

## Extraction of copper(II) and nickel(II) by long-chain aliphatic dioximes

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## EXTRACTION OF COPPER(II) AND NICKEL(II) BY LONG-CHAIN ALIPHATIC DIOXIMES

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WOLPUT and T. P. M. BEELEN\*

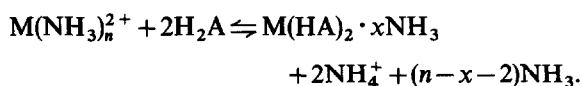
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**Abstract**—In the search for a selective nickel extractant symmetric dialkyl dioximes have been studied in the extraction of copper and nickel ions from ammoniacal and acidic solutions. Extraction from ammoniacal solutions showed great differences between copper and nickel. Because of slow kinetics for nickel, much more copper than nickel was extracted at short contact times, but since nickel forms more stable chelates, more nickel than copper was extracted after long contact times. Because of steric hindrance and solubility the extraction was also dependent on the length of the alkyl chains of the aliphatic dioximes. Two different chelates,  $\text{CuL}_2$  and  $\text{Cu}_4\text{L}_3(\text{OH})_2$ , were involved in the extraction of copper from acidic solutions. Kinetic measurements of the extraction of nickel from acidic solutions showed a first order dependence in ligand and nickel concentrations and almost zero order in  $\text{H}^+$  concentration, demonstrating that the reaction of  $\text{Ni}^{2+}$  with the first non-ionized dioxime molecule is rate determining.

From analytical chemistry it is well-known that nickel ions react with dimethylglyoxime to form quantitatively the red bis(dimethylglyoximate) nickel(II) chelate. The relatively low solubility of dimethylglyoxime in organic solvents makes this compound unattractive for extraction. Burkin and Preston<sup>1</sup> investigated some aliphatic *vic*-dioximes with alkyl groups ranging from C5 to C7 and found extremely low extraction rates for nickel, especially with compounds containing secondary alkyl groups. From previous work<sup>2,3</sup> it became clear that the use of *vic*-bicyclic dioximes increases enormously the extraction rate for nickel. Unfortunately, however, in contrast with monocyclic *vic*-dioximes, their  $\text{pH}_{1/2}$  values for copper are smaller than those for nickel. Navtanovich and co-workers<sup>4</sup> discovered that the extraction of Cu(II) and Ni(II) from ammoniacal solutions is dependent on the total number of carbon atoms. Equilibrium was not established in the extraction and re-extraction of nickel. The extraction of copper(II) and nickel(II) from ammoniacal solutions is not identical in character with the pH dependent extraction from acidic solutions.<sup>2,3</sup> Although, because of the ammonia, the pH is greater

than 7, no precipitation of metal hydroxides occurs because metal ammine complexes are formed in the water layer. The expected extraction equation is



If copper forms a much stronger ammine complex than nickel, it is perhaps possible that under special conditions  $\text{Ni}^{2+}$  is extracted, but  $\text{Cu}^{2+}$  is held in the water layer.

In this study the extraction properties of dialkyldioximes of the type  $\text{C}_n\text{H}_{2n+1}-\text{C}(\text{NOH})-\text{C}(\text{NOH})-\text{C}_n\text{H}_{2n+1}$  are described. The ammoniacal extraction is compared with the pH dependent extraction from acidic solutions.

### EXPERIMENTAL

UV-visible spectra were obtained on a Unicam Sp.800D, while ESR measurements were done at room temperature with a Varian E15 spectrometer.

The extraction experiments were carried out in a three-necked flask with a stirring device and continuous pH measurements. The starting volumes of water and organic solvent were both 250 cm<sup>3</sup>.

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Stirring was stopped when no further change of the pH was noticed, indicating that equilibrium was reached. For analysis equal small volumes of water layer and organic layer were withdrawn from the system. To measure the distribution coefficient as a function of pH thereafter a small quantity of 4N acid or base was added, and the process of stirring until equilibrium and withdrawal of small portions of the aqueous and organic solutions was repeated at a different pH. Care was taken to keep the volumes of the aqueous and organic solutions equal. Although in this procedure the electrolyte concentration does not stay constant, we preferred this model because it is convenient to execute and because in a separate experiment it was shown that in the applied concentration range the influence of the electrolyte concentration is negligible.

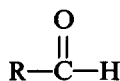
Organic solvents used were methylisobutylketone (MIBK) and chloroform and as inorganic salt metal nitrate was used. NaOH was used as base and HNO<sub>3</sub> as acid.

Kinetic measurements were carried out in a flask provided with a magnetic stirrer. The water layer containing the nickel nitrate was acidified with 4N HNO<sub>3</sub> till the desired pH and then an equal volume (50 cm<sup>3</sup>) of organic phase, in which the ligand was dissolved, was added. Under stirring 10 cm<sup>3</sup> of the mixture was withdrawn after 5, 10, 20 and 30 min. The two layers of these withdrawals separated immediately and it appeared that the volumes of both separated layers were equal (5 cm<sup>3</sup>). UV spectroscopy applied to the organic phase gave the absorption at 30,500 cm<sup>-1</sup>. Since the solvent and the ligand have no absorption below 35,000 cm<sup>-1</sup> the absorption can be ascribed to the chelate formed during the extraction. According to the Lambert-Beer's law this absorption is proportional to the chelate concentration. When plotting the absorption against the contact time a straight line was obtained for the first 20 min and only a small deviation of the straight line was visible after longer reaction times. This straight line indicated that the initial reaction rate is not, or hardly, inhibited after 20 min, so the initial rate could easily be determined from this straight line.

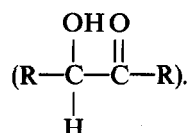
### SYNTHESIS OF DIALKYLDIOXIMES

All dioximes were prepared as described in the following general procedure.

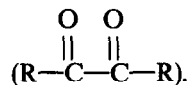
Under nitrogen 0.39 mol freshly distilled alkylaldehyde



was dissolved in 120 cm<sup>3</sup> ethanol. 0.02 mol 3-benzyl-5-(2-hydroxy-ethyl)-4-methyl-1,3-thiazolium chloride was added and subsequently 0.12 mol triethyl amine was added dropwise under vigorous stirring (Stetter synthesis).<sup>5,6</sup> After refluxing for two hours the reaction mixture was poured out into ice, filtered, washed with water and extracted with chloroform. The organic layer was washed with aqueous NaHCO<sub>3</sub>, dried with Na<sub>2</sub>SO<sub>4</sub> and distilled to give the dialkylhydroxy ketone



This dialkylhydroxy ketone was dissolved in 100 cm<sup>3</sup> 2-ethoxyethanol with 30 cm<sup>3</sup> glacial acetic acid. To this solution, heated at 80°C, 0.044 mol Bi<sub>2</sub>O<sub>3</sub> was added fast. After that the reaction mixture was heated for one and a half hours at 105°C, filtered and the residue was extracted with chloroform. The organic layer was washed with water till free from acid, dried and distilled to give the dialkyldiketone



0.4 mol NH<sub>2</sub>OH · HCl and 0.32 mol NaOAc were dissolved in 25 cm<sup>3</sup> water and 50 cm<sup>3</sup> ethanol. To this 0.135 mol dialkyldiketone was added. The reaction mixture was refluxed for half-an-hour, cooled, and the residue filtered and washed with hot water. Recrystallization from diluted alcohol gave the pure dialkyldioxime (R-C(NO<sub>2</sub>H)-C(NO<sub>2</sub>H)-R) in an overall yield of about 25%. The results of elemental analyses are presented in Table 1.

### RESULTS

In Fig. 1 the results are shown for the extraction of Cu(II) and Ni(II) from ammoniacal solutions by solutions of dialkyl dioximes in methylisobutylketone (MIBK) as a function of the number of alkyl carbon atoms at two different extraction times. Equilibrium was not yet reached after 240 min in the extraction of Ni(II) by dioximes with 5, 7 and 11 carbon atoms in the alkyl groups, but was reached after 48 h. By contrast, the equilibrium at about 80% extraction was reached within 10 min in the extraction of Cu(II) by dialkyldioximes with 3 and more carbon atoms in the alkyl groups.

The dependencies of the extractions of Cu(II) and Ni(II) by dipentyldioxime (dodecane-6,7-dione dioxime) on the NH<sub>3</sub> and NH<sub>4</sub><sup>+</sup> concentration are presented in Figs. 2 and 3.

Table 1. Synthesized dialkyl dioximes with analytical results

Compound	Found			Calc.		
	% C	% H	% N	% C	% H	% N
$C_3H_7-C(NO_2H)C(NO_2H)-C_3H_7$	55.6	9.3	16.1	55.8	9.4	16.3
$C_5H_{11}-C(NO_2H)C(NO_2H)-C_5H_{11}$	63.1	10.7	12.4	63.1	10.6	12.3
$C_7H_{15}-C(NO_2H)C(NO_2H)-C_7H_{15}$	67.5	11.2	9.9	67.6	11.1	9.8
$C_9H_{19}-C(NO_2H)C(NO_2H)-C_9H_{19}$	70.9	12.1	7.9	70.5	11.8	8.2
$C_{11}H_{23}-C(NO_2H)C(NO_2H)-C_{11}H_{23}$	73.7	12.5	6.9	72.7	12.2	7.1

The pH dependent extraction of Cu(II) from nitrate solutions by a solution of dipentylidioxime in chloroform is shown in Fig. 4.

It is clear that at pH > 5 more than 50% (which is the theoretical limit if a  $CuL_2$  chelate is formed) is extracted. The shape of the UV spectrum also changed at pH > 5. Thus it is clear that two different chelates are involved: chelate A at low pH and chelate B at pH > 5. When using an excess of Cu(II) compared to dioxime, the UV spectrum indicated that the extraction at pH = 4.3 resulted in chelate A with only a slight fraction of chelate B. Evaporation of the organic phase and recrystallization with ethanol and water gave a brown solid which was filtered and dried at 60°C. Elemental analysis of this compound gave: Cu, 13.8; N, 10.5; C, 55.2; H, 8.7%. After isolation the compound was only slightly soluble in chloroform, in contrast with the extracted chelate B. Further it was found that the extracted chelate A was unstable when the organic layer was dried with  $Na_2SO_4$ .

The ESR spectrum of the chelate A in chloroform is depicted in Fig. 5.

The extraction of excess Cu(II) at pH = 8.4 resulted, according to the UV spectrum, in an organic solution containing nearly pure chelate B. Evaporation of the organic phase and recrystallization with dioxane and water gave a green solid that was dried at 60°C. Elemental analysis of this compound gave Cu, 23.5; N, 8.0; C, 46.8; H, 7.5%. After redissolving the compound in chloroform the UV spectrum deviated somewhat from that of the extracted chelate A. No ESR spectrum could be observed for this compound in solution at room temperature.

Kinetic measurements were done on the extraction of Ni(II) from a nitrate solution by dipentylidioxime to obtain some information why this reaction is so slow (no equilibrium within days).

If Figs. 6, 7 and 8 the initial extraction rate is presented as a function of initial  $H_2A$ ,  $Ni^{2+}$  and  $H^+$  concentrations. The order in dipentylidioxime concentration is calculated from the slope in Fig. 6 as 0.90. The order in  $Ni^{2+}$  concentration calculated from the slope of the line in Fig. 7 is 0.91. Because only

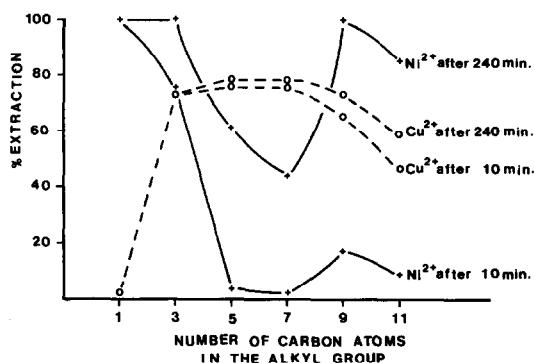


Fig. 1. Extraction of Cu(II) and Ni(II) by dialkylidioximes  $R-C(NO_2H)-C(NO_2H)-R$  as a function of the number of carbon atoms in the alkyl group R. Initial aqueous metal nitrate concentration 0.05 M. Initial dioxime concentration in methylisobutylketone (MIBK) 0.3 M. Initial  $NH_3$  concentration 1.33 M. Initial  $NH_4NO_3$  concentration 0.33 M.

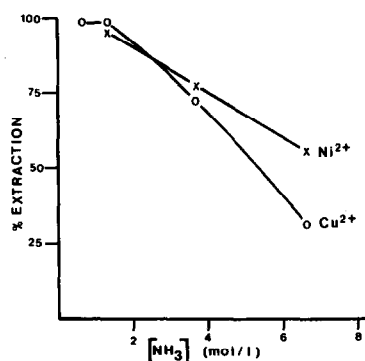


Fig. 2. Extraction of Cu(II) and Ni(II) by dipentylidioxime as a function of the initial  $NH_3$  concentration after a contact time of 240 min. Initial dioxime concentration in MIBK is 0.55 M. Initial  $NH_4NO_3$  concentration 0.33 M.

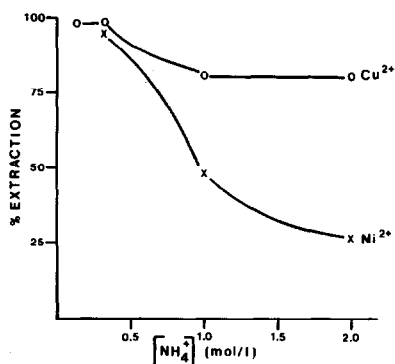


Fig. 3. Extraction of Cu(II) and Ni(II) by dipentyldioxime as a function of the initial  $\text{NH}_4\text{NO}_3$  concentration after a contact time of 240 min. Initial dioxime concentration in MIBK is 0.55 M. Initial  $\text{NH}_3$  concentration 1.33 M.

two measurements were done for the hydrogen ion dependence, the order of  $-0.16$  in  $\text{H}^+$  should be regarded as an order of magnitude estimate.

## DISCUSSION

### *Extraction of Cu(II) and Ni(II) from ammoniacal solutions by aliphatic dioximes*

From Fig. 1 it can be seen that the only dialkyl-dioxime which is really selective for nickel above copper in the extraction from ammoniacal solutions is dimethylglyoxime. However, the extracted bis(dimethylglyoximate)nickel(II) chelate precipitates in the organic layer, and the back-extraction is blocked. Caton<sup>7</sup> explains this poor solubility by nickel-nickel interactions which prevent solvation. This interaction is possible because of the close packing of molecules in the crystal, a packing that

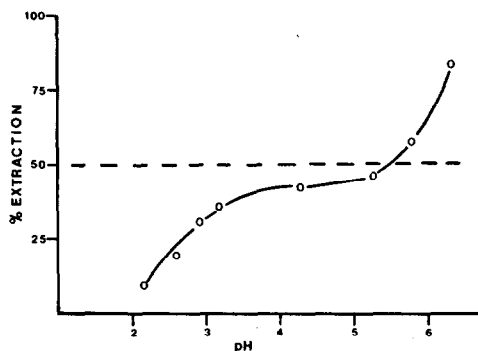


Fig. 4. Extraction of Cu(II) by dipentyldioxime as a function of the equilibrium pH. Initial aqueous copper nitrate concentration and the initial dipentyldioxime concentration in chloroform both are 0.001 M.

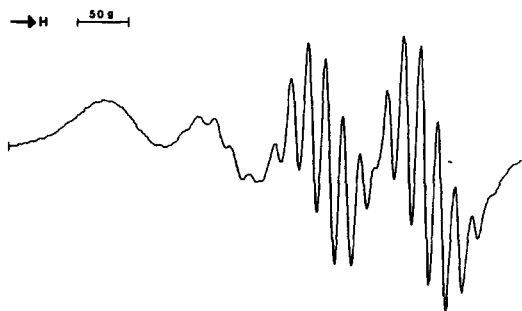


Fig. 5. ESR spectrum of the copper(II)-dipentyldioxime chelate (chelate A) in chloroform at room temperature.

cannot occur with larger alkyl groups according to Sharpe and Wakefield.<sup>8</sup> Dyrssen<sup>9</sup> stated that the bis(dimethylglyoximate)copper(II) chelate possesses two additional water molecules and that this chelate is soluble in water. The low percentage extraction of Cu(II) by dimethylglyoxime can be explained by the formation of such a hydrophilic aqua chelate. When larger alkyl groups are introduced in the dioxime the bulky hydrophobic substituents cause a change in the distribution coefficient of the copper chelate to the advantage of the organic layer. But also a destabilization of the two water molecules in the octahedral copper chelate is to be expected. In Fig. 1 it is clearly seen that from dipropyl to diheptyl dioxime these two effects keep each other in balance, but for longer alkyl groups the destabilization effect is stronger. Furthermore a small negative kinetic effect caused by steric hindrance can be seen for long alkyl groups.

In contrast with copper, nickel does not form octahedral chelates, but forms square planar chelates with dioximes. From the fact that after a contact time of 48 h the Ni extraction was almost complete, it can be concluded that the lower nickel

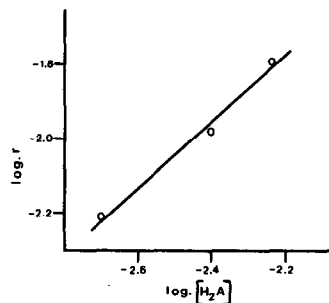


Fig. 6. Dependence of the initial rate of extraction of nickel by dipentyldioxime on the concentration of dipentyldioxime in chloroform. Initial pH is 3.52. Initial aqueous nickel nitrate concentration 0.00397 M.

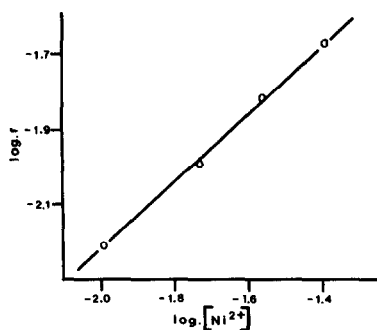


Fig. 7. Dependence of the initial rate of extraction of nickel(II) by dipentylidioxime on the concentration of  $\text{Ni}^{2+}$  in the aqueous phase. Initial dipentylidioxime concentration in chloroform is 0.00612 M. Initial pH is 3.65.

extraction observed for dioxime with pentyl, heptyl and undecyl groups after four hours is not caused by a difference in thermodynamic stability of the chelate formed, but is caused by a difference in extraction rate. This difference in extraction rate can be caused by steric hindrance. The steric hindrance from alkyl groups with 5 to 7 carbon atoms is most effective, according to Fig. 1. The reason why longer chains do not produce such a great hindrance is probably that longer chains are causing a greater insolubility of the dioxime in water, which means that the reaction takes place in the interface with the two long carbon chains pointed into the organic phase.

Comparing the extraction behaviour of Cu with that of Ni it can be noticed that after a contact time of 10 min, more Cu than Ni was extracted, because of favourable kinetics for Cu. On the other hand, after a long contact time more Ni than Cu was extracted, because Ni forms more stable chelates.

Figure 2 shows that the extraction of copper and

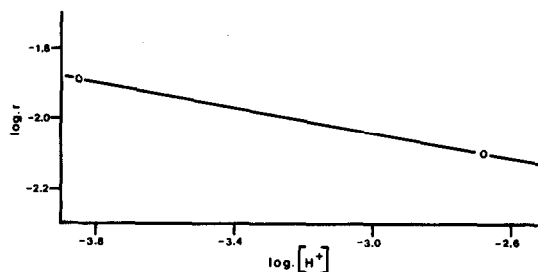


Fig. 8. Dependence of the initial rate of extraction of nickel(II) by dipentylidioxime on the concentration of hydrogen ions in the aqueous phase. Initial dipentylidioxime concentration in chloroform is 0.00415 M. Initial aqueous nickel nitrate concentration is 0.003 M.

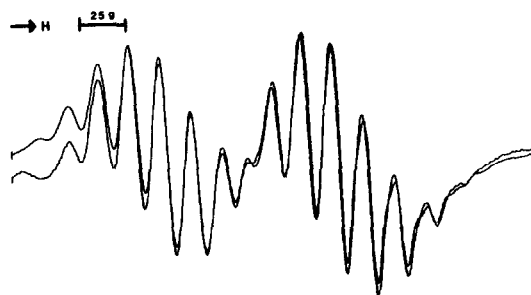
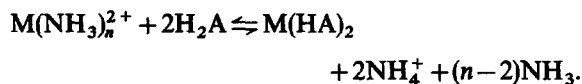


Fig. 9. The two high field copper bands from the ESR spectrum of Fig. 5 together with the computer simulation for a  $\text{CuN}_4$  chromophore. The input values for the simulation are  $A_{\text{Cu}} = 92$  G;  $A_{\text{N}} = 16.2$  G; linewidth = 10.5/8.5 G; modulation 5 G; lineform Lorentz;  $^{63}\text{Cu} = 70\%$  and  $^{65}\text{Cu} = 30\%$ .

nickel is dependent on the ammonia concentration. The dependence of copper is stronger which can be explained by the fact that copper forms more stable complexes with ammonia than nickel. Figure 3 shows that the extraction of copper and nickel also depends on the  $\text{NH}_4^+$  concentration. The expected reaction equation for the extraction is:



The extracted copper chelate will probably have two water or ammonia molecules in the axial position.

A useful selectivity for nickel above copper is not found in the extraction by dialkyldioximes from ammoniacal solutions. At high ammonia concentrations and low  $\text{NH}_4^+$  concentrations nickel is favoured but no good separation can be obtained.

#### The pH dependent extraction of Cu(II) by dipentylidioxime

The extraction (Fig. 4) and UV spectroscopic results demonstrate that two different kinds of chelate are involved in the extraction of Cu(II) by dipentylidioxime. Elemental analysis of chelate A formed at low pH values indicates that a  $\text{CuL}_2$  chelate is formed. Found: Cu, 13.8; H, 8.7; N, 10.5; C, 55.2%. Calculated for  $\text{Cu}(\text{C}_{12}\text{H}_{22}\text{N}_2\text{O}_2)_2$ : Cu, 12.3; H, 8.5; N, 10.9; C, 55.9%. The percentage of copper observed is somewhat high, probably because of the presence of a small amount of chelate B, which has a higher percentage of copper (23.5%). No additional water molecules were found, but it is not excluded that these molecules were present in the extracted chelate and disappeared during heating at 60°C. The presence of water molecules also explains

the instability in solution with  $\text{Na}_2\text{SO}_4$ , a water absorber, and the change in solubility properties after drying at  $60^\circ\text{C}$ . If  $\text{Na}_2\text{SO}_4$  absorbs the two axial water molecules, this means that these are fairly weakly coordinated and so it is not surprising that they dissociate at  $60^\circ\text{C}$ .

$\text{Cu}^{2+}$  is a  $d^9$  system with one unpaired electron, which means that four main lines can be expected in the ESR spectrum, because  $I = 3/2$  both for  $^{63}\text{Cu}$  and  $^{65}\text{Cu}$ . The normal way of coordination for unstrained dioximes is the N,N-configuration. Because  $I = 1$  for nitrogen, nine equidistant lines are to be expected on each copper line with intensity ratio of 1:4:10:16:19:16:10:4:1. Furthermore, we must take into account that copper consists of 59.1% of  $^{63}\text{Cu}$  and for 30.9% of  $^{65}\text{Cu}$  with a slight difference in magnetic moment ( $0.70904 \times 10^{-4}$  vs  $0.75958 \times 10^{-4}$  rad.  $\text{s}^{-1} \text{G}^{-1}$ ).

A computer simulation of the spectrum is shown in Fig. 9 together with the experimental spectrum and an excellent fit is noticeable.

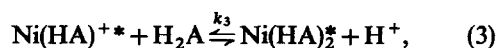
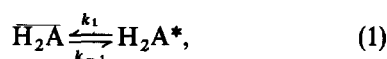
The left part of the simulation is somewhat raised compared to the observed spectrum because the overlap with the third copper band could not be taken into account with our program. This simulation proves that indeed chelate A has N,N-coordination.

Chelate B is formed at high pH values ( $\text{pH} > 5$ ) with an excess of copper. This phenomenon is also seen in the extraction of copper by  $\delta\text{-H}_2\text{CQD}$  (see Ref. 2) and in the extraction of copper by  $\alpha\text{-benzildioxime}$  (Einaga and Ishii).<sup>10</sup>

The elemental analysis of chelate B can be explained by assuming a  $\text{Cu}_4(\text{C}_{12}\text{H}_{22}\text{N}_2\text{O}_2)_3(\text{OH})_2\text{C}_4\text{H}_8\text{O}_2$  chelate. The expected elemental analysis for this chelate—Cu, 24.1; N, 8.0; C, 45.5; H, 7.2%—is in reasonable agreement with the observed values: Cu, 23.5; N, 8.0; C, 46.8; H, 7.5%. The dioxane molecule would then be introduced during the recrystallization. This would also explain why the UV spectrum changed after isolation. These results are insufficient to determine the structure of chelate B directly after extraction. The absence of an ESR spectrum points to the formation of a chelate with a strong copper-copper coupling, as was also found for the  $\text{Cu}:\text{H}_2\text{CQD} = 2:3$  chelate.<sup>2</sup> A composition of  $\text{Cu}_4(\text{C}_{12}\text{H}_{22}\text{N}_2\text{O}_2)_3(\text{OH})_2 \cdot x\text{H}_2\text{O}$  is possible for the extracted chelate but other compositions cannot be excluded. The high copper extraction as observed in Fig. 4 can readily be explained by such a chelate. The significance of this chelate B for the extraction of copper is very small, because when dipentylidioxime is used in practical processes excess ligand will be used and the pH will be kept low (to prevent copper hydroxide precipitation) and under these circumstances no chelate B will be formed.

### Kinetic measurements and pH dependency of the nickel extraction by dipentylidioxime

To find the rate-determining step kinetic measurements were performed on the extraction of nickel(II) by dipentylidioxime. From Fig. 6 the order in dipentylidioxime is calculated to be 0.90, which approximates 1 and not 2 as was found by Navtanovich and co-workers for the extraction from ammoniacal solutions. The order in  $\text{Ni}^{2+}$  is 0.91 (Fig. 7) in good agreement with the expected order of 1. The order in  $\text{H}^+$  is 0.16 (Fig. 8) which is not far from zero. These orders can be explained when we assume the following reaction scheme:



Compounds marked with an asterisk are supposed to be in the interface or in the water layer and compounds marked with bars in the organic layer.

If reaction (2) is the rate-determining step, the initial extraction rate will be given by

$$r = k_2[\text{H}_2\text{A}^*][\text{Ni}^{2+}] = k_2 \cdot K_1[\overline{\text{H}_2\text{A}}][\text{Ni}^{2+}] \quad (5)$$

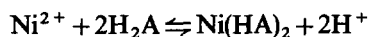
with

$$K_1 = \frac{k_1}{k_{-1}} = \frac{[\text{H}_2\text{A}^*]}{[\overline{\text{H}_2\text{A}}]}$$

This would explain the first order in  $\text{H}_2\text{A}$  and in  $\text{Ni}^{2+}$  and the zero order in  $\text{H}^+$ .

Because of the low pH value it is unlikely that the dipentylidioxime dissolves in the water layer. The reaction, therefore, presumably takes place in the interface. The acidic water layer does not make it very attractive for the dioxime part of ligand (which is acidic too) to appear at the interface. Because of this low interfacial dioxime concentration equation (2) will be the rate-determining step. In ammoniacal solutions Navtanovich and co-workers<sup>4</sup> found a second-order rate dependence in  $\text{H}_2\text{A}$ , which means that in their case the reaction of  $\text{Ni}^{2+}$  with the second  $\text{H}_2\text{A}$  molecule was rate-determining. The ammonia causes a high pH value and it is reasonable to assume that the dioxime part of the ligand is pulled to the interface and is ionized. This causes a high interfacial dioxime concentration and as a result the normally expected second order in  $\text{H}_2\text{A}$  is found.

The overall extraction equation for Ni at low pH



is completely different from the equation for the extraction from ammoniacal solutions. It is therefore not surprising that different orders are found.

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