SOLVENT EXTRACTION OF COBALT (II) FROM SULFATE MEDIUM USING CAPRIC ACID-CHLOROFORM–MIBK SYSTEM

[1]FATIMA ADJEL, [2]DJAMEL BARKAT

[1,2]Department of Industrial Chemistry, Faculty of Science and Technology, Biskra University, 07000, Biskra- Algeria
E-mail: [1]f.adjal@univ-biskra.dz, [2]barkat_djamel@yahoo.fr

Abstract— The synergistic solvent extraction of cobalt (II) from 0.33 mol dm^{-3} Na_2SO_4 aqueous solutions with capric acid (HL) using chloroform/ isobutyl ketone (MIBK) as mixed solvent was carried out at 25°C. The experimental data for the capric acid dissolved in chloroform reveal the self adduct formation, $CoL_2(HL)_2$, in the organic phase. In the presence of MIBK, a remarkable enhancement on the extraction of cobalt (II) with 0.02 mol dm^{-3} capric acid was observed upon the addition of 0.04 to 0.2 mol dm^{-3} MIBK in chloroform. From an synergistic extraction equilibrium study, the synergistic enhancement was ascribed to the adduct formation $CoL_2(HL)_2(MIBK)$. The synergistic extraction stoichiometry of cobalt (II) with capric acid and MIBK is studied with the methods of slope analysis. The value of the equilibrium constants were determined. The partition and dimerization constants have been determined in chloroform-sodium sulfate system.

Keywords— Solvent extraction, mixed solvent, MIBK, adduct formation constant, cobalt (II), Capric acid.

I. INTRODUCTION

Cobalt and its compounds have numerous applications both in laboratories and an industrial scale (environment and catalysts). Cobalt is one of the oligo-elements indispensable to the correct development and growth of most of the animals. In particular, it is part of the B-12 vitamin, or cobalamin, which is antianemic.

The removal and separation of cobalt is of great importance and relevance; with the increasing demand for cobalt metal and its compounds.

The solvent extraction of cobalt ions with carboxylic acids has been broadly investigated under a grand variety of experimental conditions.

In an investigation on the solvent extraction of cobalt with capric acid in excess, Nakasuka and his collaborator [1], have found that the monomeric species $CoL_2 4HL$ is extracted at low cobalt concentration and a dimer, $(CoL_2)_2 4HL$, at high concentration. In the case of the extraction of cobalt (II) with octanoic acid in 1-octanol and hexanoic acid in 1-hexanol, Schweitzer et al.[2] reported that the monomeric CoL_2 to be the main extracted complexes from radiotracer distribution measurements. However, Jaycock et al.[3] Has shown that cobalt (II) is extracted into heptane by octanoic acid, as $(CoL_2)_2 4HL$ at high loading of the organic phase and$(CoL_2)_2$ 2HL for 0.3/0.7mole dm^{-3} octanoic acid concentration. In the same published paper, the authors have also used long-chain carboxylic acid (versatic 911, naphthenic and decanoic acid) in heptane to extract cobalt (II) from aqueous solution, and found that the complexes $(CoL_2)_2$. 4HL appear to be the main extracted species at high percentage of acid to metal. Pedro Beneitez et al.[4] reported CoL_2.2HL to be the predominant cobalt species in the solvent extraction of cobalt ion with tert-dodecylthioglycolic acid from nitrate aqueous solution into kerozene. Shibata and Nishimura [5], studied the extraction equilibrium of cobalt (II) from aqueous sodium nitrate solution using Versatic 911. The authors have reported that the complex: $CoL_2(HL)_4$ and $(CoL_2(HL)_2)$ are extracted in the organic phase. Upon the extraction of cobalt (II) with a 1- naphtoic acid, the monomeric CoL_2 was reported to be responsible for extraction in the 1-naphtoic acid/1-octanol system [6].

synergism in solvent extraction, describing the co-operative effect of two, or more extractants where the distribution ratio for the combination is greater than the largest individual distribution ratio measured under comparable conditions.

A number of investigations on the synergistic effect of a second extractant, such as amines, non-chelating oximes and neutral oxo-donors compound on the extraction of metal carboxylates have been carried out [7–10].

The synergistic system of hydroxyoxime (LIX® 63) / versatic10 acid was used by cheng [11] to separate cobalt and nickel from the main impurities, copper, zinc, manganese, calcium and magnesium. A Significant synergistic effect was observed for all metals except for calcium and magnesium an antagonistic effect was observed. It was found that the stoichiometry of the complexes formed on the extraction of cobalt with the LIX® 63/verstic 10 acid system are $CoL_2(Ox)_2(H_2O)_2$ and $CoL_2(Ox)_4$, for an octahedral structure of cobalt. However, in the research work conducted by Preston, who used synergistic systems of non-chelating oximes/ carboxylic acids including Naphthenic acid, decanoic acid, octanoic acid and 2-ethylhexanoic acid, on the extraction of nickel(II) and cobalt(II) in xylene, and identified a species extracted as $NiL_2(oxime)_4$ and $CoL_2(oxime)_4$ [9].

The synergistic extraction of cobalt (II) with lower fatty acids as propionic, butyric and valeric acid in the presence of synergist (S) β-picoline, pyridine or quinoline has been studied by Gogia et al. [12]. The authors reported that the extracted species were found to be CoL_2 $(HL)_2S_2$ except in the butyric acid/

quinoline system, for which it is considered to be $CoL_2(HL)S_2(H_2O)$.

The aim of the present investigation was to study the effect of MIBK concentration on the solvent extraction of cobalt (II) from dilute aqueous sulfate solution, to elucidate the composition of the extracted species and to evaluate the values of the extraction constants.

.

II. DETAILS EXPERIMENTAL

A. Reagents

Capric acid (98%) and TOPO (≥97%) were purchased from Fluka, and used without further purification. Chloroform was pre-equilibrated with aqueous solution which did not contain cobalt (II). The ionic strength of the aqueous medium was assumed to be unity ($[Na_2SO_4]$ = 0.33mol dm^{-3}). The initial concentration of cobalt is 6.81×10^{-3}mol dm^{-3}.

B. Extraction and analytical procedures

All distribution equilibrium studies were carried out at 25 ±2°C. The ionic strength of the aqueous phase was maintained at 0.33mol.dm^{-3} in sodium sulfate.

The extraction procedures were carried out in a similar manner as previously described [13].

The procedure consists in putting in contact 40 ml of a solution of organic phase charged of the extractants dissolved in chloroform, with 40ml of the aqueous phase, containing the metal species to extract, in a thermostated vessel at 25°C. the two solution were shaken for 30 min. The pH of the solution was adjusted to between 6.8 and 9 by adding a few drops of 0.2 mol dm^{-3} NaOH.

The metal ion concentrations were determined in aqueous phase photometrically at 510 nm using a Philips UV-VIS SP6-36. The metal ion concentrations in the organic phase were calculated from the difference between the metal ion concentrations in the aqueous phase before and after extraction.

III. RESULTS AND DISCUSSION

A. General treatment of extraction equilibrium of cobalt(II) with capric acid The study of the extraction of cobalt(II) from a sulphate medium by capric acid in less polar solvents is described by the following equilibrium:

$$jCo^{2+} + j\,\frac{n+m}{2}(HL)_{2,org} \longleftrightarrow (CoL_n(HL)_m)_{j,org} + njH^+$$

(10)

Where, j represented the degree of polymerization of cobalt caprate in the organic phase; $(HL)_2$, extractant in dimeric form. The extraction constant can be written as the following expression

$$K_{ex} = \frac{\left[(CoL_n(HL)_m)_j\right]_{org}\left[H^+\right]^{nj}}{\left[Co^{2+}\right]_{aq}^{j}\left[(HL)_2\right]_{org}^{j(n+m)/2}} \quad (11)$$

Under the present experimental conditions, the hydrolysis and complexation of cobalt being not appreciable in the aqueous phase, the distribution coefficient D of the cobalt between the organic and aqueous phases may be expressed as follows:

$$D = \frac{[Co(II)]_{org}}{[Co(II)]_{aq}} \quad (12)$$

$$D = K_{ex}\left[Co^{2+}\right]_{aq}^{(j-1)}\left[(HL)_2\right]_{org}^{j}{}^{(n+m)/2}\left[H^+\right]^{-nj}$$

(13)

$$\log D = (j-1)\log[Co^{2+}]_{aq} + j\,\frac{n+m}{2}\log\left[(HL)_2\right]_{org} + (nj)\,pH + \log K_{ex}$$

(14)

B. Extraction of cobalt (II) with capric dissolved in chloroform:

At fixed cobalt (II) concentration, capric acid concentration and ionic strength, the effects of pH on the extraction of cobalt (II) with capric acid have been investigated. The experimental results are arranged according to equation (14).

Figure 1, shows the results obtained for the extraction of cobalt (II) with solutions of various capric acid concentrations. The degree of extraction of cobalt (II) increases with increase in pH and capric acid concentration. The plots of log D versus pH for various concentration of capric acid are straight lines with slope equal to two (nj=2). Thus, equation (14) can be written as follows:

$$\log D = (j-1)\log[Co^{2+}]_{aq} + j\,\frac{n+m}{2}\log\left[(HL)_2\right]_{org} + 2\,pH + \log K_{ex}$$

(15)

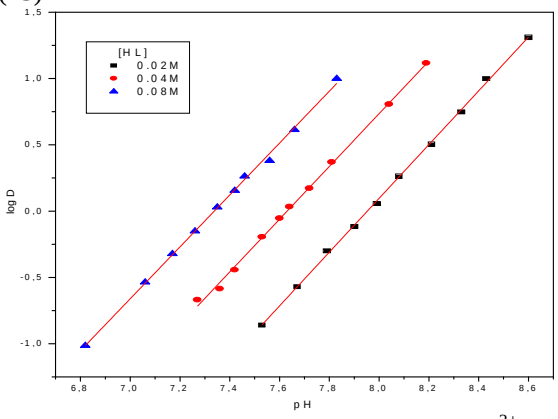


Figure 1: Effect of pH on the extraction of Co^{2+} into chloroform with capric acid from aqueous sulfate medium ($[Na_2SO_4]$ = 0.33mol. dm^{-3}). C_{Co} = 6.81×10^{-3}mol dm^{-3}, C_{HL} = 0.02, 0.04, 0.08 mol dm^{-3}.

The degree of polymerization of the extracted species is given by the slope of a plot of log D + $\log[Co^{2+}]_{aq}$ vs log $[Co^{2+}]_{aq}$ +2pH at a constant $[(HL)_2]_{org}$, the result obtained is illustrated in figure 2. The slope of this plot

is unity, i.e., j=1 then, n = 2. Thus the extracted species should mainly be in the monomeric form under the present experimental conditions.

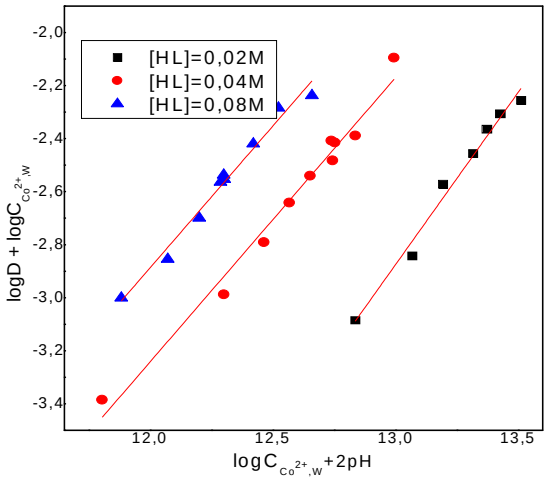


Figure 2: Determination of the degree of polymerization for cobalt (II) caprate in chloroform (confirmation of the extraction of the monomeric cobalt caprate).

If we have only one species, that is, $CoL_2(HL)_m$, equation (15) is rewritten as follows:

$$\log D = \log K_{ex} + (2+m)/2 \log\left[(HL)_2\right]_{org} + 2pH \quad (16)$$

Under the present experimental conditions, The dimeric and monomeric forms of the capric acid may be approximately related by the formula:

$[(HL)_2]=[HL]/2$.

According to equation (16), the slope of the plots of left side of equation (16) against log $[(HL)_2]_{org}$ at constant hydrogen ion concentrations, give the number of capric acid molecules involved in the extracted species. Figure 3, elucidate the variation of log D against log $[(HL)_2]_{org}$ at constant pH. As evident from Figure 3, the plot falls on the straight line with a slope of 2, i.e., m = 2, indicating that two molecules of capric acid involved in the extracted species. Thus we conclude that the extracted species is the monomeric bis (caprato)- bis (capric acid)- cobalt(II) ($CoL_2(HL)_2$), and the reaction can be given as

$$Co^{2+}_{aq} + 2(HL)_{2,org} \longleftrightarrow \left(CoL_2(HL)_2\right)_{org} + 2H^+ \quad (17)$$

With logarithmic extraction constant: log K_{ex}= -11.87. The same type of extracted species was reported by Kopach et al. [14] in the extraction of cobalt(II) with capric acid into heptane. The authors estimated the logarithmic extraction constant as -11.26. Whereas tanaka et al.[1] reported that the monomeric and demiric complex, $CoL_2(HL)_4$ and $(CoL_2(HL)_2)_2$, are responsible for the extraction of cobalt(II) into benzene solution containing capric acid from aqueous sodium sulfite media.

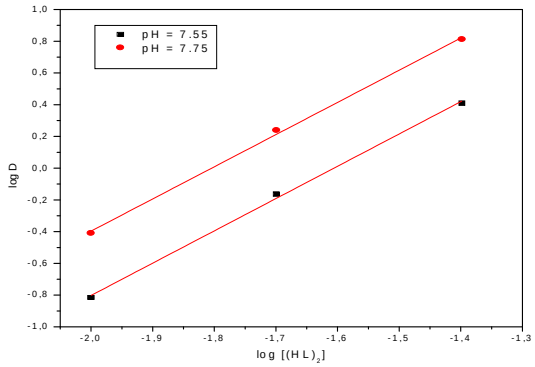


Figure 4: Determination of the number of capric acids involved in the extracted complex . C_{Co} = 6.81×10^{-3}mol dm^{-3}, C_{HL} = 0.02, 0.04, 0.08 mol dm^{-3}, pH = 7.55, 7.75.

The electronic absorption spectra of the organic phase (Figure 4) shows a broad band in the range 460–630 nm, with two maxima near 523 and 561nm.

The transition $^4T_{1g}(4F) \rightarrow {}^4T_{1g}(4P)$ (523 nm) and $^4T_{1g}(4F) \rightarrow {}^4A_{2g}(4F)$ (561 nm) suggesting the octahedral structure for Cobalt(II) ions [15, 16].

From analysis of the electronic absorption spectra we can concluded that the extracted species probably incorporate water molecule into their structure ($CoL_2(HL)_2(H_2O)_2$), occupying the octahedral sites of the complex.

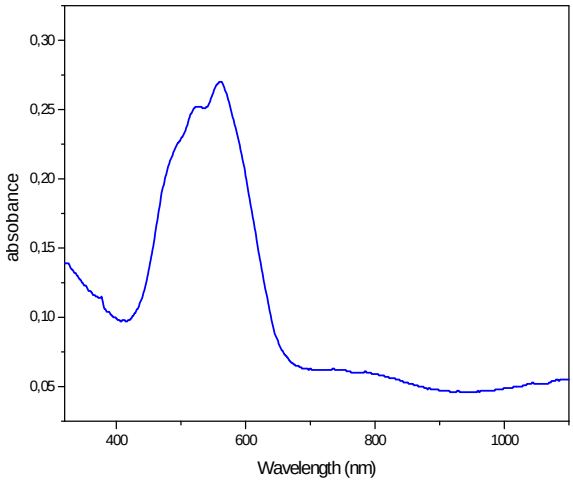


Figure 4: Electronic spectra of cobalt extracts with capric acid (2×10^{-2} mol dm^{-3}) in chloroform.

C. extraction of cobalt (II) with capric acid - chloroform-MIBK mixtures

The general reaction for synergistic extraction of cobalt by mixture of capric acid and methyl isobutyl ketone can be expressed by the following equation:

$$Co^{2+} + 2(HL)_{2,org} + s(MIBK)_{org} \longleftrightarrow CoL_2(HL)_2(MIBK)_{s,org} + 2H^+ \quad (18)$$

The equilibrium constant for the reaction is then given by,

$$K_{syn,ex} = \frac{\left[(CoL_2(HL)_2(MIBK)_s)\right]_{org}\left[H^+\right]^2}{\left[Co^{2+}\right]_{aq}\left[(HL)_2\right]^2_{org}[MIBK]^s} \quad (19)$$

It follows that

$$\log D = \log K_{syn,ex} + 2\log\left[(HL)_2\right]_{org} + s\log[MIBK] + 2\,pH \qquad (20)$$

The results concerning the pH effect on the synergistic extraction of cobalt (II) in the presence of MIBK are shown in figure 5. It should be noted that the increase in pH has a positive influence on the yield of the extraction process.

It is observed that the experimental points are practically aligned on a straight line of slope 2. Two protons are therefore exchanged during the extraction of the cobalt (II) using capric acid-MIBK-chloroform system. These curves show an exaltation of the extraction for low concentrations of MIBK (0.04 <[MIBK]< 0.2M).

When the concentration of MIBK increases ([MIBK]> 0.2M) the extraction curves move towards the higher pH, which explains that antagonism increases with increasing in MIBK concentration in the organic phase. For 0.01 M of MIBK concentration, the antagonism effect becomes more important. This phenomenon is probably due to the displacement of the equilibrium of the interaction between capric acid and the synergist MIBK in favor the formation of capric acid-MIBK complex. The nature of the interaction and the structure of the complex formed depend on the monomeric or dimeric form of the extractant. Thus, in all the synergistic systems examined to date, an excess of the synergistic reagent produces an antagonistic effect.

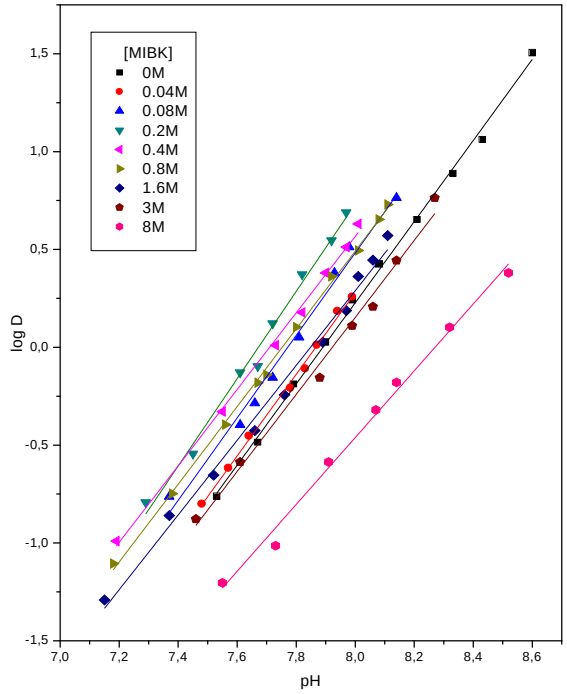


Figure 5 : Effet de pH sur l'extraction du cobalt(II) par le mélange acide caprique (0.02M) et MIBK en milieux sulfate (0.33M) dans le chloroforme

The number of MIBK molecules involved in the extracted species can be determined from the slope of the graph log D against log[MIBK]$_{org}$, at constant pH and [(HL)$_2$].

As figure 6 shows, The curve obtained is a straight line with a slope close to unity. therefore, only the complex of formula $ML_2(HL)_2(MIBK)$ is responsible during the extraction with capric acid- chloroform- MIBK system and the extraction constant (log $K_{syn,ex}$) is equal to -10.33.

the equilibrium of the synergistic effect can be described as follows:

$$CoL_2(HL)_{2org} + MIBK \rightleftharpoons CoL_2(HL)_2 MIBK_{org}$$

log K_{Syn} = 1.54

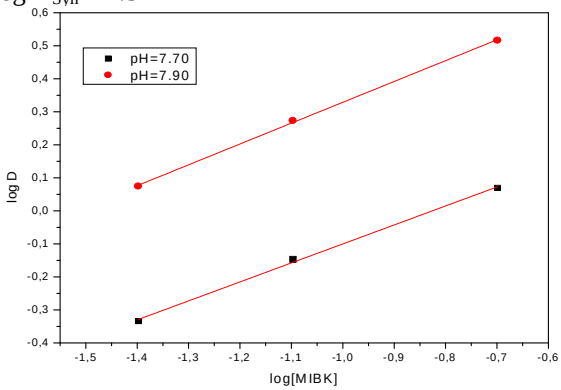


Figure 6 : Effect of MIBK concentration on the solvent extraction of cobalt(II) by mixture of capric acid (0.02M) and MIBK from sulfate media (Ionic strength μ =1) in chloroform.

CONCLUSIONS

The cobalt (II) extraction with capric acid from sulfate media using chloroform/ MIBK as mixed solvent was studied and the main following conclusion can be drawn out:

1. the extraction study of the cobalt(II) and the analysis of the organic phase by the spectrometry of UV-Visible showed that the extracted complex for this metal have an octahedral geometry with structure of $CoL_2(HL)_2(H_2O)_2$. The result obtained are in very good agreement with that reported by Kopach, S et al. [14]for the cobalt(II) extraction with capric acid into heptane.
2. it was found that the second solvent MIBK take a role as the synergistic agent especially at low concentrations of MIBK (0.04 <[MIBK]< 0.2M), followed by the decrease in the cobalt extraction efficiency, toward antagonistic effect at higher MIBK concentrations.

REFERENCES

[1] M. Tanaka, N. Nakasuka, S. Goto, extraction of some metal caprates, Solvent Extraction Chemistry. 17 (1967) 154-159.
[2] G. K. Schweitzer, L. H. Howe, The solvent extraction equilibria of some cobalt(II) chelates, J. inorg. nucl. Chem. 29 (1967) 2027 - 2032.

[3] M. J. Jaycock, A. D. Jones, C. Robinson, Solvent extraction and adsorptive bubble separation of metal ions from aqueous solution-I: Solvent extraction using carboxylic acids and their salts as extractants, J. Inorg. Nucl. Chem. 36 (1974) 887-898.

[4] P. Beneitez, J. Espejo, S. J. Ortiz, J. Ortega, Extraction of zinc, cobalt and iron with s-ter-dodecylthioglycolic acid, J. inorg, nucl. Chem. 43 (1981) 2517-2523.

[5] J. Shibata, S. Nishimura, Studies on solvent extraction of Cu, Ni and Co with Versatic acid 911. Nippon Kinzoku Gakkaishi. 39 (1975) 206-212.

[6] H. Yamada, Y. Matsui, Y. Kuroki, H. Wada, Comparison between 1-and 2-naphthoic acids as an extracting agent for cobalt (II), nickel (II) and copper (II), Analytical Sciences. 13 (1997) 237-244.

[7] K. Hirose, N. Matsumoto, M. Tanaka, Synergistic extraction of copper(II) with capric acid in the presence of pyridine, J. Inorg. Nucl. Chem. 39 (1977) 2261-2265.

[8] K. Hirose, M. Tanaka, Synergistic extraction of zinc(II) with capric acid in the presence of pyridine, J. Inorg. Nucl. Chem. 40 (1978), 1153-1157.

[9] J. S. Preston, solvent extraction of nickel and cobalt by mixtures of carboxylic acids and non-chelating oximes, Hydrometallurgy. 11 (1983) 105-124.

[10] J. Noro, T. Sekine, Solvent extraction of europium(III) with 1-Naphthoic acid into chloroform in the absence and presence of tetrabutyl ammonium ions or trioctylphosphine oxide, Bull. Chem. Soc. Jpn. 66 (1993) 2242- 2250.

[11] C. Y. Cheng, Solvent extraction of nickel and cobalt with synergistic systems consisting of carboxylic acid and aliphatic hydroxyoxime, Hydrometallurgy 84 (2006) 109–117

[12] S. K. Gogia, D. Singh, O. V. Singh, S. N. Tandon, Study on the synergistic extraction of cobalt(II) with lower fatty acids in the presence of heterocyclic amines and some metal ion separations. talanta. 34 (1987) 303-306.

[13] F. Adjel, D. Barkat, Synergistic extraction of copper(II) from sulfate medium with capric acid and tri-n-octylphosphine oxide in chloroform, Journal of coordination Chemistry. 64 (2011) 574–582.

[14] H. Yamada, M. Tanaka. Solvent extraction of metal carboxylates. In: H.J. Emeléus and A.G. Sharpe. Adv. Inorg. Chem. Radiochem.29. london: academic press. Inc, (1985) 143-164.

[15] M. Tanaka, N. Nakasuùka, S. Sasane, Extraction of nickel with capric acid, J. Inorg. Nucl. Chem. 31 (1969) 2591-2597.

[16] B. K. Tyagi, R. P. Varma, A. Kumar, Investigations into the physicochemical behaviour of cobalt(II) laurate, Phys. Chem. Liq. 31 (1996), 253-258.

★★★