Monatshefte für Chemie 118, 589—594 (1987)

Monatshefte für Chemie
Chemical Monthly

Synergistic Extraction of Cobalt(II) Complexes with Toluene-3,4-dithiol in Presence of Some Benzylamines

R. M. Mahfouz* and **S. A. Ibrahim**

Department of Chemistry, Faculty of Science, University of Assiut, Egypt

(Received 14 August 1985. Revised accepted 24 April 1986)

The synergistic extraction of cobalt(II) complexes with toluene-3,4-dithiol (*TDT*) in presence of monobenzylamine (*BA*), dibenzylamine (*DBA*) and tribenzylamine (*TBA*) has been investigated. The stoichiometry of the adducts formed was established from the extraction data. Values of the formation constant, B_{ex}, in presence of the amine ligands have been determined. It is found that the extraction ability decreases in the order *DBA* ≫ *TBA* > *BA*.

(Keywords: Synergism; Dithioles)

Synergistische Extraktion von Co(II)-*Komplexen mit Toluol-3,4-dithiol in Gegenwart einiger Benzylamine*

Es wurde die synergistische Extraktion von Kobalt(II)-Komplexen mit Toluol-3,4-dithiol (*TDT*) in Gegenwart von Monobenzylamin (*BA*), Dibenzylamin (*DBA*) und Tribenzylamin (*TBA*) untersucht. Aus den Extraktionsdaten wurden die Stöchiometrien der Addukte abgeleitet. Die Werte der Bildungskonstanten (B_{ex}) in Gegenwart der Aminliganden wurden bestimmt. Dabei ergab sich für das Extraktionsvermögen eine absteigende Reihe *DBA* ≫ *TBA* > *BA*.

Introduction

Synergistic solvent extraction of metal ions, i.e. the addition of donor molecules to increase the extraction of metal chelates has been applied successfully to the solvent extraction technique [1–6]. It has been shown that the resulting adducts are more soluble and stable in the organic phase than the parent metal chelates and are responsible for the enhancement of the extraction of metal ions by synergistic extraction.

Few attention has been focused on the extraction of metal ions with toluene-3,4-dithiol [7]. So we report now on the synergistic effect of some neutral bases, namely monobenzylamine (*BA*), dibenzylamine (*DBA*) and tribenzylamine (*TBA*) on the extraction of a representative transition metal ion, Co(II), with toluene-3,4-dithiol.

Experimental

Reagents and Apparatus: Toluene-3,4-dithiol obtained from B.D.H., having a low melting point ($\simeq 30\,°\mathrm{C}$), tribenzylamine, dibenzylamine and monobenzylamine obtained from Kock-Light Laboratories and used without further purifications. The radioisotope ^{60}Co as chloride in hydrochloric acid solution purchased from Amersham (England).

Buffer solutions of required *pH* were prepared from mixtures of acetic acid and sodium acetate in the *pH* range 4–6. In all cases the ionic strength was kept constant at 0.1 *M* ($NaClO_4$).

Procedure

The aqueous phase contained a few ppm of radioactive tracer in an acetate buffer solution. The organic phase-contained *TDT* with and without a neutral-additive (*S*). Solutions of *TDT* were freshly prepared to prevent the oxidation of this reagent. Ten ml of the aqueous phase containing the radioactive element were added to ten ml of the ligand solution in chloroform (organic phase) in a stoppered glass bottle. The bottle was shaken vigorously for 20 min using a mechanical shaker while the temperature was kept constant at 25 1 °C. After settling, 5 ml of each phase were taken and subjected to counting separately using a scintillation counter. The distribution ratio was calculated according to the following relationship.

$$\text{Distribution ratio, } D_0 = \frac{\text{Activity in the organic phase}}{\text{Activity in the aqueous phase}}$$

Results and Discussion

The solvent extraction of a metal ion with a chelating agent (H_2A) can be represented as

$$M^{+2}_{\mathrm{aq}} + M\,\mathrm{H}_2A_{\mathrm{org}} \rightleftharpoons [M(A)_m]_{\mathrm{org}} + 2m\,\mathrm{H}^+_{\mathrm{aq}} \tag{1}$$

Applying the law of mass action, Eq. (2) is obtained:

$$K_{\mathrm{ex}} = \frac{[M(A)_m]_{\mathrm{org}}\,[\mathrm{H}^+]^{2m}_{\mathrm{aq}}}{[M^{+2}]_{\mathrm{aq}}\,[\mathrm{H}_2A]^m_{\mathrm{org}}} \tag{2}$$

K_{ex} is the extraction constant and M^{+2} represents the metal ion, H_2A is the ligand and the subscripts aq and org denote aqueous and organic phases, respectively.

$$D_0 = \frac{[M(A)_m]_{\mathrm{org}}}{[M^{+2}]_{\mathrm{aq}}} \tag{3}$$

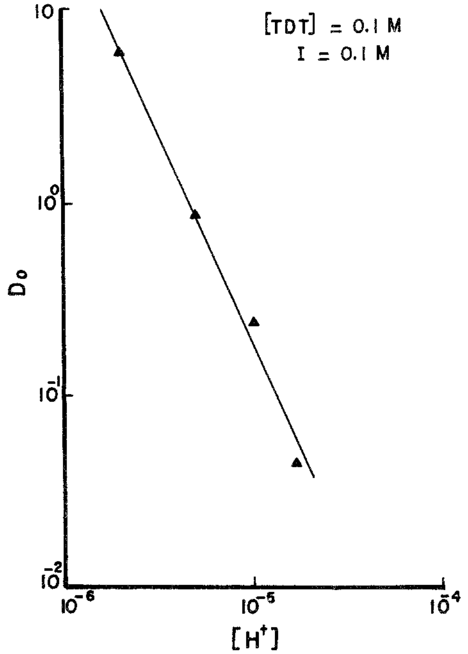
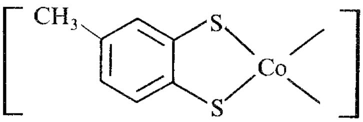


Fig. 1. Variation of the distribution ratio D_0 as a function of hydrogen ion concentration $[H^+]$ for the extraction of Co(II) with *TDT* in chloroform

From Eqs. (2) and (3) we obtain

$$\log K_{ex} = \log D_0 - m \log H_2 A_{org} - 2\,m\,pH \qquad (4)$$

Accordingly the extraction behaviour of cobalt(II) with *TDT* can be followed either by a plot of the logarithm of the distribution ratio against *pH* with constant ligand concentration or by a plot of the logarithm of the distribution ratio against the logarithm of ligand concentration at constant *pH* (Figs. 1, 2). The plots are drawn on a log-log paper. The number of the hydrogen ions liberated during chelate formation is indicated by the first plot while the number of ligand molecules involved in the extracted species is indicated by the second plot. The plots of $\log D_0$ against *pH* at constant ligand concentration (0.1 *M*, *TDT*) and plots of $\log D_0$ against $\log(H_2A)$ at constant *pH*(5.0) gave straight lines with slopes equal to 2.0 ± 0.1 and 1.0 ± 0.2 indicting that the structural formula of the extracted species can be represented by



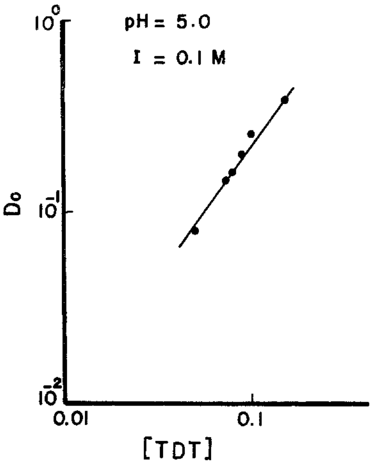


Fig. 2. Variation of the distribution ratio D_0 with *TDT* concentration on the extraction of Co(II) at constant *pH* and total ionic strength

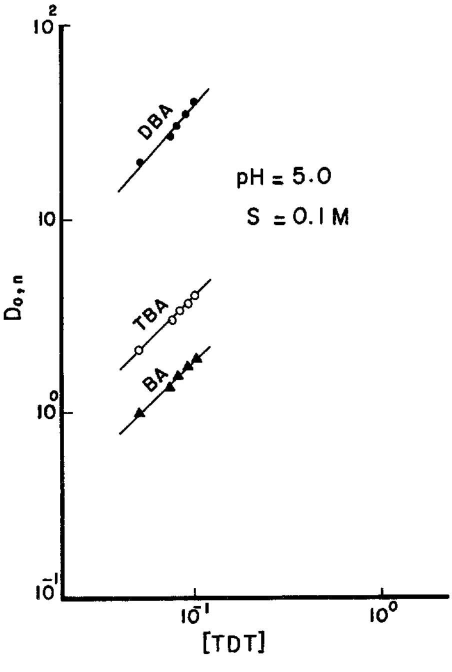


Fig. 3. Variation of the distribution ratio $D_{o,n}$ with [*TDT*] on the extraction of Co(II) at constant [*S*] and constant *pH*

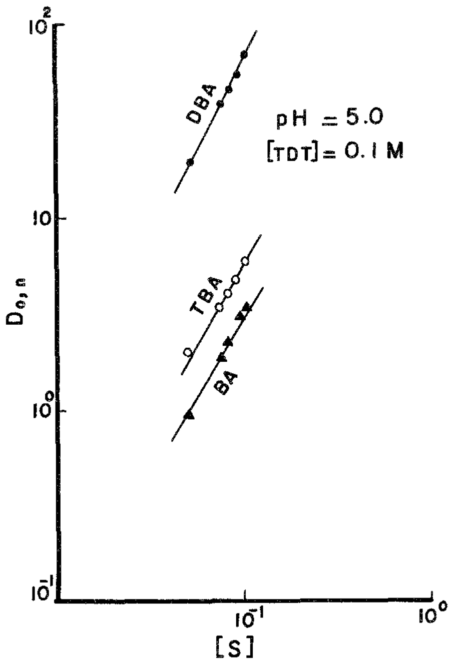


Fig. 4. Variation of the distribution ratio $D_{o,n}$ with $[S]$ at constant $[TDT]$ and constant pH

In synergistic systems employing neutral additives (S) the extraction equilibrium may be represented by the equation

$$M^{+2}_{aq} + m\,H_2A_{org} + XS_{org} \rightleftharpoons MA_m S_{x_{org}} + 2m\,H^+ \qquad (5)$$

The extraction constant K'_{ex} is given by

$$K'_{ex} = \frac{[MA_m S_x]_{org}[H^+]^{2m}_{aq}}{[M^{+2}]_{aq}[H_2A]^m_{org}[S]^x_{org}} \qquad (6)$$

The distribution ratio in the synergistic system, $D_{o,n}$, may be given by

$$D_{o,n} = \frac{[MA_m S_x]_{org}}{[M^{+2}]_{aq}} \qquad (7)$$

and

$$\log K'_{ex} = \log D_{o,n} - m \log [H_2A]_{org} - 2m\,pH - X \log [S]_{org} \qquad (8)$$

Then, from the plots of log $D_{o,n}$ versus log $[S]$ at constant pH and TDT concentration the number of molecules of amine entering into the extracted species can be determined. From the results of experiments on the variation of log $[TDT]$ at constant amine concentration and constant *pH* the number of *TDT* molecules incorporated in the adduct formation can be also determined.

Figure 3 represents the plots of $\log D_{o,n}$ vs. $\log [S]$ at constant $[TDT]$ while Fig. 4 represents the plots of $\log D_{o,n}$ vs. $\log [TDT]$ at constant $[S]$ using a *pH* value of 5.0 and total ionic strength 0.1 *M*. From these figures it could be seen that straight lines are obtained in both cases with slope values of 2.0 ± 0.1 and 1.0 ± 0.2, respectively, which indicate that $CoAS_2$ is the main species extracted in the organic phase where *A* stands for *TDT* and *S* for amine ligands.

Table 1. *Extraction constant K'_{ex} and adduct formation constant B_{ex} for the extraction of cobalt(II) with TDT in presence of neutral additives*

Neutral additives	K'_{ex}	B_{ex}
DBA	$1.45 \cdot 10^{-5}$	$6.4 \cdot 10^{4}$
TBA	$1.50 \cdot 10^{-5}$	$6.6 \cdot 10^{3}$
BA	$7.26 \cdot 10^{-7}$	$3.2 \cdot 10^{3}$
without additive	$2.27 \cdot 10^{-10}$	—

From the distribution data extraction constants and adduct formation constants have been calculated and are listed in Table 1. The very large increase in the distribution coefficient in the presence of these auxiliary ligands indicated the phenomenon of synergism in such system.

It is also clear that the enhancement in the synergism takes the order $BA < TBA \ll DBA$ which indicates that the basicity order for the three classes of amines ($BA > DBA > TBA$) has no effect on the synergistic behaviour [8]. The high synergistic enhancement of *DBA* over *BA* can be related to its higher symmetry relative to *BA*, where the steric hindrance in the latter contributes to the decrease of its basicity.

References

[1] *Irving H, Edgington DN* (1969) Proc Chem Soc London 360
[2] *Irving H, Edgington DN* (1960) J Inorg Nucl Chem 15: 158
[3] *Li NC, Wang SM, Walker WR* (1963) J Inorg Nucl Chem 27: 2263
[4] *Irving H, Edgington DN* (1961) Chem Ind 77
[5] *Healy TV* (1961) J Inorg Nucl Chem 10: 314–328
[6] *Walker WR, Li NC* (1965) J Inorg Nucl Chem 27: 411
[7] *Hobart GH, Freiser H* (1969) Anal Chem 41: 10
[8] *Aly HF, Mohamed S, Abdel Rassoul AA* (1976) Radiochem Radioanal Lett 27: 79