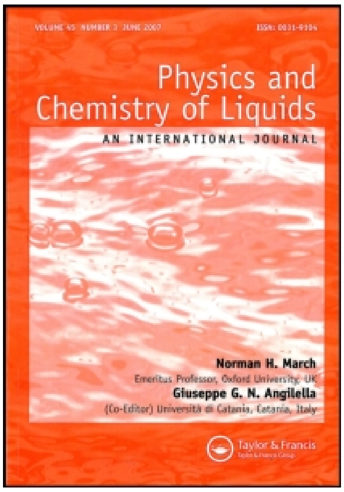

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Liquid–liquid extraction of Cu(II), Co(II) and Ni(II) with salicylidèneaniline from sulphate media

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For a fundamental study on the development of novel extraction divalent metal, the extraction behaviour of copper(II), cobalt(II) and nickel(II) is studied with salicylidèneaniline (SAN). The phenol group in the Schiff base moiety leads to a large increase in the percentage of transition metal ions. SAN has both good reactivity towards metal ions and solubility in organic solvents. The solvent extraction of copper(II), cobalt(II) and nickel(II) with salicylidèneaniline from sulphate media is studied with the following parameters: pH, concentration of the extractant and the nature of diluent. The stoichiometry coefficients of the extracted species are determined by the slope analysis method. The extraction reaction proceeds by cation exchange mechanism and the extracted species are: CuL_2HL, CoL_2HL and NiL_2. The extaction constants are evaluated for the different diluents. Under suitable conditions of pH, the solvent extraction of cobalt(II) and nickel(II) in different diluents leads to third phase formation. This tendency is confirmed from numerical extraction constants for both metal cations ($\log K_{ex} = -15.10 \pm 0.03$ for nickel(II) in $CHCl_3$) and ($\log K_{ex} = -12.56 \pm 0.04$ for cobalt(II) in $CHCl_3$). The extraction efficiency is found to follow the order Cu(II) > Co(II) > Ni(II).

Keywords: Liquid–liquid extraction; Cu(II); Co(II); Ni(II); Salicylidèneaniline; Schiff bases; Third phase formation

1. Introduction

Schiff base compounds are often used as ligands in coordination chemistry because they are generally known for their metal binding ability and, in particular, salicylaldimines are useful for the synthesis of transitional metal complexes. Noteworthy examples include Cu(II) [1–2], Fe(II)[3] and complexes. The Schiff's bases derived from salycilaldehyde are known to form very stable complexes with transitional metal

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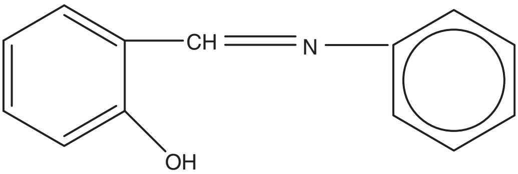

Figure 1. Scheme of the chemical formula of *N*-salicylideneaniline.

ions [4–5]. The resulting complexes are frequently used as catalysts in such diverse processes as mediating organic redox reactions [6], enantioselective epoxidation [8] and aziridation [9]. Important and numerous studies have been carried out in liquid–liquid extraction of divalent metal cations. The use of Schiff base extraction favours the formation of extractible stable chelates [10–17]. However, the use of SAN for solvent extraction of metal(II) cations has not been reported so far. SAN acts mainly as bidentate ligand and its chemical formula is illustrated in figure 1.

The present work describes the results obtained from the extraction of copper(II), cobalt(II) and nickel(II) with salicylidèneaniline in sulphate aqueous solutions. The aim of the work is to determine the stoichiometry coefficients of the extracted complexes and their extraction constants.

2. Experimental

2.1. *Reagents*

SAN was synthesised in our laboratory according to the literature procedure [18]. Equimolar quantities of salicylic aldehyde and aniline are dissolved in the minimum pure ethanol inside a balloon tricol provided with a magnetic stirrer, a cooling agent and a graduated thermometer. The unit is maintained with the backward flow and under agitation for approximately 2 h. The mixture is cooled at room temperature and then concentrated by elimination of solvent using a rotary evaporator. The solid product obtained is filtered and then re-crystallised in the minimum pure ethanol.

Chloroform, toluene and cyclohexane were pre-equilibrated with aqueous solution which did not contain any metal. The ionic strength of the aqueous medium was assumed to be unity with the concentration of Na_2SO_4 equal to 0.33 M. The initial metal concentrations in the aqueous phase in all the experiments were:

$$[Cu^{+2}] = 1.575 \times 10^{-3} M, \quad [Co^{+2}] = 1.88 \times 10^{-3} M, \quad [Ni^{+2}] = 6.81 \times 10^{-3} M.$$

2.2. *Extraction and analytical procedures*

The distribution measurements were performed in thermostated vessels, with a temperature fixed at $25.0 \pm 0.2^\circ C$. Equal volumes, $40\,cm^3$ 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 the phase separation by gravity, the metal concentration in the aqueous phases was determined photometrically using a Shimadzu UV-VIS 211. The pH of the aqueous phase was measured by a pH-meter with an accuracy equal to 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, and the temperature was measured with an accuracy of 0.2°C.

3. Results and discussion

3.1. *Extraction of Cu(II), Co(II) and Ni(II) with SAN*

3.1.1. Effect of equilibrium pH. The overall reaction in the extraction of copper(II), cobalt(II) and nickel(II) with SAN (HL) from sulphate aqueous medium may be expressed as

$$M^{2+} + (n+m)HL_{org}\ DML_n(HL)_{m\ org} + nH^+(1) \tag{1}$$

$(M = Cu(II), Co(II), Ni(II))$; (org) denotes the species in organic phase.

The extraction constant, K_{ex}, is defined as equation (2) and is rewritten as equation (3) by using the distribution ratio, D_M, of the metals

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

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

Experimental plots $\log D_M$ *versus* pH for each metal cation with SAN in chloroform are straight lines of slope equal to 2 in figure 2. The curves obtained show that the extraction of each metal increases with the concentration of SAN.

The study of the effect of pH on the liquid–liquid extraction of Co(II) and Ni(II) leads to third phase formation which was already found for Zn(II) [19] and Cd(II) [20]. Tayeb *et al.* [19] reported the formation of a third phase during the extraction of Zn(II) by acidic chelating extractants. The addition of TOPO to the solvent leads to a synergistic enhancement of the extraction, mainly due to the extracted species. A review of third phase formation in extraction of actinides by neutral organophosphorus extractants was previously established by Vasudeva Rao [21].

3.1.2. Effect of SAN concentration. The variation of $\log D_M$ *versus* $\log[HL]_{i\,org}$ to pH constants for each metal cation is represented in figure 3. The curves are straight lines with slope equal to 3 for both Cu(II) and Co(II). However, for Ni the slope is less, with a value equal to 2. This finding explains the number of molecules of HL coordinated to the metal cation in the extracted complexes. The extraction process may be described by the following equilibrium reactions:

$$Cu^{+2} + 3\overline{HL} \rightleftarrows \overline{CuL_2HL} + 2H^+$$

$$Co^{+2} + 3\overline{HL} \rightleftarrows \overline{CoL_2HL} + 2H^+$$

$$Ni^{+2} + 2\overline{HL} \rightleftarrows \overline{NiL_2} + 2H^+$$

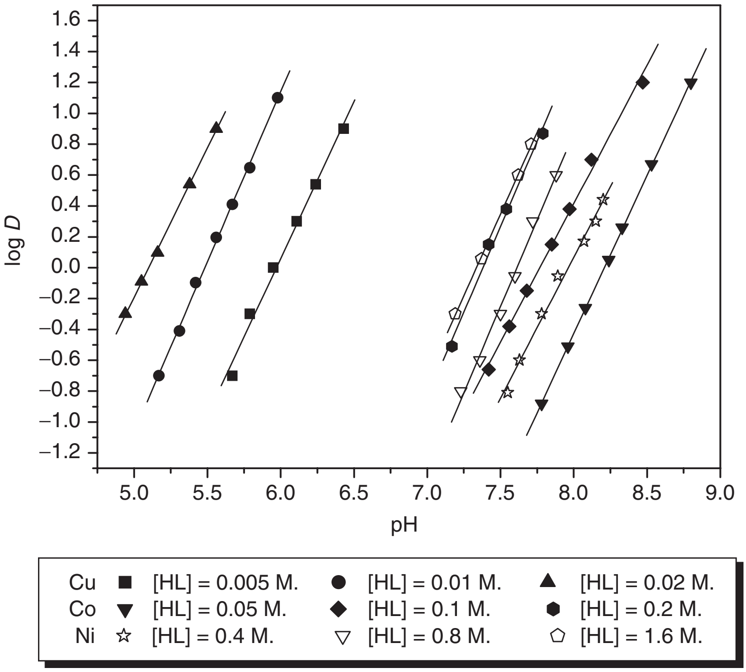

Figure 2. pH effect on Cu^{2+}, Co^{2+} and Ni^{2+} extraction with SAN in chloroform. Sulphate medium 0.33 M.

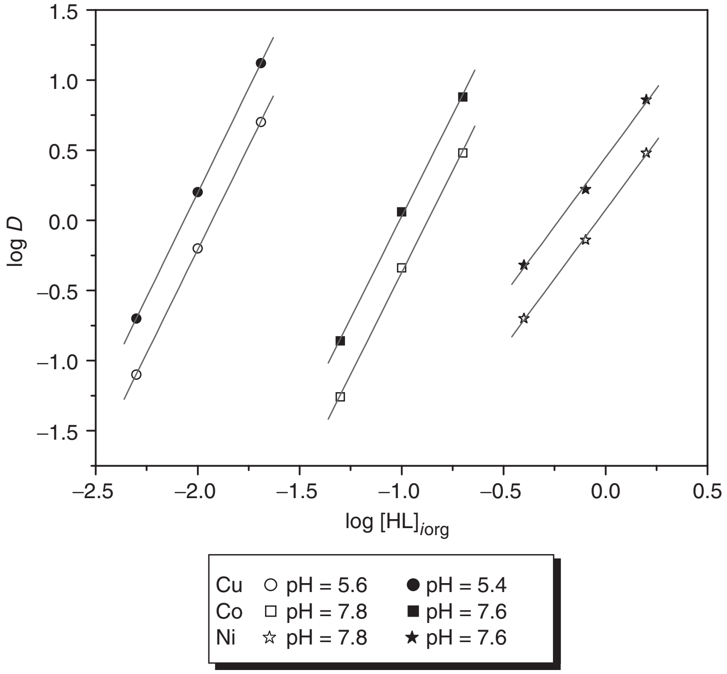

Figure 3. Concentration effect of SAN in chloroform on Cu^{2+}, Co^{2+} and Ni^{2+} extraction. Sulphate medium 0.33 M.

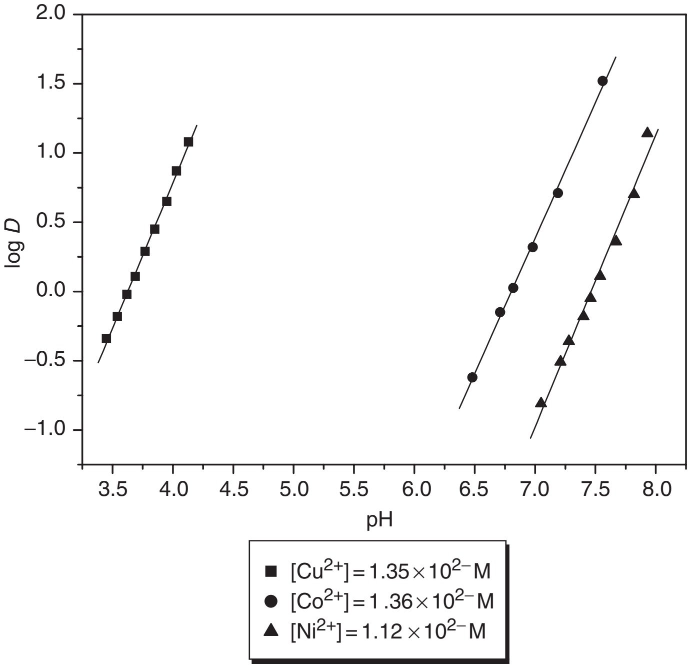

Figure 4. Extraction of Cu^{2+}, Co^{2+} and Ni^{2+} with SAN in chloroform. Sulphate medium 0.33 M.

Table 1. $\log K_{\mathrm{ex}}$ of Cu(II), Co(II) and Ni(II) in different diluents at 25°C.

Diluent	$\log K_{\mathrm{ex,Cu(II)}}$0.02	$\log K_{\mathrm{ex,Co(II)}}$0.03	$\log K_{\mathrm{ex,Ni(II)}}$0.04
Cyclohexane	−4.24	−11.36	−13.31
Toluene	−4.57	−11.85	−14.55
Chloroform	−4.77	−12.56	−15.10

Comparing the stoichiometry of the extracted species of Cu(II) found in this work with those obtained by Adams [22] and Prenesti [23], the same set of species are found for Cu(II) and Co(II) in similar experimental conditions. Moreover, by using the distribution ratio, D_{M}, of the metals, the extraction constants, K_{ex} may be defined as:

$$\log K_{\mathrm{ex,Cu(II)}} = \log D_{\mathrm{M}} - 3\log[\overline{\mathrm{HL}}] + 2\mathrm{pH} \quad \text{with} \quad [\overline{\mathrm{HL}}] = [\overline{\mathrm{HL}}]_i - 3[\mathrm{Cu}^{2+}]$$

$$\log K_{\mathrm{ex,Co(II)}} = \log D_{\mathrm{M}} - 3\log[\overline{\mathrm{HL}}] + 2\mathrm{pH} \quad \text{with} \quad [\overline{\mathrm{HL}}] = [\overline{\mathrm{HL}}]_i - 3[\mathrm{Co}^{2+}]$$

$$\log K_{\mathrm{ex,Ni(II)}} = \log D_{\mathrm{M}} - 2\log[\overline{\mathrm{HL}}] + 2\mathrm{pH} \quad \text{with} \quad [\overline{\mathrm{HL}}] = [\overline{\mathrm{HL}}]_i - 3[\mathrm{Ni}^{2+}]$$

The overlined symbols refer to the organic phase. The index (i) denotes initial concentration before contacting the phases. The extraction of copper(II), cobalt(II) and nickel(II) from sulphate solution with SAN is shown in figure 4. Comparison between the formation constants given in table 1 revealed that the stability of the ligand (SAN) varies according to the sequence

$$\mathrm{Cu}^{2+} > \mathrm{Co}^{2+} > \mathrm{Ni}^{2+}$$

It is known that both the relative size of the cations to the cavity of (SAN) and hard–soft acid–base character of the cation and the donating sites of the ligand are among the most important parameters affecting the stability of cation–(SAN) complexes.

The order of the extrabilities between the metals does not coincide with the Irving–Williams series of stability [24] because both Cu^{2+} and Co^{2+} ions seem to have the suitable size to fit well inside the cavity of the ligand used. The Co^{2+} ion forms a more stable complex than the Ni^{2+} ion does, obviously due to its least softer acid character than the Ni(II) ion [25]. The extraction ability decreases in the order: Cu(II) > Co(II) > Ni(II). This can be explained by assuming the formation of CuL_2HL for Cu(II), CoL_2HL for Co(II) and NiL_2 for Ni(II). This respective sequence is probably due to a better lipophilicity of both CuL_2HL and CoL_2HL than NiL_2.

3.1.3. Effect of diluent. It is well known that the diluent plays an important role in solvent extraction by affecting the efficiency of the extraction process. Extraction of Cu^{+2}, Co^{+2} and Ni^{+2} with SAN is achieved by using the diluents chloroform, toluene and cyclohexane which are described in figure 5. Dreisinger and Cooper studied the effect of diluent upon the extraction of nickel(II) and cobalt(II). They showed that the choice of the diluent could influence the extraction [26]. A more detailed study of diluent effect was carried out by Brunette [27–29] and Komasawa [30,31] who found polar or non-polar diluents could greatly affect the extraction of metal cations. When cyclohexane was used as the diluent, $\log K_{ex}$ values for each metal were found clearly improved. The best extraction was according to the following order: cyclohexane > toluene > choroform. The results of extraction of the three solvents

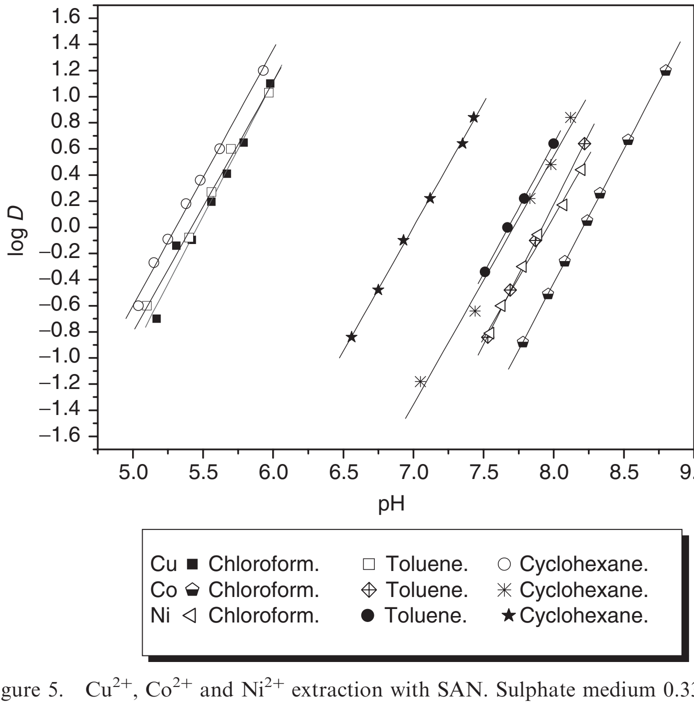

Figure 5. Cu^{2+}, Co^{2+} and Ni^{2+} extraction with SAN. Sulphate medium 0.33 M.

Table 2. Comparison of $\log K_{ex}$ of Cu(II), Co(II) and Ni(II) in different diluents at 25°C.

	Cu(II)	Co(II)	Ni(II)	Cd(II)	Zn(II)	In(III)	Ln(III)
$\Delta\log\beta$	0.2	0.71 1.12 [27]	0.55	0.05 [32]	0.01 [32]	0.61 [28]	
$\Delta\log\beta'$	0.33	0.49	1.24				
$\Delta\log\beta^*$					2.42 [19]		
$\Delta\log\beta'^*$		0.99 [27]				0.58 [28]	3.45 [33] 3.06 [33]

$\Delta\log\beta'^* = \log K_{(ex,M(II))Toluène} - \log K_{(ex,M(II))Chloroforme}$.
$\Delta\log\beta' = \log K_{(ex,M(II))Cyclohexane} - \log K_{(ex,M(II))Toluène}$.
$\Delta\log\beta' = \log K_{(ex,M(II))Dichloroethane} - \log K_{(ex,M(II))Chloroforme}$.
$\Delta\log\beta'^* = \log K_{(ex,M(II))Nitrobenzene} - \log K_{(ex,M(II))Chloroforme}$.

were calculated, the best extraction was obtained with cyclohexane, toluene and chloroform; the extraction of Co(II), Cu(II) and Ni(II) in chloroform is worse. The drive of water molecules in the organic phase is more significant in chloroform than in toluene [32] and cyclohexane. As a result, when cyclohexane was used as a diluent, the extraction was clearly improved. In order to interpret the results, we compare the variation among $\log K_{(ex,M(II))}$ and list the results in table 2. As it is shown in table 2, $\Delta\log\beta'$ is larger than $\Delta\log\beta$ for Ni(II), which is in good agreement with reference [28]. The literature values range from 0.01 to 0.61 for $\Delta\log\beta$ and 0.58 to 3.45 for $\Delta\log\beta'^*$ depending on the experimental conditions. A considerable improvement of the extraction constants, especially for nickel(II), was brought about by changing diluent from polar to non-polar nature. Cyclohexane is observed to be a good solvent for the extraction of Ni(II) ($\Delta\log\beta' = 1.24$). This improvement may be explained by the fact that the water molecules which accompany the metal complex in organic phase are possibly raised.

4. Conclusion

SAN has been found to be a good chelate extractant for Cu(II), Co(II) and Ni(II). The extraction of these metal cations by SAN in sulphate medium was studied using the following parameters:

- The equilibrium pH: The effect of the pH on extraction of Co(II) and Ni(II) leads to third phase formation by standing solid at the interface liquid–liquid.
- Concentration of SAN: The extraction of Cu(II), Co(II) and Ni(II) by SAN increases with the concentration of SAN. The stoichiometry of the extracted species and their equilibrium constants is elucidated by graphical and numerical methods and appears to be CuL_2HL, CoL_2HL, NiL_2.
- Solvent: The extraction is better according to the following order:

$$\text{cyclohexane} > \text{toluene} > \text{choroform}.$$

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