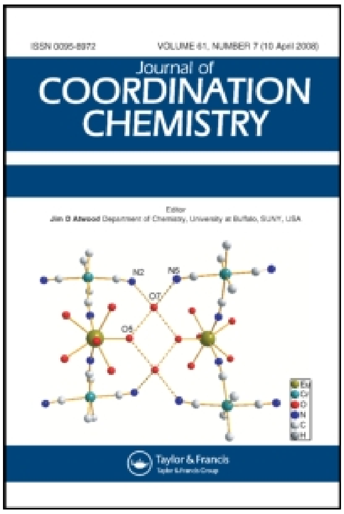

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Solvent extraction of copper(II) from sulfate medium with *N*-(2-hydroxybenzylidene)aniline

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Solvent extraction of copper(II) from sulfate medium with *N*-(2-hydroxybenzylidene)aniline is studied with the following parameters: pH, concentration of the extractant, nature of diluent, and temperature. The extraction of copper(II) proceeds by a cation exchange mechanism and the extracted species are CuL_2 in cyclohexane and toluene and CuL_2 with some CuL_2HL in chloroform. The equilibrium constants have been calculated as well as thermodynamic parameters ΔH°, ΔS°, and ΔG°. The temperature effect on the solvent extraction of copper(II) with *N*-(2-hydroxybenzylidene)aniline in cyclohexane is discussed.

Keywords: Solvent extraction; Copper(II); Sulfate medium; *N*-(2-hydroxybenzylidene)aniline; Temperature effect

1. Introduction

Several salicylidene Schiff bases have been reported including electronic spectra [1, 2], protonation equilibria [3–8], tautomeric properties [9, 10], and liquid–liquid extraction of various metal cations [11–13].

In previous studies [14, 15], we investigated the extraction of transition metal ions with *N*-(2-hydroxybenzylidene)aniline from sulfate and perchlorate media. It has been shown that the extraction of copper(II) with *N*-(2-hydroxybenzylidene)aniline from sulfate medium is less efficient than that in a perchlorate aqueous medium. This arises from the fact that the perchlorate is noncomplexing and the sulfate is moderately complexing. *N*-(2-hydroxybenzylidene)aniline has been found to be a good chelate extractant for Cu(II), Co(II), and Ni(II).

In a recent paper, we reported [16] the liquid–liquid extraction of copper(II) from sulfate medium with Schiff bases derived from salicylaldehyde. Their extraction constants show dependence on the position of substituent present on the aniline ring.

In this work, we study the solvent extraction of copper(II) from sulfate medium with *N*-(2-hydroxybenzylidene)aniline to investigate the effect of temperature on the extraction of copper(II).

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2. Experimental

2.1. *Reagents and solutions*

N-(2-hydroxybenzylidene)aniline (N2HBA) was prepared by refluxing salicylaldehyde with aniline and purified by recrystallization from ethanol [15]. Salicylaldehyde, aniline, and all chemicals used in this work were purchased from Merck and used as received. Chloroform, toluene, and cyclohexane were pre-equilibrated with aqueous solution which did not contain copper(II). The initial compositions of the phases were as follows: aqueous phase: $[Cu^{2+}]_i = 1.5 \times 10^{-3}\,mol\,L^{-1}$; $[Na_2SO_4] = 0.33\,mol\,L^{-1}$; organic phase: $[N2HBA]_i = 0.01$, 0.02, and $0.04\,mol\,L^{-1}$.

2.2. *Extraction and analytical procedure*

Extractions were performed on thermostated vessels. Equal volumes, 30 mL each of aqueous and organic phases, were shaken with a magnetic stirrer for 30 min, a period found to be adequate to reach equilibrium. After phase separation by gravity, the metal concentration in the aqueous phases was determined photometrically at 820 nm using a Shimadzu UV-VIS 1240. The pH of the aqueous phase was measured by a pH-meter with an accuracy of 0.02 pH unit. The pH was adjusted to the desired level by the addition of sodium hydroxide. The ionic strength was maintained at 1 with Na_2SO_4.

3. Results and discussion

3.1. *Extractant concentration and pH dependencies*

The overall reaction in the extraction of copper(II) with N2HBA (HL) in cyclohexane, toluene, and chloroform from the sulfate aqueous medium of ionic strength $(I = 1.0\,mol\,kg^{-1})$ may be expressed as

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

where org denotes species in the organic phase.

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

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

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

Plots of $\log D_{Cu}$ *versus* pH for various concentrations of N2HBA are linear with a slope equal to 2, as shown in figures 1–3. Likewise, in all the extraction systems, plots of $\log D_{Cu}$ *versus* $\log[HL]_{org}$ at constant pH are also linear with a slope equal to 2 in cyclohexane and toluene and 2.3 in chloroform, as shown in figures 4–6. These results

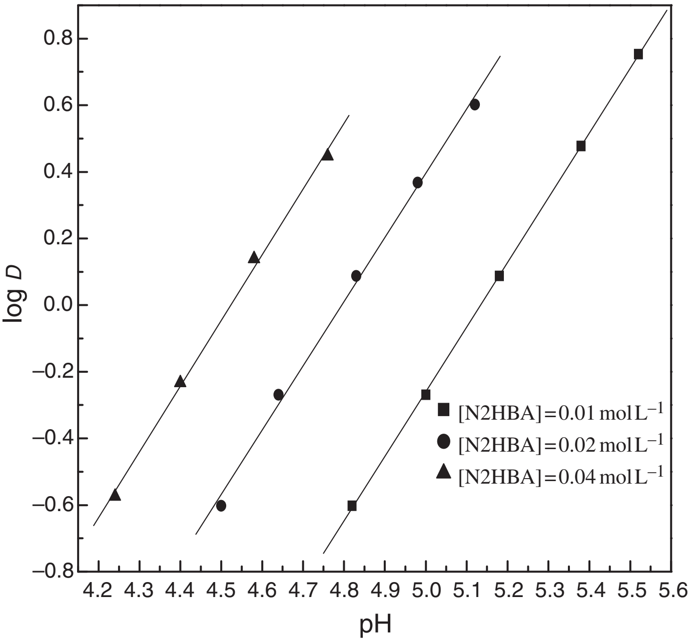

Figure 1. Effect of pH on the extraction of copper(II) from sulfate medium with *N*-(2-hydroxybenzylidene)aniline in chloroform at 25°C.

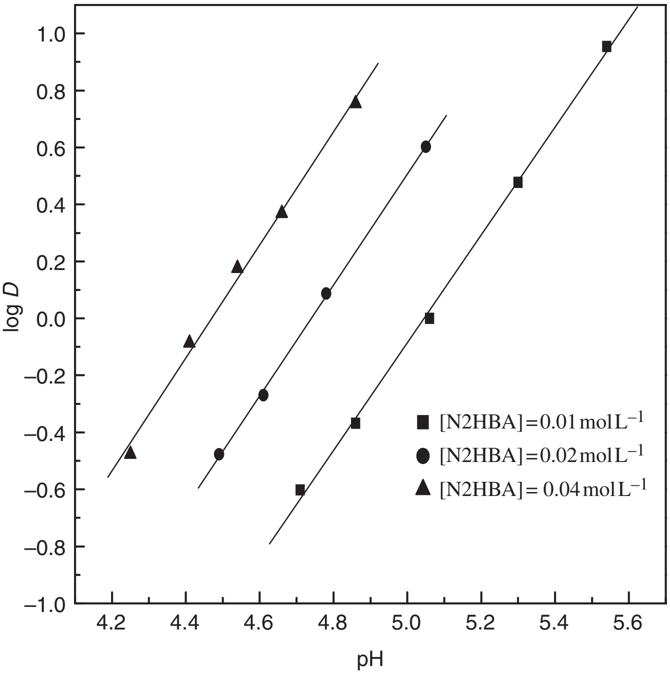

Figure 2. Effect of pH on the extraction of copper(II) from sulfate medium with *N*-(2-hydroxybenzylidene)aniline in toluene at 25°C.

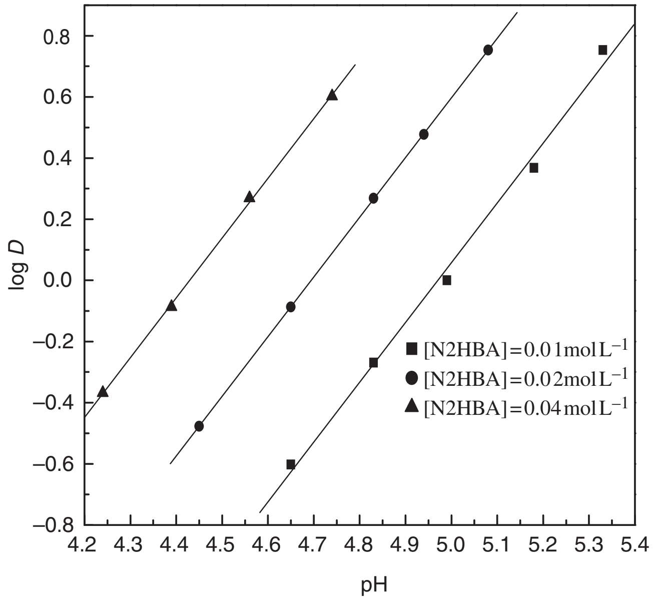

Figure 3. Effect of pH on the extraction of copper(II) from sulfate medium with *N*-(2-hydroxybenzylidene)aniline in cyclohexane at 25°C.

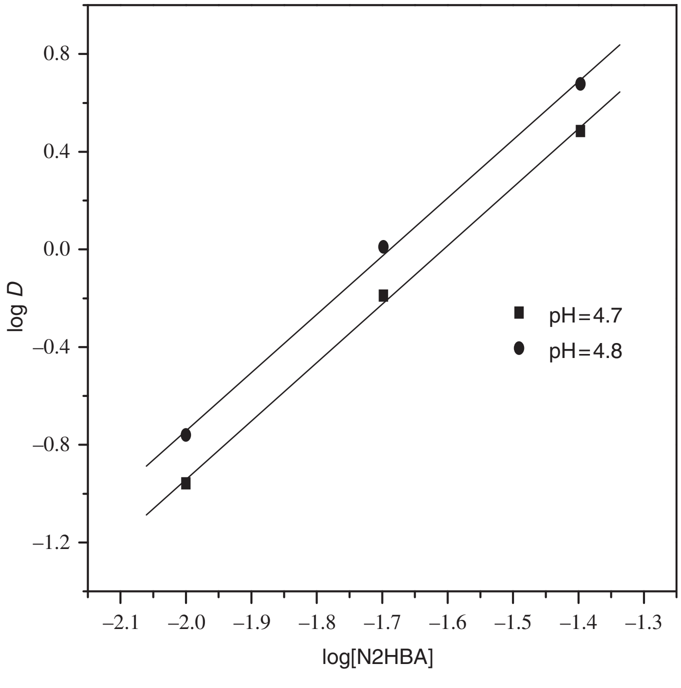

Figure 4. Effect of the extractant concentration on the extraction of copper(II) in chloroform at 25°C.

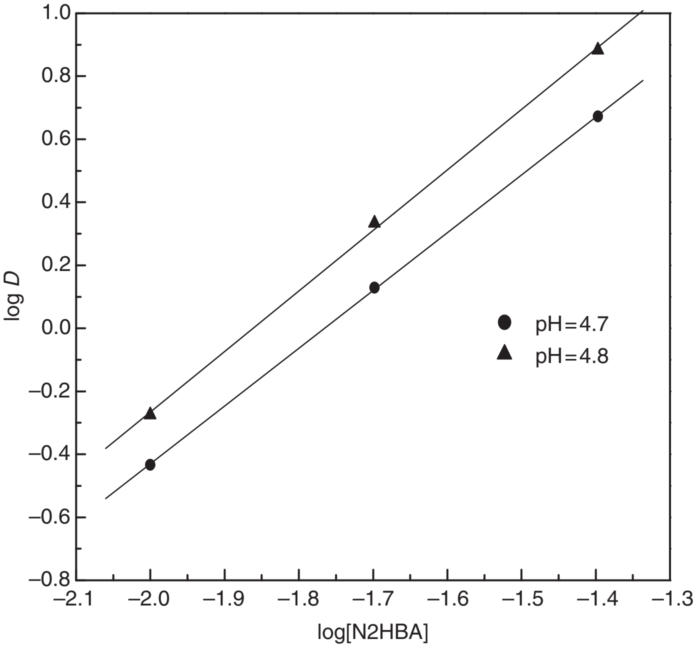

Figure 5. Effect of the extractant concentration on the extraction of copper(II) in toluene at 25°C.

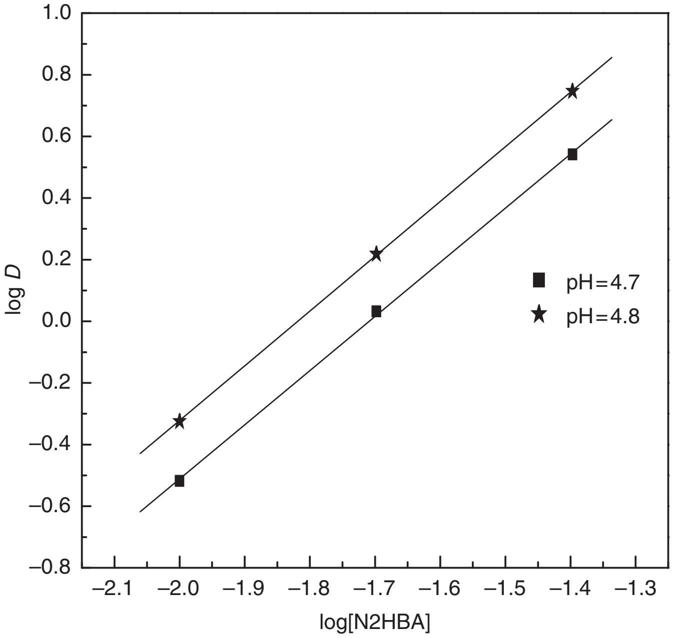

Figure 6. Effect of the extractant concentration on the extraction of copper(II) in cyclohexane at 25°C.

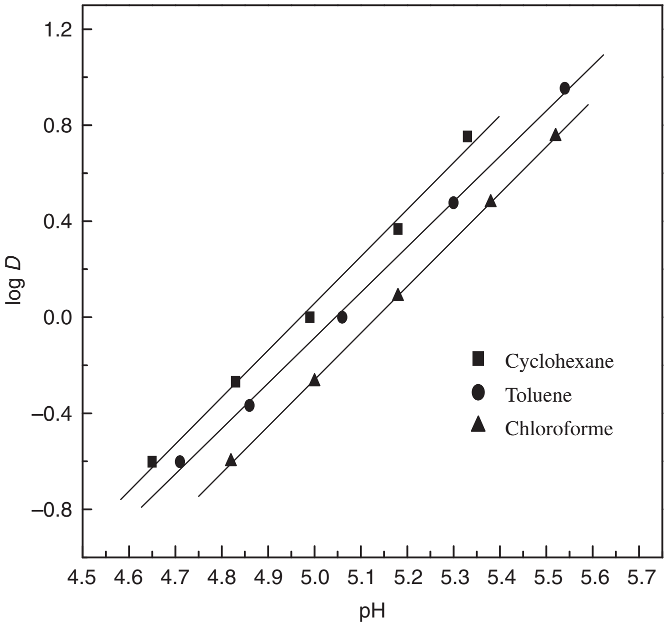

Figure 7. Effect of diluents on the extraction of copper(II) at 25°C from sulfate medium with *N*-(2-hydroxybenzylidene)aniline 0.01 mol L^{-1}.

give $n=2$ and $m=0$ or 0.3, which are readily replaced in equation (1). This means that two types of complexes are extracted that depend on the nature of diluent; CuL_2 is extracted into cyclohexane and toluene and CuL_2 with some CuL_2HL in chloroform.

In a previous paper, the extraction of copper(II) by di(2-ethylhexyl)phosphoric acid in different solvents were reported [17]. The stoichiometry coefficients of the extracted complexes and their extraction constants were dependent on the nature of the diluents. Comparing the stoichiometry of the extracted species of copper(II) found in this work with those obtained by Boukraa [15] and Ghebghoub [17], the same set of species are found for copper(II) in similar experimental conditions. The extraction process may be described by the following equilibrium:

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

The extraction constants, K_{ex}, may be defined as

$$\log K_{ex} = \log D_{Cu} - 2\log [HL]_{org} - 2pH \tag{5}$$

3.2. *Effect of diluent*

It is well known that diluent plays an important role in solvent extraction by affecting the efficiency of the extraction process. Extraction of copper(II) with N2HBA is achieved by using chloroform, toluene, and cyclohexane as diluents (described in figure 7). Ghebghoub and Barkat [17] studied the effect of diluent upon the extraction

Table 1. Log K_{ex} values of copper(II) in different diluents at 25°C.

Diluent	Cyclohexane	Toluene	Chloroform
log K_{ex}	−5.94	−6.09	−6.27

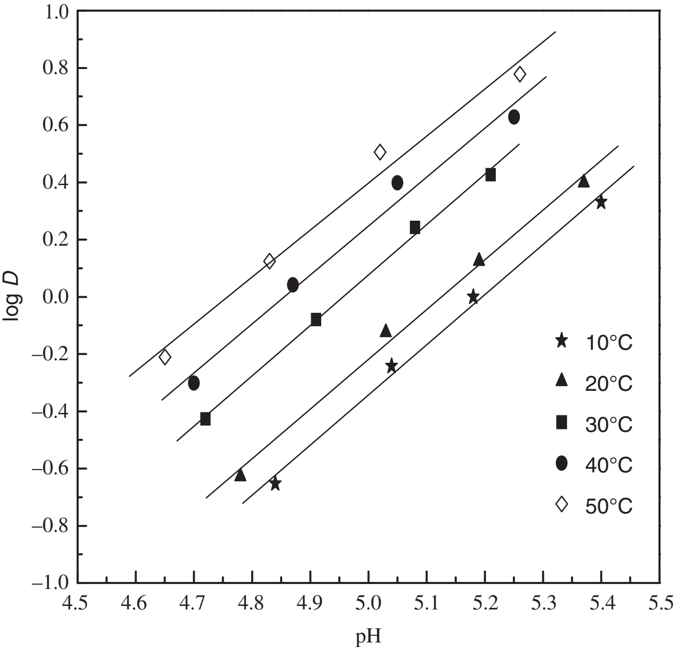

Figure 8. Effect of temperature on the extraction of copper(II) from sulfate medium with *N*-(2-hydroxybenzylidene) aniline 0.01 mol L^{-1} in cyclohexane.

of copper(II) with di(2-ethylhexyl)phosphoric acid, showing that the choice of diluent influences the extraction. A more detailed study of diluent effect was carried out by Brunette [18] and Komasawa [19, 20], who found that polar or non-polar diluents could greatly affect the extraction of metal cations.

When cyclohexane was used as diluent, log K_{ex} values for copper(II) clearly improved (table 1). The best extraction order was: cyclohexane > toluene > choroform.

3.3. *Temperature dependency*

Figure 8 represent the plots of log D_{Cu} *versus* pH obtained during the extraction of copper(II) at different temperatures. As shown in this figure, the extraction of the metal increases with increasing temperature.

The values of log K_{ex} at different temperatures calculated from equation (5) are listed in table 2. Within the limited temperature range investigated, the relation between log K_{ex} and the thermodynamic parameters can be expressed as

$$\log K_{ex} = \frac{\Delta H^\circ}{2.303RT} + \frac{\Delta S^\circ}{2.303R} \tag{6}$$

Table 2. Values of the extraction constants of copper(II) at different temperatures.

T (K)	283	293	303	313	323
$\log K_{ex}$	−6.37	−6.24	−5.91	−5.74	−5.58

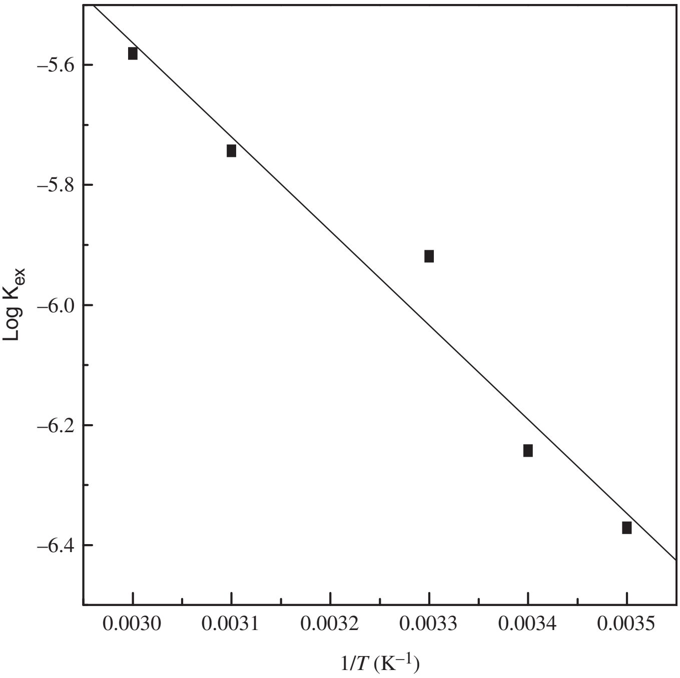

Figure 9. Variation of equilibrium constant with temperature on the extraction of copper(II) with *N*-(2-hydroxybenzylidene)aniline.

Table 3. Thermodynamic parameters for copper(II) extraction.

ΔH° (kJ mol^{-1})	ΔS° (J K^{-1}mol^{-1})	ΔG°(kJ mol^{-1})
30.05	−16.37	34.56

where ΔH° is extraction enthalpy of copper(II), T is temperature, ΔS° is extraction entropy of copper(II), and R is gas constant. A plot of $\log K_{ex}$ against $1/T$ gives a straight line of slope $-\Delta H^\circ/2.303R$ and a y-intercept of $\Delta S^\circ/2.303R$ (figure 9). The values of ΔH° and ΔS° of the extraction processes and free energy calculated from $\Delta G^\circ = -2.303RT \log K_{ex}$ are tabulated in table 3.

The results show that the extraction of copper(II) from sulfate medium with *N*-(2-hydroxybenzylidene)aniline in cyclohexane is endothermic. The positive values of ΔG° imply that the reaction is not spontaneous. Further, it is clear from the experimental data that the extraction increases with increasing temperature.

4. Conclusion

The solvent extraction of copper(II) from sulfate medium with *N*-(2-hydroxybenzylidene)aniline was studied in the following parameter functions:

- Extractant concentration and pH dependencies: CuL_2 is extracted into cyclohexane and toluene and CuL_2 (major) with CuL_2HL in chloroform.
- Solvent: the extraction is better in the following order: cyclohexane > toluene > chloroform.
- The results of the copper(II) distribution studies using N-(2-hydroxybenzylidene)aniline are in general agreement with previously reported data for Cu(II), with di(2-ethylhexyl)phosphoric acid and salicylideneaniline as extractants [15, 17].
- Temperature dependency: the extraction increases with increasing temperature. The extraction is endothermic.

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