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Extraction of Copper(II) with Salicylideneaniline from Sulphate and Perchlorate Media

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The liquid-liquid extraction of copper(II) from sulphate and perchlorate media by salicylideneaniline (HSA) in chloroform is studied. The ionic strength effect of the aqueous phase shows that the extraction of copper(II) increases with decreasing concentration of sulphate. At initially 10^{-4} M in the aqueous phase, Cu(II) is extracted as the complex $Cu(SA)_2 \cdot HSA$. Sulphate complex of Cu(II) is formed in the aqueous phase. The copper-sulphate interaction has been made in evidence by using the Debye-Hückel extended limiting law of ionic activity coefficient.

Key Words: Liquid-liquid extraction, Ionic strength, Copper(II), Salicylideneaniline, Activity coefficient.

INTRODUCTION

Liquid-liquid extraction of metals in sulphate medium has not been studied widely because of its complexity[1]. However, this medium remains very important from a practical point of view and the metallic extractions undertaken from sulphuric acid solution are preferred in industrial applications.

At initially about 10^{-6} M in the aqueous phase, Zn^{2+} is extracted as the complex $ZnA_2 \cdot 2HA$. The monosulphate, disulphate and trisulphate complexes of Zn^{2+} are formed in the aqueous phase in the presence of less than 0.25 M sulphate[2].

Previously, it has been shown that the extraction of a metal using a sulphate medium is less better than that in a perchlorate aqueous medium. This arises from the fact that the perchlorate is a non-complexing medium and the sulphate is a moderate complexing commonly used medium[3, 4]. Besides, the extraction of sulphuric acid as well as metallic sulphates is generally very weak because of the hydrophilic character of sulphate anions[5].

In the present work, the study of the liquid-liquid extraction of copper(II) from sulphate and perchlorate media with salicylideneaniline (HSA) in chloroform is carried out. Our interest is to study the effect of ionic strength of the aqueous sulphate and perchlorate media on the extraction of Cu^{2+} and to see if the complexes of copper could be formed in the aqueous phase using three different concentrations of sulphate 0.033, 0.16 and 0.33 M.

The Debye-Hückel extended limiting law of ionic activity coefficient has been introduced in order to gain information about the copper-sulphate interaction.

EXPERIMENTAL

Salicylideneaniline was prepared by refluxing salicylaldehyde with aniline and was purified by recrystallization from ethanol[6]. Chloroform was pre-equilibrated with aqueous solution which did not contain copper(II). The initial compositions of the phases were as follows:

Aqueous phase: $[Cu^{2+}]_i = 10^{-4}$ M;

$[Na_2SO_4] = 0.033, 0.16$ and 0.33 M;

$[NaClO_4] = 0.01, 0.1$ and 1 M;

Organic phase: $[HSA]_{i,\,org} = 0.005, 0.01$ and 0.02 M in chloroform.

Extraction and analytical procedure

Extractions were performed on thermostated vessels at 25°C. Equal volumes (40 mL) of both phases were contacted under magnetic stirring until the equilibrium was attained (max 30 mn) and then separated by gravity. The pH was adjusted by NaOH 0.1 M solutions of suitable compositions. For each experimental point, aliquots of the two phases were withdrawn and the metal was stripped from the organic aliquot with 0.1 M H_2SO_4 or $HClO_4$. Copper concentrations were determined after suitable dilution by flame atomic absorption using a 2380 Perkin-Elmer spectrophotometer.

RESULTS AND DISCUSSION

Liquid-liquid extraction of copper(II) with HSA in chloroform from sulphate medium at constant ionic strength

The overall reaction in the extraction of copper(II) with HSA (HL) in chloroform from sulphate aqueous medium of ionic strength ($I = 1.0$ mol. kg^{-1}), may be expressed as

$$Cu^{2+} + (n+m)HL_{org} \overset{K_{ex}}{\rightleftharpoons} CuL_n(HL)_{m\,org} + nH^+ \qquad (1)$$

org denotes species in organic phase.

The extraction constant, K_{ex}, is defined as Eq. (2) and is rewritten as Eq. (3) by using the distribution ratio, D_{Cu}, of copper(II).

$$K_{ex} = \frac{[CuL_n(HL)_m]_{org}[H^+]^n}{[Cu^{2+}][HL]_{org}^{n+m}} \qquad (2)$$

$$\log D_{Cu} = \log \frac{[Cu]_{org}}{[Cu]} = \log K_{ex} + (n+m)\log [HL]_{org} + n\,pH \qquad (3)$$

Plots of the log D_{Cu} *vs.* pH, for various concentrations of HSA, were linear with a slope of 2, as shown in Fig. 1. Likewise, plots of log D_{Cu} *vs.* log $[HL]_{org}$ at constant pH values were also linear with a slope of 3 in all the extraction systems, as shown in Fig. 2. These results reveal that $n = 2$ and $m = 1$ in Eq. (1), *i.e.*, only a complex $CuL_2 \cdot HL$, is extracted into chloroform. The logarithmic values of K_{ex} of copper(II) can therefore be calculated for each experimental point ($\log K_{ex} = -4.07$).

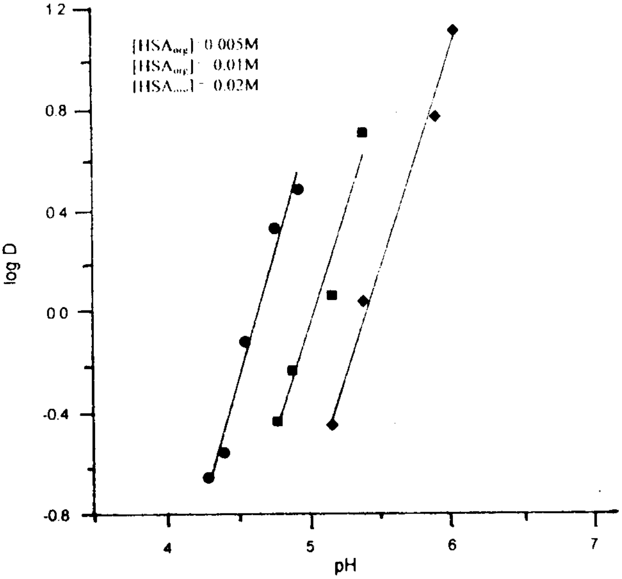

Fig. 1. pH effect on the Cu^{2+} extraction with HSA in chloroform; sulphate medium 0.33 M

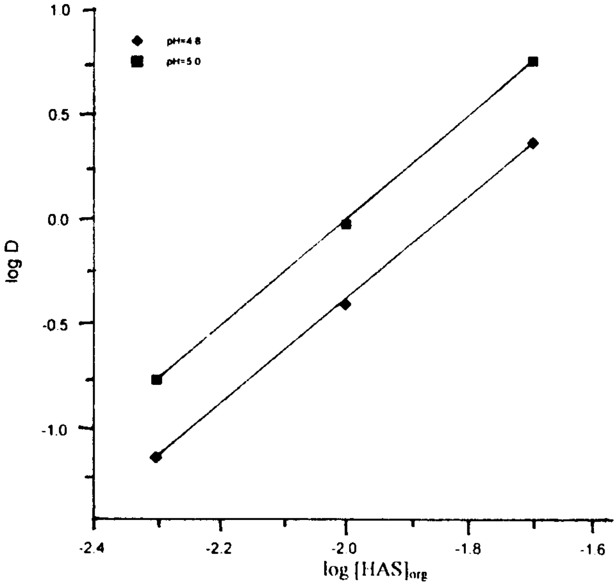

Fig. 2. Concentration effect of HAS in chloroform on the Cu^{2+} extraction; sulphate medium 0.33 M

Liquid-liquid extraction of copper(II) with HSA in chloroform from sulphate and perchlorate media for various ionic strengths

Figs. 3 and 4 represent plots of log D_{Cu} *vs.* pH obtained during the extraction of copper(II) at various ionic strengths 0.01, 0.1 and 1.0 mol kg^{-1}. As it is shown on these figures, the extraction of Cu(II) from sulphate medium increases when the ionic strength decreases and, therefore, the extraction from perchlorate medium is independent of the ionic strength.

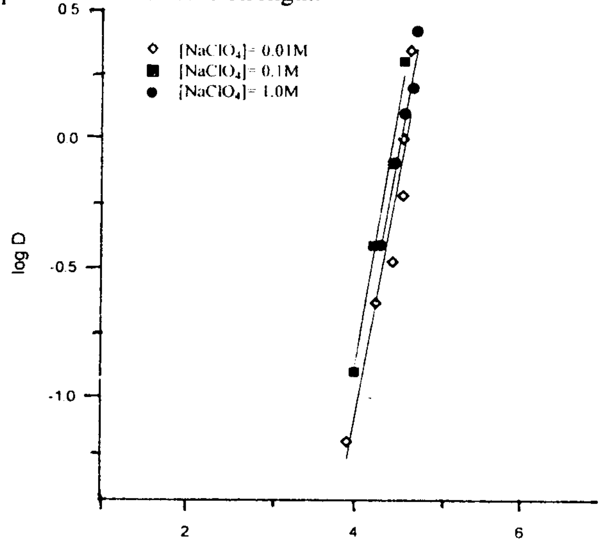

Fig. 3. Ionic strength effect on the Cu^{2+} extraction with HAS 0.01 M in chloroform from perchlorate medium

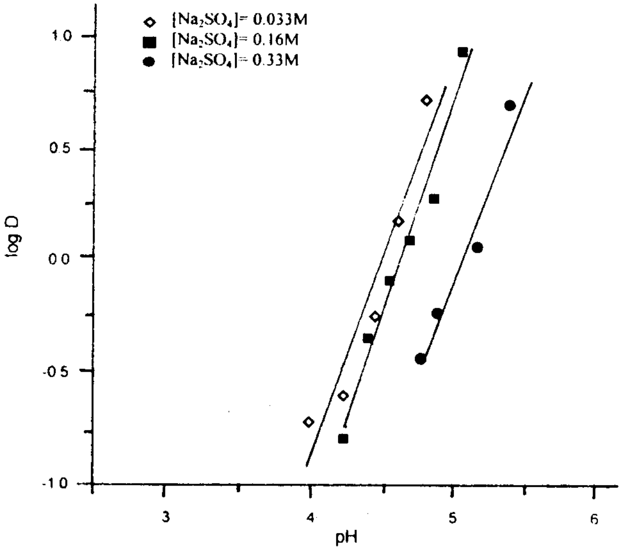

Fig. 4. Ionic strength effect on the Cu^{2+} extraction with HAS 0.01 M in chloroform from sulphate medium

The activity coefficient may be introduced as a useful parameter to explain the effect of the ionic strength upon the liquid-liquid extraction of copper(II) from sulphate medium into chloroform.

The extraction process may be decribed by the following equilibrium:

$$Cu^{2+} + 3HL_{org} \overset{K_{ex}}{\rightleftharpoons} CuL_2{\cdot}HL_{org} + 2H^+ \tag{4}$$

The extraction constant K_{ex}, describing this process, may be expressed in terms of the activity coefficients, *i.e.*,

$$K_{ex} = \frac{[CuL_2{\cdot}HL]_{org}[H^+]\gamma_{CuL_2}{\cdot}HL_{org}\gamma^2_{H^+}}{[Cu^{2+}][HL]^{n+m}_{org}} \tag{5}$$

The logarithmic values of D_{Cu} can, therefore, be deduced:

$$\log D_{Cu} = \log K_{ex} + 3 \log [HL]_{org} + 2pH + \log \frac{\gamma^3_{HL_{org}}}{\gamma_{CuL_2{\cdot}HL_{org}}} + \log \frac{\gamma^2_{Cu^{2+}}}{\gamma^2_{H^+}} \tag{6}$$

log $(\gamma^3_{HL_{org}}/\gamma_{CuL_2{\cdot}HL_{org}})$ of the organic phase does not vary because it is independent of the ionic strength of the aqueous phase. Therefore, at constant pH the values of log D_{Cu} depends upon log $(\gamma_{Cu^{2+}}/\gamma^2_{H^+})$.

The ionic activity coefficients can be determined using the Debye-Hückel extended limiting law by taking into account the size of the ions[7] (a_i)

$$-\log \gamma_A = \frac{A_m z_A^2 I_m^{1/2}}{1 + B_m a_i I_m^{1/2}} \tag{7}$$

where, on the molality scale, the constants A_m and B_m are defined by

$$A_m = \frac{(2\pi N d_0)^{1/2}}{(1000)^{1/2}} \frac{e^3}{2.3026(kTD)^{3/2}} \tag{8}$$

and

$$B_m = \frac{(8\pi N d_0)^{1/2}}{(1000)^{1/2}} \frac{e}{(kTD)^{1/2}} \tag{9}$$

In the formulae (8) and (9), e, N, d_0, k, T, D and z_A represent the magnitude of the electron charge, the Avogadro constant, the density of the solvent, the Boltzmann constant, the absolute temperature, the dielectric constant of the solvent and the valency of the cation, respectively.

Since, in Eq. (7), the ionic size (a_i) is not clearly defined[7, 8], it has been introduced by us as the radius of hydrated cation. The values of the hydrated radii $(a_i = r_H)$ used for the tabulation of the ionic activity coefficient values of Cu^{2+} and H_3O^+ are taken from (9). The calculated values of these ionic activity coefficients are summarized in Table-1.

As it is shown in Table-1, log $(\gamma_{Cu^{2+}}/\gamma^2_{H^+})$ decreases with increasing values of the ionic strength and, therefore, log D decreases according to Eq. (6). This result agrees satisfactorily with experimental values shown in Fig. 5.

TABLE-1
THE CALCULATED VALUES OF THE IONIC ACTIVITY COEFFICIENTS
OF Cu^{2+} AND H^+ AT 25°C

Ionic strength (mol kg^{-1})	Ionic activity coefficient γ_{H^+}	Ionic activity coefficient $\gamma_{Cu^{2+}}$	$\log(\gamma_{Cu^{2+}}/\gamma^2_{H^+})$
0.01	0.9134	0.6756	−0.0916
0.10	0.8257	0.4011	−0.2304
1.00	0.7439	0.2067	−0.4292

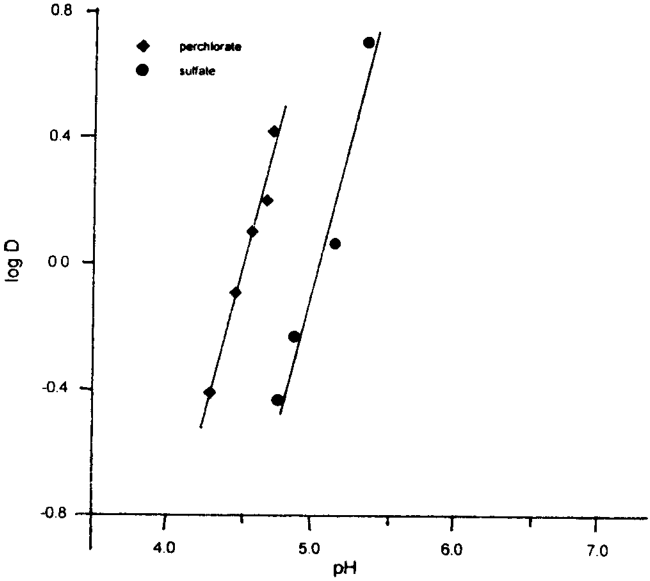

Fig. 5. Cu^{2+} extraction with HAS 0.01 M in chloroform from sulphate and perchlorate aqueous media (I = 1.0 mol kg^{-1}).

In addition, $\Delta \log D_{Cu}$ between two different ionic strengths for copper(II) are deduced graphically from this figure. Their values are reported along with those of $\Delta \log(\gamma_{Cu^{2+}}/\gamma^2_{H^+})$ in Table-2.

TABLE-2
COMPARISON BETWEEN VALUES OF $\Delta \log(\gamma_{Cu^{2+}}/\gamma^2_{H^+})$ AND $\Delta \log D_{Cu}$

Ionic strength	$\Delta \log D_{Cu}$	$\Delta \log(\gamma_{Cu^{2+}}/\gamma^2_{H^+})$
0.01 → 0.1	0.25	0.1388
0.10 → 1.0	0.72	0.1988
0.01 → 1.0	0.94	0.3376

It is noticed in Table-2 that values of $\Delta \log D_{Cu}$ are always different from those of $\Delta \log(\gamma_{Cu^{2+}}/\gamma^2_{H^+})$. This difference may be due to the fact that the $Cu^{2+}-SO_4^{2-}$ interaction has not been taken into account, *i.e.*, ($a_i = r_H$) during the calculation of the ionic activity coefficients using the extended Debye-Hückel limiting law (Eq. (7)).

The curves illustrated by Fig. 5 could be in good agreement with the formation of the complexes $CuSO_4$ not extractible, which could reduce the concentration of Cu^{2+} and thus decrease their extraction.

In the experimental conditions, this hypothesis becomes valid when the interaction constant of Cu^{2+}–SO_4^{2-} is taken into account [equation (10)].

$$Cu^{2+} + SO_4^{2-} \overset{K_{int}}{\rightleftharpoons} CuSO_4 \qquad (10)$$

The interaction constant value of Cu^{2+}–SO_4^{2-} is equal to 0.085. It was determined by making the difference between the extraction constants of copper(II) in sulphate ($\log K_{ex, SO_4^{2-}} = -4.07$) and perchlorate aqueous media ($\log K_{ex, ClO_4^-} = -3.0$).

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