

## STUDY OF THE COMPLEX OF COBALT WITH $\alpha$ -FURILMONOXIME

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Received May 2nd, 1972

The binary complex of cobalt with  $\alpha$ -furlmonoxime (HL) was studied; the dissociation constant of HL in 20% ethanol ( $I = 0.1$ ) and its distribution constant in the system water (0.1M-NaClO<sub>4</sub>)-benzene were determined. The complexes Co(III)L<sub>2</sub><sup>+</sup> and Co(III)L<sub>3</sub> are formed during the extraction of Co<sup>2+</sup> by a solution of HL in benzene; the stability constants of these complexes as well as the distribution constant of CoL<sub>3</sub> in the system benzene-water (0.1M-NaClO<sub>4</sub>) were determined.

$\alpha$ -Furilmonoxime is used as a reagent for the determination of small amounts of cobalt<sup>1-3</sup> and palladium<sup>4</sup>. Properties of this reagent are described in some other papers<sup>5,6</sup>. Cobalt is oxidized to the trivalent form on its reaction with  $\alpha$ -furlmonoxime<sup>1,3</sup> and in that form it forms a complex, orange coloured salt at pH 8-9. In the solid state, the formula of the compound is<sup>1</sup> Co(C<sub>10</sub>H<sub>6</sub>NO<sub>4</sub>)<sub>3</sub>. This salt is low-soluble in water and it can be extracted by organic solvents, e.g. benzene, toluene, chloroform<sup>1</sup>, etc. The complex formation has been followed<sup>2</sup> in dependence on various factors (the amount of the reagent, pH of the aqueous phase, etc.), and the composition of the complexes formed at pH 9 and pH 5 has been determined (CoL<sub>3</sub> and CoL<sub>2</sub><sup>+</sup>, resp.).

The aim of this work was to study the equilibria in solutions containing the complex of cobalt with  $\alpha$ -furlmonoxime during its extraction. By using the information obtained, the mechanism of the extraction of cobalt by  $\alpha$ -furlmonoxime<sup>1</sup> and accordingly also the cause of the lower reproducibility of the extraction-photometric determination of cobalt by that reagent could be explained.

### EXPERIMENTAL

#### Chemicals and Apparatus

Cobaltous perchlorate was obtained from cobaltous acetate by repeated evaporation with perchloric acid and recrystallization from water. All the other chemicals, solvents, and  $\alpha$ -furlmonoxime were p.a. purity (Lachema, Brno). A pH-meter type OP-205 (Radelkis, Budapest) with a glass electrode of the same make and a saturated calomel electrode (Radiometer, Copenhagen) was used for the pH measurements. Spectrophotometric measurements were carried out by using the instrument Spekol (Zeiss, Jena) for the visible region and the spectrophotometer SF 4 (U.S.S.R.) for the UV region. The temperature was kept at  $25 \pm 1^\circ\text{C}$  during the measurements.

## Procedures

The determination of the concentration of HL in the aqueous and benzene phases was performed spectrophotometrically, by measuring the absorbance at 283 nm ( $\lambda_{\max}$  for the benzene phase and the isobestic point for the aqueous phase<sup>6</sup>). Water and benzene served as the reference solvents for the measurements of the aqueous and benzene solutions of  $\alpha$ -furylmonoxime, resp. The content of HL was determined by using calibration curves.

The dissociation constant of HL was determined potentiometrically<sup>7</sup> using a solution in 20% ethanol. The solution of the reagent ( $10^{-2}\text{M}$ ) was titrated by  $0.1\text{M-NaOH}$  at  $I\ 0.1$  ( $\text{NaClO}_4$ ) in nitrogen atmosphere at  $25^\circ\text{C}$ . The  $\text{p}K_a$  value was obtained as the intercept of the plot  $\log . ([L]/[HL])$  vs  $-\log [\text{OH}^-]$ . The glass electrode was calibrated according to Biedermann and Sillén<sup>8</sup>, so that the pH values measured correspond to the concentration of hydrogen ions.

For the determination of the distribution constant of the reagent between water and benzene at  $I\ 0.1$  ( $\text{NaClO}_4$ ),  $t\ 25^\circ\text{C}$ , the distribution of the reagent between the two solvents was determined at various pH values. 10 ml aqueous or benzene solution of  $\alpha$ -furylmonoxime ( $5 \cdot 10^{-5}\text{M}$ ) were shaken with 10 ml benzene or water, resp., until equilibrium was attained (1 h). After the phases were separated, the pH value of the aqueous phase was measured and the concentration of the reagent in one or the two phases was determined spectrophotometrically.

The content of cobalt in the organic phase was determined spectrophotometrically from the absorbance value at  $\lambda_{\max}$  405 nm. The accuracy of the cobalt concentration found was verified by analyzing an aliquot of the organic phase, which was evaporated, and the residue incinerated with oxalic acid. The ignited residue was dissolved in nitric acid, the excess of the latter was evaporated and the content of cobalt determined by means of nitroso-R-salt.<sup>9</sup> The cobalt concentration was directly read from the plot of the absorbance of the organic phase at 405 nm vs. the molar concentration of cobalt in that phase.

Extractions of the complex were carried out in solutions with the initial cobalt concentration  $5 \cdot 10^{-6}$ – $10^{-4}\text{M}$  and the initial HL concentration  $1.25 \cdot 10^{-3}$ – $4.5 \cdot 10^{-3}\text{M}$ . The pH values of the solutions were adjusted by NaOH or  $\text{HClO}_4$ . The ionic strength of the solutions was set to  $0.1$  ( $\text{NaClO}_4$ ). The volume of the two phases used for extraction was 10 ml.

## RESULTS AND DISCUSSION

For the determination of the concentration of  $\alpha$ -furylmonoxime in the organic and aqueous phases, resp., its absorption spectra were measured in the aqueous and benzene solutions in the regions of 230–340 and 275–340 nm, resp. The spectra exhibit  $\lambda_{\max}$  283 nm in both cases, with  $\epsilon_{283}$   $1.88 \cdot 10^4$  and  $2.24 \cdot 10^4 \text{ mol}^{-1} \text{ cm}^2$  in water and in benzene, resp. These  $\lambda_{\max}$  values approach those found for chloroform (280 nm, cf.<sup>5</sup>, or 276 nm, cf.<sup>6</sup>). A somewhat poorer agreement appears between the absorption coefficient determined by us for the aqueous solution and value given by Peshkova<sup>5</sup> ( $\epsilon_{280}$   $2.533 \cdot 10^4 \text{ mol}^{-1} \text{ cm}^2$ ); our value, however, fits better the series of molar absorption coefficient decreasing in solvents of increasing polarity: benzene–chloroform<sup>6</sup>–water.

Although the absorbance of benzene found at  $\lambda_{\max}$  is not negligible (Fig. 1), this solvent was used for the extraction, because, among the solvents tested, benzene required the shortest time for attaining the equilibrium in the extraction of the com-

plex (benzene 1 h, toluene 3 h, chloroform 6 h). The absorbance of the blank at 283 nm, due to benzene, can be compensated without an essential lack of sensitivity of the equipment or of the spectral homogeneity of the radiation used.

The dissociation constant of  $\alpha$ -furylmonoxime was determined potentiometrically in 20% ethanol, as the reagent is low-soluble in water. The value  $p(K_a)_c = 9.22 \pm 0.02$  was found. The reliability of this value as well as of the  $K_D$  value of the reagent is given by the confidence interval with the 95% probability. This  $p(K_a)_c$  value was recalculated to the thermodynamic value by means of the simplified Debye-Hückel equation ( $pK_a$  8.98) and compared with the equally recalculated values determined spectrophotometrically<sup>6</sup> ( $pK_a$  8.96). The agreement is very good. The  $p(K_a)_c$  value calculated from the extraction data<sup>6</sup> could not be recalculated to  $pK_a$ , with regard to the high ionic strength ( $I$  0.15) used in the extraction process.

The distribution constant of  $\alpha$ -furylmonoxime in the system water (0.1M-NaClO<sub>4</sub>)-benzene was determined from the distribution ratios  $D$  in the pH range of 3–6, where the relation  $D = K_D$  holds true with a 1% error for the reagent used. The following  $D$  values were found for various pH values:

pH:	3.28	3.51	3.56	6.12	6.16	6.24	6.26	6.98
$D$ :	3.54	3.55	3.56	3.62	3.58	3.65	3.69	3.65

From the average of the  $D$  values,  $K_D = 3.60 \pm 0.04$  was calculated, which is a considerably lower value than that in the chloroform-water system<sup>6</sup>. As mentioned above, the equilibrium of extraction of the Co-HL complex is established more quickly during the extraction by benzene than during that by chloroform. This can be thus related to the lower  $K_D$  value of the reagent in the former case, which is in ac-

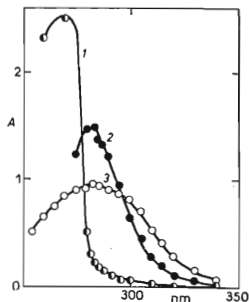


FIG. 1  
Dependence of Absorbance of  $\alpha$ -Furylmonoxime (HL)  
on Wavelength

Cell 1 cm, 1 benzene, 2  $7.5 \cdot 10^{-5}$  M-HL in benzene,  
3  $3.5 \cdot 10^{-5}$  M-HL in water.

cordance with the observations by Zolotov<sup>10</sup> for the extraction of various complexes of  $\beta$ -diketones and benzoylphenylhydroxylamine by chloroform, benzene, and tetrachloromethane. Although the extraction of the Co—HL complex by benzene proceeds in the shortest time, it is slow in comparison with other extraction systems of metal chelates.

During the study of the extraction it was at first verified that the distribution ratio remains constant at the Co concentrations lying in the range of  $5 \cdot 10^{-6}$ – $10^{-4}$  mol  $l^{-1}$  other conditions being constant, hence mononuclear complexes<sup>11</sup> are formed in the aqueous phase in the  $c_{Co}$  range indicated. The dependence  $\log D = f(\text{pH})$  (Fig. 2) for the extraction of the Co—HL complex by benzene or toluene in the pH range of 7.5–9 indicates that the ratio of the  $D$  values for the two solvents is constant; thus the assumption was confirmed that the chelate in that system is not solvated by the organic solvent<sup>12</sup>. The dependence  $\log D = f(\text{pL})$  was then investigated (Fig. 3). In the region of pH 7.5–8.9 and with a hundredfold excess of the reagent with respect to cobalt, the shape of the curve obtained is independent of the concentration of HL. From the slope of the ascending part of the curve (Fig. 3) it follows<sup>12–14</sup> that the complex  $\text{CoL}_3$  is extracted; this result is in accordance with those of other authors<sup>2</sup>. So the complex  $\text{CoL}_3$  predominates in the aqueous phase, but the existence of the  $\text{CoL}_2^+$  and  $\text{CoL}^{2+}$  forms can be also assumed. The presence of the

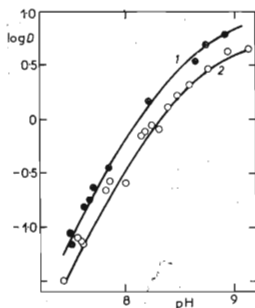


FIG. 2

Dependence  $\log D = f(\text{pH})$  for the Extraction of the Complex Co— $\alpha$ -Furilmonoxime  
1 Extraction by benzene, 2 extraction by toluene.

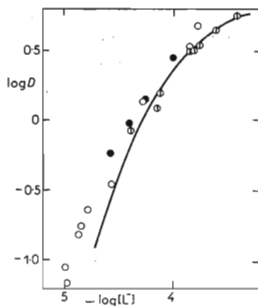


FIG. 3

Dependence  $\log D = f(\text{pL})$  for the Extraction of the Complex Co— $\alpha$ -Furilmonoxime  
 $c_{Co} 10^{-5} \text{M}$ ,  $c_{HL}$  ●  $1.25 \cdot 10^{-3} \text{M}$ , ○  $2.5 \cdot 10^{-3} \text{M}$ , ●  $4.5 \cdot 10^{-3} \text{M}$ . — Curve calculated from the  $\beta_n$  and  $K_D$  values found.

complex with the ratio  $\text{Co} : \text{L} = 1 : 2$  was ascertained<sup>15</sup> in isomolar series during the study of isochromes<sup>16</sup> of the system  $\text{Co(II)}\text{-HL-pyridine}$ .

The distribution ratio of Co in the system studied is given by

$$D = \frac{[\text{CoL}_3]_{\text{org}}}{[\text{Co}^{2+}] + [\text{CoL}^{2+}] + [\text{CoL}_2^+] + [\text{CoL}_3]} \quad (1)$$

where the subscript org denotes the concentrations in the organic phase, the concentration data without any subscript refer to the aqueous phase. The hydroxo complexes of cobalt are not involved in Eq. (1), since the coefficient of the side reaction<sup>17</sup>  $\alpha_{\text{Co(OH)}}$  approaches one in the pH range applied ( $\alpha_{\text{Co(OH)}} = 1$  and 1.10 for pH 8 and 8.9, resp., as calculated by using the values  $\log \beta_{\text{Co(OH)}^{2+}} = 1.8$ ,  $\log \beta_{\text{Co(OH)}_2^+} = 9.2$ , and  $\log \beta_{\text{Co(OH)}_3} = 10.5$ ). On substituting for  $K_D$  and  $\beta_n$  in Eq. (1) we obtain

$$D = K_D \beta_3 [\text{L}^-]^3 / \sum_0^3 \beta_n [\text{L}^-]^n \quad (2)$$

Using  $[\text{L}^-] = x$ ,  $D^{-1} = y$ , and  $\beta_n / K_D \beta_3 = a_n$  we rearrange the relation (2) to

$$x^3 y = a_0 + a_1 x + a_2 x^2 + a_3 x^3 \quad (3)$$

The  $x$  value was calculated from the initial analytical concentration of the reagent, and the amount of the reagent bound in the complex was neglected regarding its excess with respect to the metal. The coefficients  $a_0 - a_3$  were calculated by means of a computer ( $a_0 = 3.32 \cdot 10^{-14}$ ,  $a_1 =$  negative value,  $a_2 = 3.39 \cdot 10^{-5}$ ,  $a_3 = 9.29 \cdot 10^{-2}$ ). The relations  $a_2/a_0 = k_1 k_2 = \beta_2$ ,  $a_3/a_2 = k_3$ , and  $1/a_3 = K_D$  hold true. The values of the constants calculated (and their definition relations) are:

Constant	Definition relation	Value
$\beta_2$	$[\text{CoL}_2^+]/[\text{Co}^{3+}][\text{L}^-]^2$	$1.02 \cdot 10^9$
$k_3$	$[\text{CoL}_3]/[\text{CoL}_2^+][\text{L}^-]$	$2.74 \cdot 10^3$
$\beta_3$	$[\text{CoL}_3]/[\text{Co}^{3+}][\text{L}^-]^3$	$2.79 \cdot 10^{12}$
$K_D$	$[\text{CoL}_3]_{\text{org}}/[\text{CoL}_3]$	10.76

The precision of the experimental data was not sufficient for the determination of the two stepwise stability constants of the lower complexes,  $k_1$  and  $k_2$ , which predominate in the range of the lowest  $D$  values; only the  $\beta_2$  value could be determined. Although the existence of the  $\text{CoL}^{2+}$  complex is probable, we were not able to prove it experimentally. Fig. 3 shows the curve  $\log D = f(\text{pL})$ , the course of which was calculated by using the constants found. The experimental points lie close enough to the calculated curve (in the limits of errors of the methods used) with the exception of the points corresponding to the lowest  $[\text{L}^-]$  concentration.

It can be concluded that in the pH range 8–9, suggested for the analytical extraction of cobalt with  $\alpha$ -furlimonoxime, the binary chelate  $\text{CoL}_3$  is formed in the system cobalt–reagent; it is sufficiently stable and has a sufficiently high value of the distribution factor. It is, however, extracted very sluggishly.

*We wish to thank the staff of the computer center of the Department of Physical Chemistry, Institute of Chemical Technology, Prague, for performing the calculations on the Hewlett-Packard computer.*

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Translated by P. Adámek.