by separate experiments in the absence of copper and K_{ex} from distribution of the metal, both at various pH.

The material balance of the ligand L is based on its known total concentration in the system with equal volumes of the phases and consists of the sum of concentrations of various forms

$$c_L = [\text{HL}]_{\text{org}} + 2[\text{CuL}_2]_{\text{org}} + [\text{HL}]_w + [\text{L}^-]_w + [\text{H}_2\text{L}^+]_w + 2[\text{CuL}_2]_w. \quad (2)$$

The analysis of the aqueous phase has shown the over-all concentration of the ligand L in various forms

$$c_{L,w} = [\text{HL}]_w + [\text{L}^-]_w + [\text{H}_2\text{L}^+]_w \quad (3)$$

and, similarly, of copper

$$c_{\text{Cu},w} = [\text{Cu}^{2+}]_w + [\text{CuL}^+]_w + [\text{CuL}_2]_w. \quad (4)$$

It was assumed that copper is present only in the form of CuL_2 in the organic phase and therefore,

$$c_{\text{Cu},\text{org}} = [\text{CuL}_2]_{\text{org}}. \quad (5)$$

From Eq. (2) in the absence of copper, the relation between the concentration of the extractant in the aqueous phase and its acidity at known total concentration of the extractant can be derived

$$c_{L,w} = c_L \left/ \left(1 + \frac{K_D(\text{HL})}{1 + [\text{H}^+]_w/K_{a1} + K_{a2}/[\text{H}^+]_w} \right) \right. \quad (6)$$

Eq. (6) represents an implicit model of equilibrium with parameters $K_D(\text{HL})$, K_{a1} and K_{a2} , which can be evaluated from measured values of variables $[\text{L}]_w$, c_L and $[\text{H}^+]_w$. The optimum values of these parameters were estimated by the maximum likelihood method. Deming's algorithm²⁷ was used for finding the minimum of the objective function defined by the sum of weighted squares

$$S = \sum_i (1/s_i^2) \sum_j e_{ij}^2, \quad (7)$$

where e_{ij} denotes deviation of i -th variable in j -th experiment, under the constraint given by Eq. (6). The resulting values of the parameters are summarized in Table I. The agreement between calculated and experimental values of D_L is seen from Fig. 1, where their dependence on pH is shown.

For the measurements of the distribution of copper, Eqs (8) and (9) follow from the definitions of equilibrium constants and Eqs (4) and (5)

$$c_L = 2c_{Cu,org} + \frac{[HL]_{org} \{K_D(HL) + 1 + K_{a2}/[H^+]_w + [H^+]_w/K_{a1}\}}{K_D(HL)} + c_{Cu,w} \frac{\{\beta_1 K_{a2}/K_D(HL)\} ([HL]_{org}/[H^+]_w) + 2\{\beta_2 K_{a2}^2/K_D^D(HL)\} ([HL]_{org}/[H^+]_w)^2}{1 + \{\beta_1 K_{a2}/K_D(HL)\} ([HL]_{org}/[H^+]_w) + \beta_2 K_{a2}^2 ([HL]_{org}/[H^+]_w)^2} \quad (8)$$

TABLE I

Equilibrium and rate parameters at 25°C for the system water-chloroform

Compound	$\log K_D(HL)$	$\log K_{a1}$	$\log K_{a2}$	$\log K_{ex}$	$\log \Theta$ $m^2 s^{-2}$	k_{org} $m s^{-1}$	$J^0 \cdot 10^6$ $kmol m^{-2} s^{-1}$
<i>I</i>	2.63	-5.07	-10.00	1.80	-8.0	50	4.03
<i>II</i>	3.22	-5.51	-10.16	-1.41	—	—	—
<i>IIIa</i>	3.71	-4.52	-10.07	1.97	-8.4	39	3.13
<i>IIIb</i>	4.20	-4.94	-9.80	1.43	-11.7	38	1.55
<i>IIIc</i>	4.49	-4.51	-10.03	1.22	-11.8	34	1.49
<i>IVa</i>	4.48	-4.66	-11.34	2.80	-11.1	39	2.44
<i>IVb</i>	3.82	-3.57	-11.63	2.42	—	—	—
<i>V</i>	5.38	-3.01	-9.70	2.10	-10.7	35	2.63

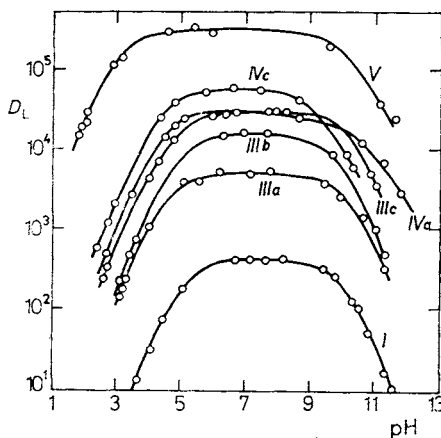


FIG. 1

Dependence of distribution ratios of 8-quinolinol extractants in the system water-chloroform on pH at 25°C. Points are experimental, curves are calculated using Eq. (6)

$$\left(\frac{[\text{HL}]_{\text{org}}}{[\text{H}^+]_{\text{w}}}\right)^2 \left(1 - \frac{K_{\text{D}}(\text{HL}) K_{\text{ex}}}{D_{\text{Cu}} \beta_2 K_{\text{a}2}^2}\right) + \frac{[\text{HL}]_{\text{org}} \beta_1 K_{\text{D}}(\text{HL})}{[\text{H}^+]_{\text{w}} \beta_2 K_{\text{a}2}} + \frac{K_{\text{D}}^2(\text{HL})}{\beta_2 K_{\text{a}2}^2} = 0 \quad (9)$$

Equations (8) and (9) are implicit expressions for the relationship between the experimental variables $c_{\text{Cu,w}}$, $c_{\text{Cu,org}}$ and $[\text{H}^+]_{\text{w}}$ at given total concentration of the extractant c_{L} .

With the knowledge of $K_{\text{D}}(\text{HL})$, $K_{\text{a}1}$ and $K_{\text{a}2}$, the data for copper extraction equilibria, i.e. measured values of $c_{\text{Cu,w}}$, $c_{\text{Cu,org}}$, $[\text{H}^+]_{\text{w}}$ and c_{L} , were evaluated using Eqs (8) and (9), and parameters K_{ex} , β_1 and β_2 were estimated by the optimization method mentioned above. Because of the very low sensitivity of the objective function (7) to parameters β_1 and β_2 , their values could not be estimated with sufficient accuracy ($\beta_1 \approx 10^{12}$, $\beta_2 \approx 10^{23}$) and therefore only K_{ex} values are given in Table I.

Kinetics of Extraction

The measurement of time course of the extraction of copper by the extractants I to V were treated by a model based on the assumption that the formation of the complex CuL_2 proceeds under the conditions of our experiments in the regime of rapid irreversible reaction occurring in the diffusion film of the aqueous phase at the phase boundary. The corresponding rate equation has the form

$$r = k_{\text{r}} c_{\text{HL,org}} c_{\text{Cu,w}} / c_{\text{H}^+, \text{w}} \quad (10)$$

where $c_{\text{HL,org}} = c_{\text{L}} - 2c_{\text{Cu,org}}$. Under these assumptions, the rate of extraction J is described by the approximate relation²⁵

$$J = \frac{c_{\text{HL,org}}/2}{1/k_{\text{org}} + (\Theta c_{\text{Cu,i}}/c_{\text{H}^+, \text{i}})^{-0.5}} \quad (11)$$

where the concentrations of components at the interface are

$$c_{\text{H}^+, \text{i}} = c_{\text{H}^+, \text{w}} + 2J/k_{\text{w}} \quad (12)$$

$$c_{\text{Cu,i}} = c_{\text{Cu}^{2+}, \text{w}} = J/k_{\text{w}} \quad (13)$$

and the combined rate parameter is

$$\Theta = k_{\text{r}} \mathcal{D}_{\text{HL}} / K_{\text{D}}^2(\text{HL}) \quad (14)$$

k_{w} and k_{org} denote mass transfer coefficients for the metal ion in the aqueous phase and for the extractant in the organic phase, respectively.

This model has been tested in a series of experiments with 8-quinolinol (*I*) at three concentrations c_L and c_{Cu} , and two pH values (4.0 and 4.5) with satisfactory result. With other extractants, two initial extractant concentrations ($2.0 \cdot 10^{-3}$ and $1.0 \cdot 10^{-3} \text{ mol l}^{-1}$) and two initial copper concentrations ($1.0 \cdot 10^{-3}$ and $5.0 \cdot 10^{-4} \text{ mol l}^{-1}$) were used at constant pH 4.5. The ionic strength was adjusted to 0.1 mol l^{-1} , the temperature was 25°C . The obtained copper concentration-time dependences were worked up by numerical integration of differential rate equations (11)–(12). For the determination of the values of parameters of the model, the data concerning all extractants were pooled. The coefficient k_w was evaluated as a common parameter, the mass transfer coefficient $k_{org,j}$ for the extractant *j* was related to the value for 8-quinolinol $k_{org,I}$ as reference compound by the relation

$$k_{org,j} = k_{org,I} \sqrt{(\mathcal{D}_{org,j}/\mathcal{D}_{org,I})}. \quad (15)$$

The ratios of diffusion coefficients in Eq. (15) calculated by means of Wilke–Chang correlation²⁶ and the coefficient $k_{org,I}$ was evaluated as a common parameter from the data. The combined kinetic parameter Θ (Eq. (14)) was determined for each extractant separately.

The optimum parameter values were found by minimalization of the weighed sum of squared deviations of experimental and calculated copper concentrations in the organic phase. The found values of $\log \Theta$ and $k_{org,j}$ are given in Table I, together with the values of the initial extraction rates J^0 which were determined as slopes of the tangents to the concentration–time curves at $t = 0$. A comparison of calculated and experimental kinetic dependences for three representative extractants is demonstrated in Fig. 2.

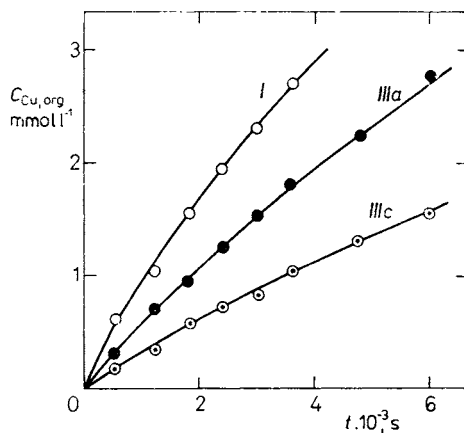


FIG. 2
Examples of experimental (points) and calculated (by Eq. (13)) dependences of copper concentration in the chloroform phase on time at 25°C

Influence of Extractant Structure

Effect of 2-methyl substituent. The introduction of methyl group in position 2 of the 8-quinolinol molecule causes a decrease of the extraction constant K_{ex} by three orders of magnitude from 63 for *I* to 0.039 for *II*. This large effect seems to be steric in nature. In accordance with our finding is the report by Irwing and Rossotti²⁸ who have found much lower complex stability formed from 2-methyl-8-quinolinol than from 8-quinolinol and divalent ions. This was later confirmed by Gerson and coworkers²⁹.

Effect of the size of 7-alkenyl substituents. The values of both the extraction constant K_{ex} and the initial rate of copper extraction J^0 for the series of compounds *III* and *IV* show a decrease within each series with increasing size of the 7-alkenyl group. This is clearly connected with poorer solvation of the extractant by water due to increasing length of the alkenyl group. The trend in the distribution constant $K_D(HL)$ of the compounds *III* confirms this influence. The series *IV* is not consistent for similar consideration because compound *IVb* has branched chain on the double bond.

The complex formation constant β_u in water is related to the extraction constant K_{ex} by the equation

$$K_{ex} = \beta_u K_D(CuL_2) / K_D^2(HL) \quad (16)$$

which follows from the definitions of the extraction constant (Eq. (1)), the distribution constants $K_D(CuL_2)$ and $K_D(HL)$ and stability constant β_u .

Assuming that the ratio $\gamma = K_D(CuL_2) / K_D(HL)$ is independent of the structure of the extractant in a series of similar derivatives, Eq. (16) simplifies to

$$K' = K_{ex} K_D(HL), \quad (17)$$

where $K' = \beta_u \gamma$. Now, as the electronic influence on equilibrium (cf. values of Hammett's sigma constants for alkyl and alkenyl groups in³⁰) of the three alkenyl substituents in the series *III* must be practically the same, we may expect constant value of b (or K') and, consequently of the product $K_{ex} K_D(HL)$. This is fulfilled with sufficient agreement: for compounds *IIIa-c*, $\log(K_{ex} K_D(HL))$ is equal to 5.68, 5.63, 5.71, respectively. This confirms that within a series of structurally related extractants, the value of K_{ex} is given by the distribution constant $K_D(HL)$, because $K_{ex} K_D(HL) \approx \text{const.}$

However, the question arises how closely the extractants must be kindred in order to fulfill this rule. A comparison of the compounds *IIIa* and *IVa* ($\log(K_{ex} K_D(HL)) = 5.68$ or 6.24 , respectively), which differ only by the position of the double bond, shows that the requirement on structural relation is rather strict.

Effect of the position of C=C bond. Aromatic hydroxy compounds with some substituents in *ortho* position differ from *meta* and *para* isomers by their ability to form intramolecular hydrogen bonds. Therefore, the behaviour of the 7-alkenyl-8-quinolinols may be influenced by the type and strength of bonding interactions between the hydroxyl group and either the hydrogens of the alkenyl group or the π electrons of the double bond. With the allyl type substituents, the double bond can interact with hydrogen of the hydroxyl group whereas with the propenyl type substituents, such bonding would require substantial distortion of the bond angles. Therefore, only the weaker hydrogen bonding between oxygen of the hydroxyl group and hydrogen on the 3 carbon atom is possible. In our case, the values of K_{ex} for the allyl derivatives *III* are by one order of magnitude lower than those for propenyl derivatives *IV*. We suggest that the intramolecular hydrogen bonding competes with the complex formation and that the competition is stronger with 7-allyl derivatives.

Also the rate of extraction is slightly influenced by the position of the double bond, as well as by other structural features. In the previous paper¹³ we have suggested that the rate should be related to the distribution constant of the extractant. Fig. 3 shows the plot of initial rates J^0 against partition coefficients. The expected correlation has been obtained only within the series of compounds *III* and probably also *IV* (however, identical slopes support the hypothesis). We assume that the separation of the points for the compounds *I* and *V* is caused by the different degree of intramolecular and intermolecular hydrogen bonding. It should be stressed that these interactions influence both the distribution constants and extraction rate parameters.

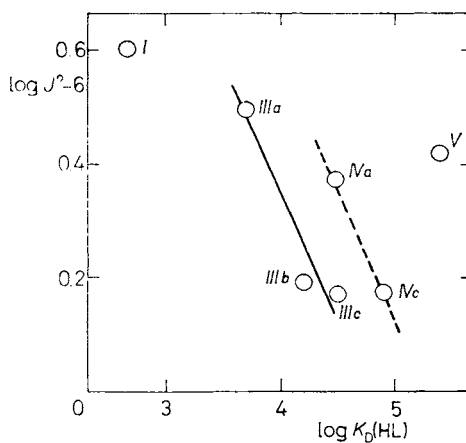


FIG. 3
Plot of initial extraction rate on partition coefficient for different extractants

LIST OF SYMBOLS

c_j	concentration of the species j , kmol m^{-3}
\mathcal{D}_j	diffusivity of the species j , $\text{m}^2 \text{s}^{-1}$
$D_{\text{Cu}} = c_{\text{Cu,org}}/c_{\text{Cu,w}}$	distribution ratio of copper, —
$D_{\text{L}} = c_{\text{L,org}}/c_{\text{L,w}}$	distribution ratio of the reactant HL, —
I	ionic strength, kmol m^{-3}
J	extraction rate, $\text{kmol m}^{-2} \text{s}^{-1}$
J^0	initial extraction rate, $\text{kmol m}^{-2} \text{s}^{-1}$
$K_{a1} = [\text{HL}]_{\text{w}}[\text{H}^+]_{\text{w}}/[\text{H}_2\text{L}^+]_{\text{w}}$	acid-base equilibrium constant, kmol m^{-3}
$K_{a2} = [\text{L}^-]_{\text{w}}[\text{H}^+]_{\text{w}}/[\text{HL}]_{\text{w}}$	acid-base equilibrium constant, kmol m^{-3}
$K_{\text{D}}(\text{CuL}_2) = [\text{CuL}_2]_{\text{org}}/[\text{CuL}_2]_{\text{w}}$	distribution constant of CuLa , —
$K_{\text{D}}(\text{HL}) = [\text{HL}]_{\text{org}}/[\text{HL}]_{\text{w}}$	distribution constant of HL, —
K_{ex}	extraction equilibrium constant (Eq. (1)), —
$k_{\text{org}}, k_{\text{w}}$	mass transfer coefficients, m s^{-1}
k_r	rate constant, s^{-1}
r	reaction rate, $\text{kmol m}^{-3} \text{s}^{-1}$
s	standard deviation, kmol m^{-3}
t	time, s
$\beta_1 = [\text{CuL}^+]_{\text{w}}/[\text{Cu}^{2+}]_{\text{w}}[\text{L}^-]_{\text{w}}$	formation constant, $\text{kmol}^{-1} \text{m}^3$
$\beta_2 = [\text{CuL}_2]_{\text{w}}/[\text{Cu}^{2+}]_{\text{w}}[\text{L}^-]_{\text{w}}$	formation constant, $\text{kmol}^{-1} \text{m}^3$
$\beta_{\text{u}} = [\text{CuL}_2]_{\text{w}}[\text{H}^+]_{\text{w}}/[\text{Cu}^{2+}]_{\text{w}}[\text{HL}]_{\text{w}}$	equilibrium constant, —
$\gamma = K_{\text{D}}(\text{CuL}_2)/K_{\text{D}}(\text{HL})$	ratio of distribution constants, —
Θ	combined rate parameter, (Eq. (14)), $\text{m}^2 \text{s}^{-2}$
$[]$	equilibrium concentrations, kmol m^{-3}

Subscripts

org	chloroform phase
w	water phase

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