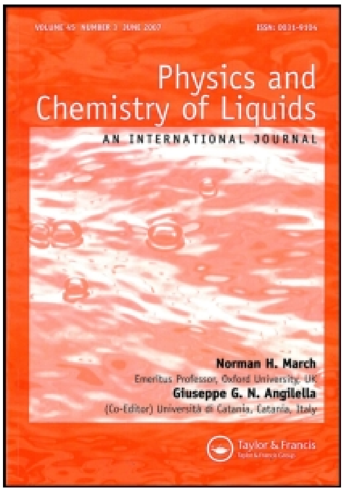

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Temperature effect on the solvent extraction of copper(II), cobalt(II) and nickel(II) with salicylideneaniline from sulphate media

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The temperature effect on the solvent extraction of copper(II), cobalt(II) and nickel(II) by Schiff base salicylideneaniline (SAN) in chloroform from sulfate aqueous medium of constant ionic strength was studied. The temperature dependence of the extraction equilibrium constants were investigated to estimate the variation of enthalpy (ΔH) and entropy (ΔS). These thermodynamic functions were, as a result, calculated and discussed in conjunction with the structure of the extracted species. It was found that the extraction of each metal increased with increase in temperature. Besides ΔH and ΔS have been discussed in connection with the nature of bonding and also the symmetry of the metal complexes. It was established through this study that the types of bonding in the complexes formed in the aqueous solution are clearly reflected by the values of ΔH and ΔS for the complex formation reaction.

Keywords: liquid–liquid extraction; transition metals; thermodynamic properties

1. Introduction

Schiff base SAN is an efficient extractant for transition divalent metal from sulfate media. In our previous work [1] Cu(II), Co(II) and Ni(II) have been extracted by means of SAN in three different diluents and investigated in detail. The stoichiometry of the extraction of these species was determined by the slope analysis method. The extraction reaction proceeded by cation exchange mechanism and the extraction species were CuL_2HL, CoL_2HL and NiL_2. by extending this investigation, the effect of temperature up on the extraction have been introduced and the mechanism of the extraction process were carried out and discussed in the light of the results obtained.

The effect of temperature on the extraction of Cu(II), Co(II) and Ni(II) has been studied by several authors. The temperature effect on the extraction of transition divalent metals such as Cu(II), Co(II) and Ni(II) reported was investigated by means of the extraction of these metals with mixture of HTTA and TBP and TOPO [2–6]. Data of the temperature influence on extraction of Cu(II), Co(II), Ni(II) with neutral organophosphorus extractants were already published [7]. Schiff base complexes were chosen in order to capitalise on the reversible nature of imine bond formation Schiff bases complex

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stability is typically higher in organic solvents such as chloroform. Schiff base ligands have been successfully used for extraction of metal ions from aqueous to organic solutions [8,9]. The thermodynamic parameters have been discussed in connection with the nature of bonding and the symmetry of the metal complexes [10]. The different types of bonding in complexes formed in aqueous solution were clearly reflected by the values of ΔH and ΔS for the complex formation reaction [11]. The present work was undertaken to study further the influence of temperature on the extraction of Cu(II), Co(II) and Ni(II) by SAN in chloroform from sulphate media.

2. Experimental

2.1. *Reagents and solutions*

SAN was synthesised in our laboratory according to the procedure given in reference [12]. Chloroform $CHCl_3$ was pre-equilibrated with an aqueous solution which did not contain any metal. The ionic strength of the aqueous medium was assumed to be unity ($I = 1$) ($[Na_2SO_4] = 0.33$ M). The initial compositions of the phases were as follows:

Aqueous phases : $[Cu^{+2}] = 1.575\,10^{-3}$ M, $[Co^{+2}] = 1.88\,10^{-3}$ M, $[Ni^{+2}] = 6.81\,10^{-3}$ M
Organic phase : $[SAN]_{i,\mathrm{org}} = 0.2$ M in chloroform.

2.2. *Extraction and analytical procedures*

Extraction is performed in thermostated vessels. Equal volumes 40 cm^3 each of aqueous and organic phases were shaken mechanically for 30 nm; a period found to be adequate for equilibrium. The pH was adjusted to the desired level by the addition of sodium hydroxide. The pH of the aqueous phases was measured by pH-meter with an accuracy of 0.02 pH unit. The ionic strength was maintained at 1 with Na_2SO_4. The temperature was measured with an accuracy of 0.2°C. After phase separation by gravity, the solutions were then allowed to settle a little while in the bath. These were carried out at room temperature ±25°C. After this, the aqueous solution was analysed photometrically using shimadzu UV-VIS 211.

3. Results and discussion

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

$$M^{2+} + (n+m)\ HL_{\mathrm{org}} \rightleftarrows ML_n(HL)_{m\mathrm{org}} + nH^+, \tag{1}$$

(M =, Cu(II), Co(II), Ni(II)); (org) denotes 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

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

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

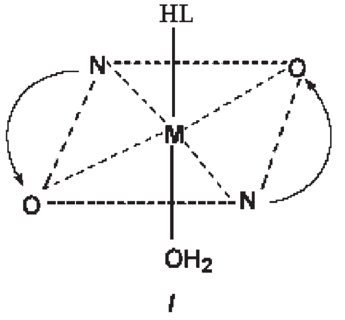
In a previous work [1], the extraction of Cu(II), Co(II) and Ni(II) with SAN (HL) in chloroform have been described by the following extraction equilibrium:

$$\mathrm{Cu}^{+2} + 3\mathrm{HL}_{i\mathrm{org}} \rightleftarrows \mathrm{CuL_2HL} + 2\mathrm{H}^{+} \tag{4}$$

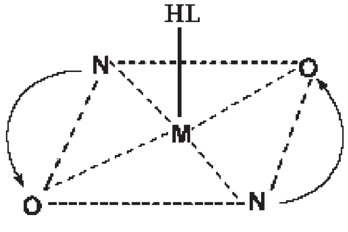
$$\mathrm{Co}^{+2} + 3\mathrm{HL}_{i\mathrm{org}} \rightleftarrows \mathrm{CoL_2HL} + 2\mathrm{H}^{+} \tag{5}$$

$$\mathrm{Ni}^{+2} + 2\mathrm{HL}_{i\mathrm{org}} \rightleftarrows \mathrm{NiL_2} + 2\mathrm{H}^{+}. \tag{6}$$

The experimental data for the extraction of Cu(II), Co(II) and Ni(II) with SAN in chloroform are given in Figures 1–3. The obtained curves show that the extraction of Cu(II), Co(II) and Ni(II) increase with the temperature. The plots of log $D = f$ (pH) are linear of slopes close to two in all cases. It should be mentioned that the obtained results reflect that, the temperature has no effect on the stoichiometry of the extracted complexes. The values of the extraction constants for each metal were favoured as the temperature was increased from 25 to 45°C. These values were calculated experimental data. The thermodynamic parameters for the organic phase can be determined from the equation from the dependence of the formation constants upon the temperatures according to the Van't Hoff relationship, with the assumption that both the enthalpy and entropy changes are constant in the ranges of the temperature applied thus, $\log K_{\mathrm{ex}} = -(\Delta H/2{,}303RT) + (\Delta S/2{,}303R)$ where: ΔH: extraction enthalpy of metal, ΔS: extraction entropy of metal. The plot of log $K_{\mathrm{ex}} = f(1/T)$ should result in straight lines with slope equal to $-(\Delta H/2{,}303RT)$ and an intercepts equal to $\Delta S/2{,}303R$. The enthalpy and entropy of complexation were determined from the temperature dependence of the formation constant as shown in Figure 4. The ΔH and ΔS values are grouped in Table 1. Thus, the sequence of ΔH values are: Ni(II) > Co(II) > Cu(II). This sequence might be attributed to the geometrical change of Cu(II) from "six-coordinate" to "four-coordinate" as a result of the Jahn Teller effect [13]. This interpretation was confirmed by the visible spectral data of Cu(II) ion in the presence of the SAN ligand where the d→d transition($\lambda = 685$ nm) indicates that the geometrical shape of the higher species ($\mathrm{CuL_2HL}$) is square pyramidal [14,15]. However, the other metal complexes, on the other hand would retain their most probable octahedral structure. The electronic spectrum of Co(II) complex displayed band at $\lambda = 900$ nm, Ni(II) complex showed absorption at $\lambda = 625$ nm. These, as result, can be suggest octahedral geometry [14]; water molecules would complete the coordination sphere. On the basis of this interpretation, the plausible structures of the complexes under investigation are **I** and **II**.



I



II

In aqueous solutions, it was assumed that the decrease in entropy was largely due to the rearrangement of water structure upon the metastasis of a small inorganic cation into

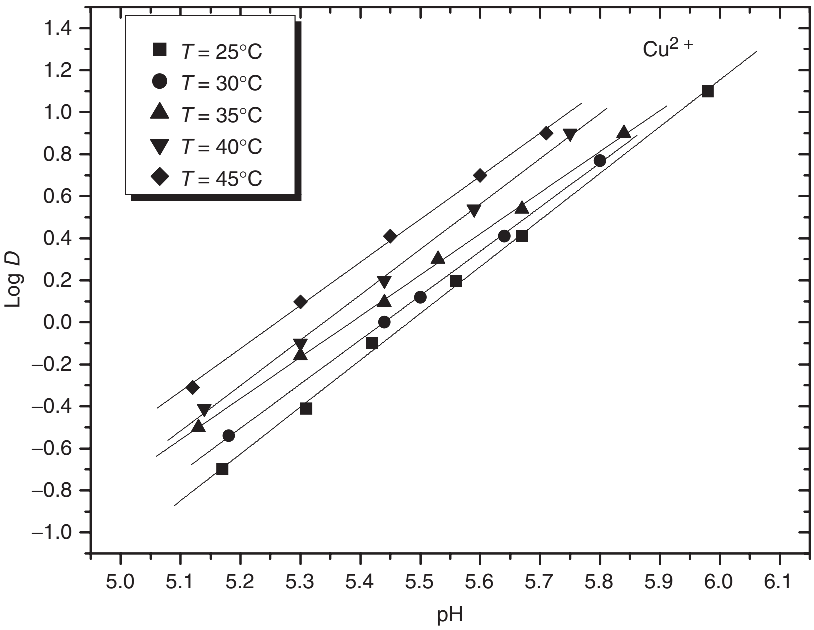


Figure 1. Effect of pH on extraction of Cu^{2+} with SAN in chloroform (sulfate medium 0.33 M).

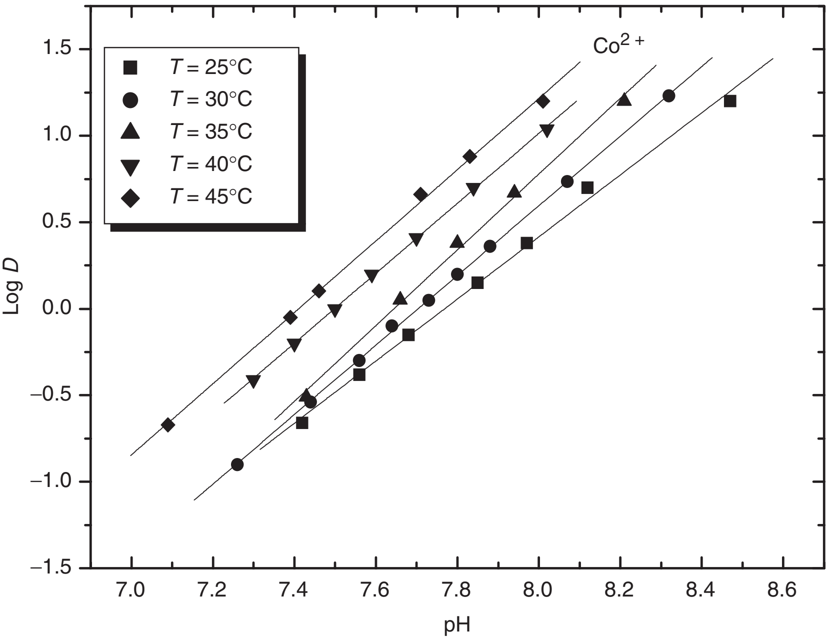


Figure 2. Effect of pH on extraction of Co^{2+} with SAN in chloroform (sulfate medium 0.33 M).

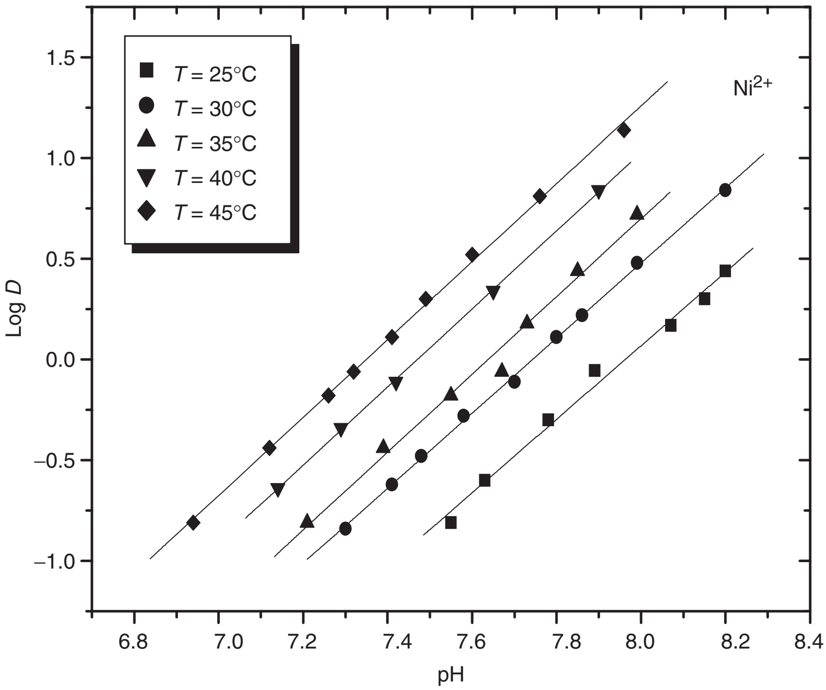


Figure 3. Effect of pH on extraction Ni^{2+} with SAN in chloroform (sulfate medium 0.33 M).

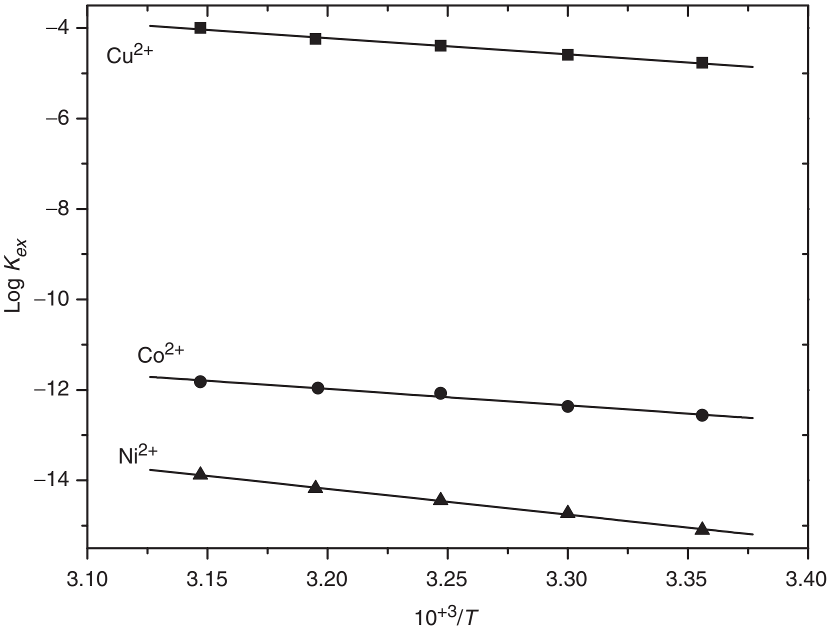


Figure 4. Temperature effect on the solvent extraction of Cu^{2+}, Co^{2+} and N^{2+} with SAN in chloroform (sulphate medium 0.33 M).

Table 1. Thermodynamic parameters for extraction of Cu(II), Co(II) and Ni(II) by SAN in chloroform at different temperatures.

Metal ion	Corr. coeff.	ΔH (J mol^{-1})	ΔS (KJ mol^{-1} K^{-1})
Cu(II)	−099648	+69.11	−140.28
Co(II)	−099042	+69.5	−7.023
Ni(II)	−099901	+109.60	−78.80

large hydrophobic organic cation [16]. This trend has been supported by Indira and Parameswaran's studies [17]. In addition, the complexes have a more ordered structure than the reactant [18]. The negative entropy finding values indicate an increase in order as the metal cation is surrounded by the bidentate SAN. Thus, it is reasonable to assume that the entropic contribution in the organic phase is ruled by the degree of order which is gained as a consequence of the highly ordered chelate structure which is formed between the metal ions and the SAN ligand. Therefore, it is not surprising to observe that Cu^{+2} ion with the best condition of complexation with SAN [1] will result the most negative ΔS in the series. It should be noted that, to the best of our knowledge, there are no published values of ΔH and ΔS for complexation of SAN available to be able to compare with the results obtained here. Thence, it seems reasonable to assume that the main reason for the negative entropy of complexation is the decrease in the conformational entropy of the Schiff's base (SAN) brought about upon complexation from a rather flexible free state to a relative structured rigid complex [19,20].

4. Conclusion

The thermodynamic values obtained for the system studied indicated the following:

(a) Enthalpy (ΔH) for the chelate equilibrium are positive and reflected the endothermic character of the complexes reactions. For this kind of interaction, the large amount of energy required to break the metal ion and ligand –water bonds is not compensated by the formation of the new metal–SAN bonds.

(b) The entropic contribution, shows that the degree of order which lost during the dehydration of the cation is not compensated by the order caused by the hydration of the proton [21,22]. Thus, it is reasonable to assume that the entropic contribution in the organic phase is ruled by the degree of order which is gained as a consequence of the highly ordered chelate structure which is formed between the metal ions and the SAN ligand.

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