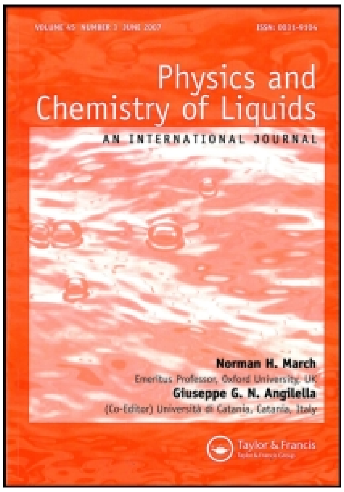

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Liquid–liquid extraction of copper(II) with Schiff's bases derived from salicylaldehyde

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The liquid–liquid extraction of copper(II) with Schiff's bases from salicylaldehyde and aniline and its derivatives in chloroform is studied. Slope analysis results are consistent with the extraction of copper(II) as complexes of the type $CuL_2(HL)$. Their extraction constants show dependence on the position of substituent present on the aniline ring.

Keywords: Liquid–liquid extraction; Schiff's base; Copper(II); Salicylaldehyde; Aniline; Substituent

1. Introduction

Several salicylidene Schiff's bases have been synthesised previously. Earlier studies have included electronic spectra [1,2], protonation equilibria [3–8], tautomeric properties [9,10], and liquid–liquid extraction of various metal cations [11–13].

In a previous paper [14], it has been shown that the extraction of copper(II) with salicylideneaniline from sulphate medium is not as good as in a perchlorate aqueous medium. This arises from the fact that the perchlorate is a non-complexing medium and the sulphate being a moderate-complexing commonly used medium.

In the present work, the study of the liquid–liquid extraction of copper(II) with Schiff's bases derived from salicylaldehyde is carried out. Our interest is to investigate the effect of position of the substituent on the extraction of copper(II).

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2. Experimental

2.1. *Reagents and solutions*

Salicylideneaniline (HSA), salicylidene-*o*-methoxyaniline (HSOMA), salicylidene-*m*-methoxyaniline (HSMMA), salicylidene-*p*-methoxyaniline (HSPMA) and salicylidene-*o*-methylaniline (HSOT) were prepared by refluxing salicylaldehyde with the corresponding amine and were purified by recrystallisation from ethanol [15]. Chloroform was pre-equilibrated with aqueous solution which did not contain copper(II). The initial compositions of the phases were as follows:

Aqueous phase: $[\mathrm{Cu}^{2+}]_i = 10^{-4}\,\mathrm{M}$; $[\mathrm{Na_2SO_4}] = 0.33\,\mathrm{M}$;
Organic phase: $[\mathrm{HL}]_{i,\mathrm{org}} = 0.005$, 0.01 and 0.02 M in chloroform.

2.2. *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 min) and then separated by gravity. The pH was adjusted by NaOH 0.1M 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 0.1M H_2SO_4. Copper concentrations were determined, after suitable dilution, by flame atomic absorption using a 2380 Perkin-Elmer spectrophotometer.

3. Results and discussion

3.1. *Liquid–liquid extraction of copper(II) with HSA in chloroform*

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

$$\mathrm{Cu}^{2+} + (n+m)\mathrm{HL}_{\mathrm{org}} \overset{K_{\mathrm{ex}}}{\rightleftarrows} \mathrm{CuL}_n(\mathrm{HL})_{m\,\mathrm{org}} + n\mathrm{H}^+, \tag{1}$$

Subscript org denotes species in organic phase.

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

$$K_{\mathrm{ex}} = \frac{[\mathrm{CuL}_n(\mathrm{HL})_m]_{\mathrm{org}}[\mathrm{H}^+]^n}{[\mathrm{Cu}^{2+}][\mathrm{HL}]^{n+m}\mathrm{org}} \tag{2}$$

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

Plots of the $\log D_{\mathrm{Cu}}$ *versus* pH for various concentrations of HSA, are linear with a slope equal to 2, as shown in figure 1. Likewise, in all the extraction systems, plots of $\log D_{\mathrm{Cu}}$ *versus* $\log[\mathrm{HL}]_{\mathrm{org}}$ at constant pH values are also linear with a slope equal to 3, as shown in figure 2. These results allow to obtain $n = 2$ and $m = 1$, which are readily replaced in equation (1).

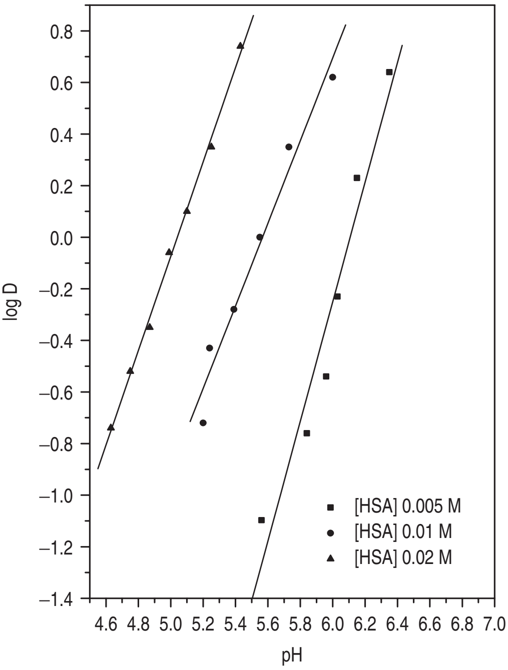

Figure 1. pH effect on the Cu^{2+} extraction with HSA in chloroform; sulphate medium 0.33 M.

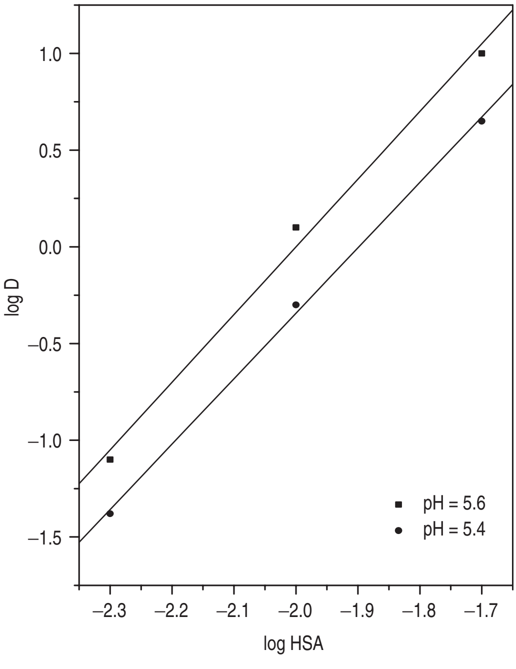

Figure 2. Concentration effect of HSA in chloroform on the Cu^{2+} extraction; sulphate medium 0.33 M.

This means that only the complex $CuL_2(HL)$, is extracted into chloroform. The logarithmic values of K_{ex} of copper(II) can, therefore, be calculated for each experimental point ($\log K_{ex} = -5.08$).

3.2. *Liquid–liquid extraction of copper(II) with substituted salicylideneanilines in chloroform*

In the aim to study the effect of substituent on the extraction of copper by salicylideneanilines, we have chosen Schiff's bases carrying successively the groups *o*-OCH_3, *m*-OCH_3, *p*-OCH_3 and *o*-CH_3.

For each case, we have followed the evolution of $\log D$ when the pH varied in the sulphate–chloroform medium.

The various curves in figure 3 allow us, as a result, to evaluate the effects of the substituents and to compare them between each other. We remark that besides the HSA, this figure exhibits only the curves relative to HSMMA and HSPMA. However, the remaining Schiff's bases, namely HSOMA and HSOT do not allow any extraction of copper(II).

We have not, so far, observed any extraction with the compounds carrying *o*-OCH_3 and *o*-CH_3 groups. The absence of extraction with these two compounds is not, certainly, due to their electronic effects, since that the same methoxy in positions meta and para, characterised by the same feed mesomer effect as in position ortho, leads to the extraction of copper(II).

Effectively, for the extractions with HSPMA and HSMMA, in chloroform–sulphate medium, the study of $\log D$ as a function of pH, leads to straight lines (figure 3).

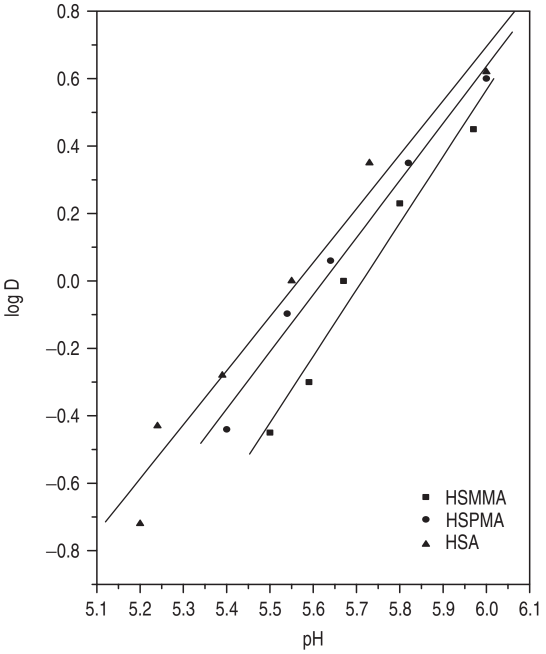

Figure 3. Extraction of Cu^{2+} with salicylideneanilines 0.01 M in chloroform; sulphate medium 0.33 M.

Table 1. Values of the extraction constants of copper (II), obtained from three extractants.

Extractant	HSA	HSPMA	HSMMA
$\log K_{ex}$	−5.08	−5.22	−5.42

These latter have the same slope equal to 2, as in the case of HAS not substituted, suggesting the exchange of two protons between the metal cation and the extractant.

The set of the lines obtained, allows to establish for the three Schiff's bases, the following increasing order HSMMA < HSPMA < HSA. Indeed, this sequence is confirmed by the extraction constant values of the three extractants, calculated from equation (4). These values are summarised in table 1.

$$\log K_{ex} = \log D - 2\,\mathrm{pH} - 3\log[\mathrm{HL}]_{org} \tag{4}$$

The best extraction is observed with HSA not substituted. This could be due to its higher distribution ability, as it has been already proved in a previous study [16].

Finally this study allows to suggest that the absence of extraction with HSMMA and HSOT, would be due to an encumbered steric effect, engendered by the same position. The substituents in ortho would encumber the coordination sites in the ligand and would, perhaps, prevent the complexation of the metal ion.

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