Liquid–liquid extraction of copper(II) with substituted salicylideneanilines from sulfate media

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The liquid–liquid extraction of copper(II) with Schiff bases in chloroform from sulfate media is studied for pH and concentration of the extractant. Stoichiometry coefficients of the extracted species are determined by the slope analysis method. With salicylideneaniline, the copper(II) is extracted as a mixed chelate complex, CuL_2HL. In the presence of substituent, the copper is extracted as simple chelates, CuL_2. The trends in the values of extraction constants were explained in terms of the nature of the substituents.

Keywords: Liquid–liquid extraction; Copper(II); Schiff bases; Substituent effect

1. Introduction

During the past two decades, attention has been paid to metal complexes of Schiff bases containing nitrogen and other donors [1–4]. This may be attributed to their stability, biological activity [5] and potential applications in oxidation catalysis [6], and electrochemistry [7]. The use of liquid–liquid extraction technique involving Schiff-base extractants is receiving increasing attention. Schiff bases have been used for the extraction of metal ions from aqueous to organic solutions [8, 9]. Salicylideneaniline (SAN) can be used for the extraction of metal species from sulfate aqueous to organic solutions. In our previous paper [10], we reported using SAN as an excellent extractant in liquid–liquid extraction of copper(II), cobalt(II), and nickel(II) from sulfate media which depends on pH, concentration of the extractant, and the nature of diluent. The stoichiometry coefficients of the extracted species are determined by the slope analysis method. Extraction proceeds by cation exchange mechanism and the extracted species are CuL_2HL, CoL_2HL, and NiL_2. Extraction constants were evaluated for different diluents; the best extraction was with cyclohexane. Under suitable conditions of pH, extraction of cobalt(II) and nickel(II) in different diluents leads to third phase formation. We recently [11] reported the thermodynamic parameters ΔH and ΔS of the complexes in solutions of copper(II), cobalt(II), and nickel(II) with SAN from

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Table 1.   Scheme of the chemical formulas of SANs.

X	Schiff base	
H	Salicylideneaniline	SAN
4-CH$_3$	Salicylidene-4-methylaniline	*p*-CH$_3$SAN
4-OCH$_3$	Salicylidene-4-methoxylaniline	*p*-OCH$_3$SAN
4-Br	Salicylidene-4-bromoaniline	*p*-Br SAN
4-NO$_2$	Salicylidene-4-nitroaniline	*p*-NO$_2$SAN

sulfate media. The thermodynamic functions were calculated and discussed together with the structures of the extracted species. The extraction of each metal increased with increase in temperature. It is important to know how to design an optimal system for metal extraction, select the extractant to obtain maximum extraction, obtain data bases for solvent extraction systems, and find correlations between the overall equilibrium constants. Therefore, investigation about the steric effect around donors in SANs is very important. These ligands are bidentate in the extraction system, the substituents raise the hydrophobicity of the ligands, and the extractability can be controlled by introduction of substituents near the imine-N donor. In this research, we investigate the effect of substituents in the Schiff base on the extraction of copper(II). It was found that a Schiff base analog, SAN, can be used for the extraction of copper(II). SANs are bidentate ligands and chemical formulas are listed in table 1. In this research, we investigate the effects of several electron donating and withdrawing substituents on the extractability of a number of Schiff bases, studying the effect of methyl, bromo, nitro, and methoxy groups on the extractability of copper(II). This study describes the results from the extraction of copper(II) with SANs in sulfate aqueous solutions. The aim is to determine the stoichiometry coefficients of the extracted complexes and their extraction constants.

2. Experimental

2.1. *Reagents*

SANs were synthesized by literature procedure [12]. Refluxing equimolar quantities of salicylicaldehyde and corresponding aniline dissolved in minimum pure ethanol is done inside a balloon tricol provided with a magnetic stirrer, a cooling agent, and a graduated thermometer. The unit is maintained with backward flow and under agitation for approximately 2 h. The mixture is cooled at room temperature and then concentrated by the elimination of solvent using a rotary evaporator. The solid product obtained is filtered and then recrystallized in minimum pure ethanol.

Chloroform was pre-equilibrated with an aqueous solution which did not contain any copper. The ionic strength of the aqueous medium was assumed to be unity with a concentration of Na_2SO_4 equal to $0.33\,mol\,L^{-1}$. The initial concentration of metal in the aqueous phase in all experiments was $[Cu^{2+}] = 1.575 \times 10^{-3}\,mol\,L^{-1}$.

2.2. *Extraction and analytical procedures*

Distribution measurements were performed in thermostated vessels at $25.0 \pm 0.2°C$; $40\,cm^3$ each of aqueous and organic phases were shaken with a magnetic stirrer for 30 min, a period adequate to reach equilibrium. After 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. *Liquid–liquid extraction of copper(II) with SAN in chloroform*

3.1.1. Effect of equilibrium pH. The overall reaction in the extraction of copper(II) with SAN (HL) from sulfate aqueous medium may be expressed as:

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

(M = Cu(II); (org) denotes species in organic phase)

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

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

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

Plots of $\log D_{Cu}$ *versus* pH for various concentrations of SAN are linear with a slope equal to 2, as shown in figure 1. The curves obtained show that the extraction of copper(II) increases with the concentration of SAN.

3.1.2. Effect of SAN concentration. Likewise, in all extraction systems, plots of $\log D_{Cu}$ *versus* $\log [\overline{HL}]_i$ at constant pH are also linear with a slope equal to 3.04 ± 0.02, as shown in figure 2. Therefore, the extraction of Cu^{2+} with SAN in chloroform can be established as the following extraction equilibrium:
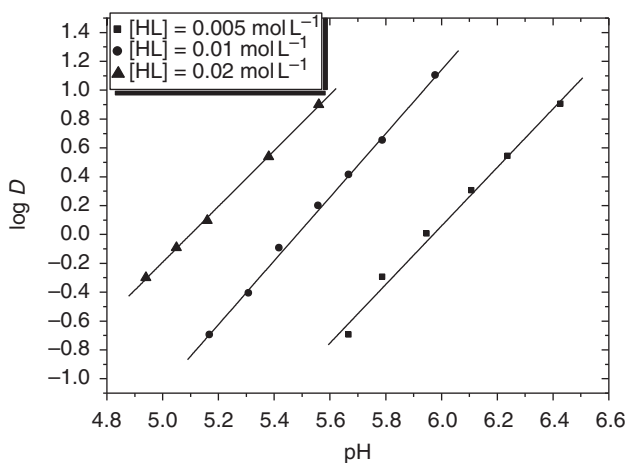
$$Cu^{2+} + 3[\overline{HL}]_i \rightleftharpoons \overline{CuL_2HL} + 2H^+$$
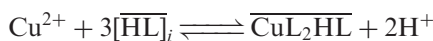
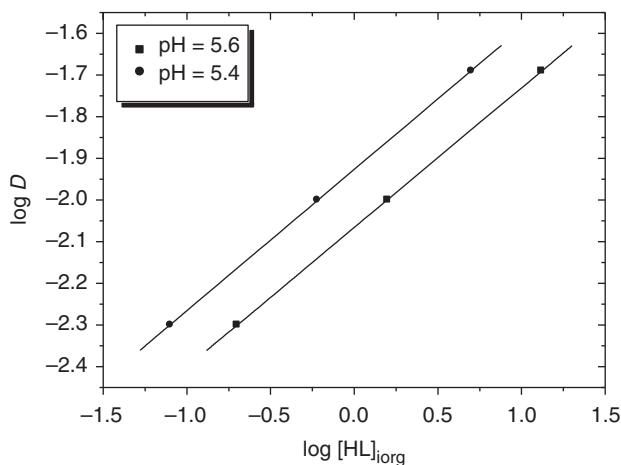Figure 1.   Extraction of Cu^{2+} with SAN in chloroform. Sulfate medium $0.33 \, mol \, L^{-1}$.

Figure 2.   Plots of log $D_{Cu^{2+}}$ as a function of the logarithmic initial concentration of SAN in chloroform. Sulfate medium $0.33 \, mol \, L^{-1}$.

This means that only $\overline{CuL_2HL}$ is extracted into chloroform. Taking into account the lowering of the free extraction with respect to the initial conditions due to the complex formation gives:

$$[\overline{HL}] = [\overline{HL}]_i - 3\overline{[Cu^{2+}]}$$

The overlined symbols refer to the organic phase. The index (*i*) denotes initial concentration before contacting the phases. The logarithmic values of K_{ex} of copper(II) can, therefore, be calculated for each experimental point from equation (4).

$$\log K_{ex} = \log D_{Cu} - 2pH - 3\log [\overline{HL}]_i$$
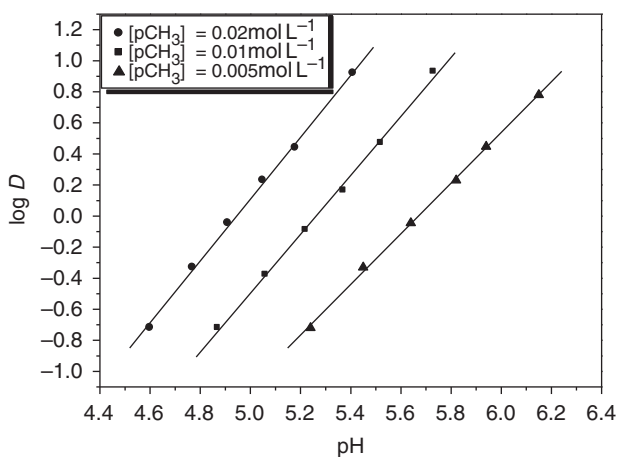$$\log K_{ex} = -4.77$$

(4)

Figure 3.　Extraction of Cu^{2+} with pCH_3 in chloroform. Sulfate medium $0.33\,mol\,L^{-1}$.
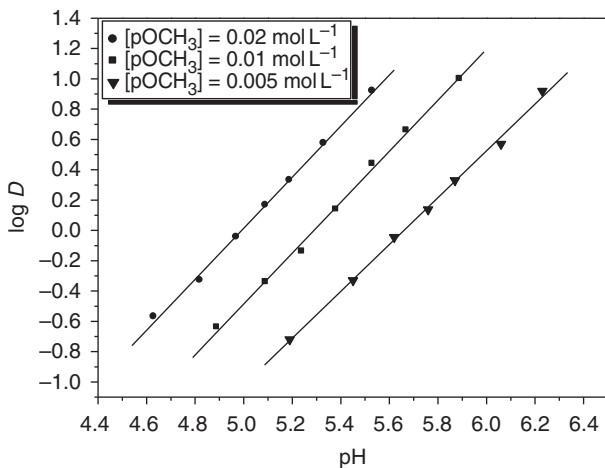

Figure 4.　Extraction of Cu^{2+} with $pOCH_3$ in chloroform. Sulfate medium $0.33\,mol\,L^{-1}$.

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

3.2.1. Effect of equilibrium pH.　For extractions with pCH_3, $pOCH_3$, pBr, and pNO_2, in chloroform–sulfate medium, $\log D$, as a function of pH, leads to straight lines (figures 3–6) of the same slope (2.00 ± 0.02) as in the case of unsubstituted SAN, suggesting exchange of two protons between the metal cation and the extractant. The various curves in figure 7 allow us, as a result, to evaluate the effects of the substituents and to compare them. SAN is always more efficient in these systems. The difference of extraction allows accurate determination of extraction constants of copper(II).

3.2.2. Effect of substituted SAN concentration.　Plots of $\log D_{Cu}$ *versus* $\log[\overline{HL}]_i$ at constant pH are also linear with a slope equal to 2.01 ± 0.05, as shown in figures 8–11. This finding explains the number of molecules of HL coordinated to copper in the
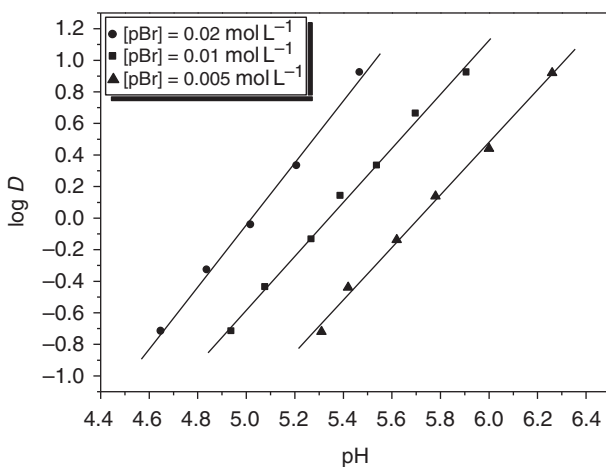
Figure 5. Extraction of Cu^{2+} with pBr in chloroform. Sulfate medium $0.33\,mol\,L^{-1}$.
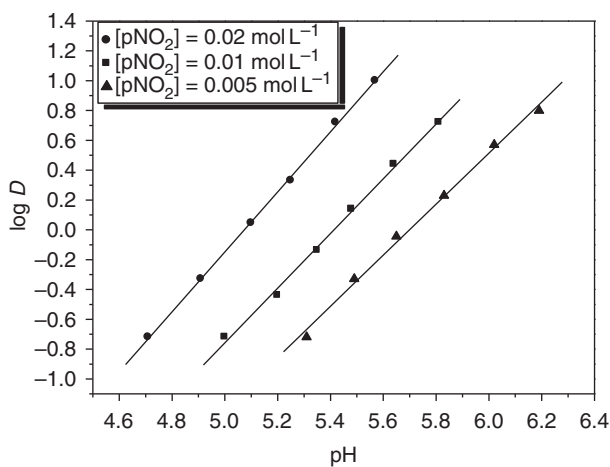

Figure 6. Extraction of Cu^{2+} with pNO_2 in chloroform. Sulfate medium $0.33\,mol\,L^{-1}$.

extracted complex. Therefore, the extraction of Cu^{2+} with SAN in chloroform can be established as the following extraction equilibrium:

$$Cu^{2+} + 2[\overline{HL}]_i \rightleftharpoons \overline{CuL_2} + 2H^+$$
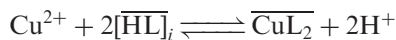
Thus, only $\overline{CuL_2}$ is extracted into chloroform. Taking into account the lowering of the free extraction with respect to the initial conditions due to the complex formation, we have

$$[\overline{HL}] = [\overline{HL}]_i - 2\overline{[Cu^{2+}]}$$

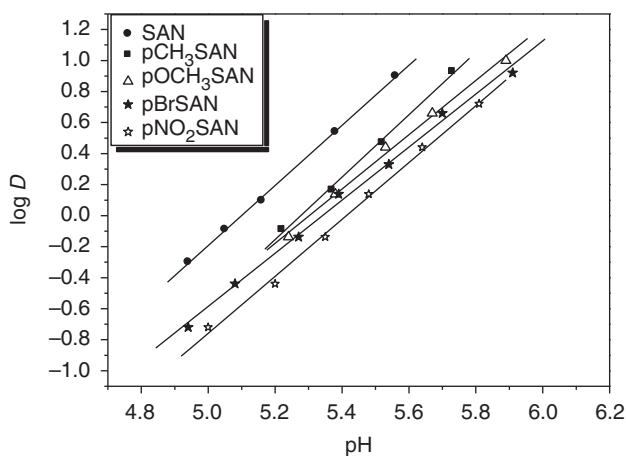Figure 7. Extraction of Cu^{2+} with salicylideneanilines $0.001\,mol\,L^{-1}$ in chloroform. Sulfate medium $0.33\,mol\,L^{-1}$.

Figure 8. Plots of log $D_{Cu^{2+}}$ as a function of the logarithmic initial concentration of pCH$_3$ in chloroform. Sulfate medium $0.33\,mol\,L^{-1}$.

The logarithmic values of K_{ex} of copper(II) can, therefore, be calculated for each experimental point from equation (5). All calculated extraction constants are summarized in table 1.

$$\log K_{ex} = \log\ D_{Cu} - 2pH - 2\log [\overline{HL}]_i \qquad (5)$$

Comparison of the extraction constants in table 2 revealed that the extractability of copper(II) with SANs varies in the following sequence:
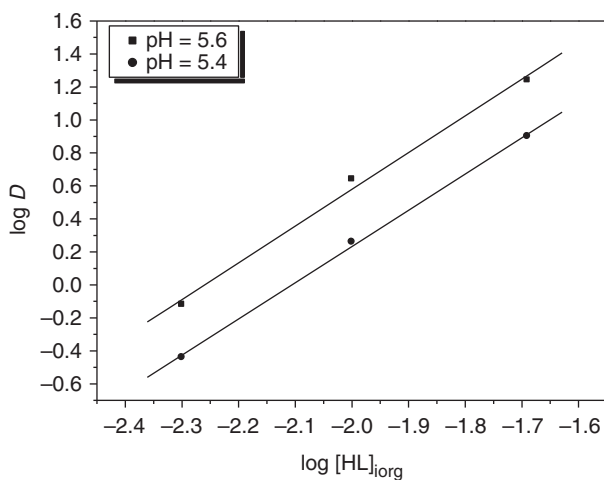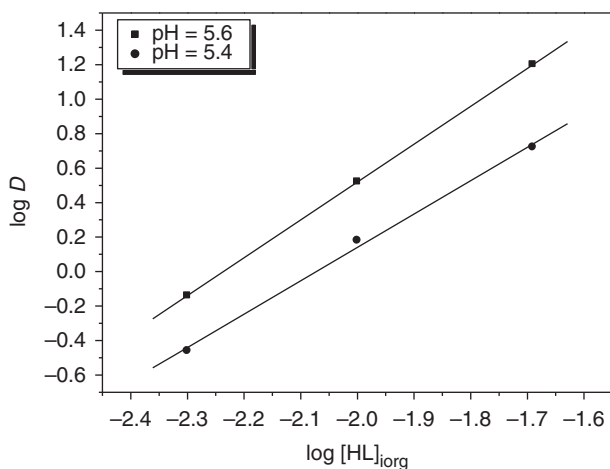
$$SAN > pCH_3 > pOCH_3 > pBr > pNO_2.$$

Figure 9. Plots of log $D_{Cu^{2+}}$ as a function of the logarithmic initial concentration of pOCH$_3$ in chloroform. Sulfate medium 0.33 mol L^{-1}.
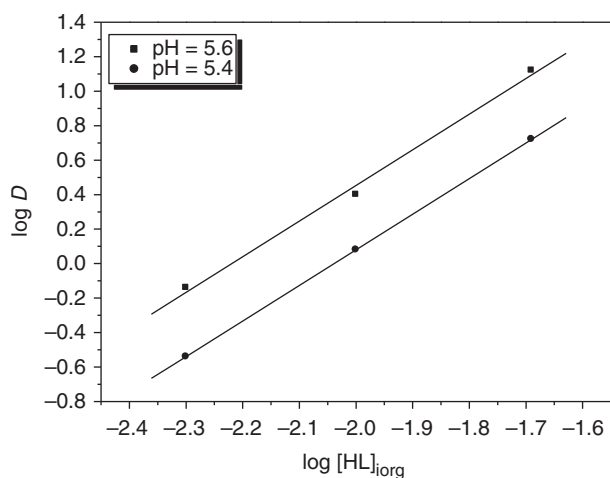
Figure 10. Plots of log $D_{Cu^{2+}}$ as a function of the logarithmic initial concentration of pBr in chloroform. Sulfate medium 0.33 mol L^{-1}.

The behavior of these Schiff base extractants is described by their acidity constant in aqueous phase pK_a, and for a given diluent, by their partition constant log K_d. The obtained values of pK_a and log K_d are listed in table 3 [13]. SAN is always a more efficient extractant than pCH$_3$, in spite of the electron-withdrawing inductive effect of methyl. The distribution constants of HL are significantly (if not much) different: $(\Delta \log K_d(HL)) = 0.11$. This difference is enough to explain the noticeably lower extraction of pCH$_3$. The lower extraction rate is obviously caused by the high hydrophobicity of pCH$_3$ which limits the formation of the extractable complex.

Figure 11.   Plots of log $D_{Cu^{2+}}$ as a function of the logarithmic initial concentration of pNO$_2$ in chloroform. Sulfate medium 0.33 mol L^{-1}.
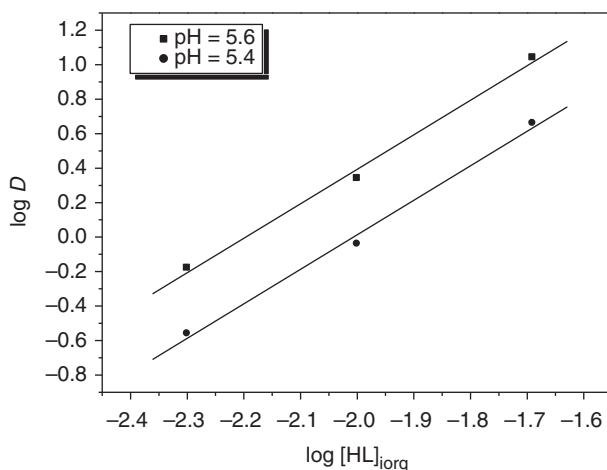
Table 2.   Values of the extraction constants of copper(II) obtained from five extractants.

Extractant	SAN	*p*-CH$_3$SAN	*p*-OCH$_3$SAN	*p*-BrSAN	*p*-NO$_2$SAN
log K_{ex}	−4.77	6.60	6.66	6.70	6.76

Table 3.   Values of the distribution constants log K_d for SANs obtained in chloroform–water, aqueous phase: $[H_2SO_4] = 10^{-2}$ mol L^{-1}; $[Na_2SO_4] = 0.33$ mol L^{-1}; organic phase: $[HL]_{i,org} = 2 \times 10^{-2}$ mol L^{-1} and protonation pK_a constants of substituted SANs at $25.0 \pm 0.1^{\circ}$C in ethanol–water mixtures ($I = 1$, [NaCl] = 1 mol L^{-1}) at 25°C [13].

X	pK_a	log K_d
H	9.30	3.24
4-CH$_3$	9.40	3.35
4-OCH$_3$	9.60	3.170
4-Br	9.80	2.87
4-NO$_2$	10.40	2.38

The high distribution constant of SAN might be attributed to its extra-solubilization in chloroform, increasing both the expected stability and lipophilicity of CuL$_2$HL, and hence the corresponding extraction constant, and explain the high extraction constant of copper(II) by SAN. Methoxy derivative of SAN is more basic. This can be used as an indication of the extent of the contributions of the methoxy group to the basicity of azomethine nitrogen. This is as expected in light of the resonance and the electronic effect of the methoxy group. The obtained log K_{ex} value of pOCH$_3$ is lower than those in SAN and pCH$_3$, obviously caused by its high hydrophobicity, and might be attributed to the decrease of organic concentration of free pOCH$_3$ by complexation

with copper(II) and by dissolving and dissociating in the aqueous phase. The reason that the pBr is the least effective for extraction might be the strong negative inductive effect of the halogen. It is generally believed that the resonance effect is greater than the inductive effect. However, the resonance effect of the halogen is generally very weak. It seems reasonable to assume that the main reason for the low extraction rate of the bromine derivative is the very strong electron-withdrawing character of bromine influencing the electron density in azomethine nitrogen. This would decrease both the expected stability and lipophilicity of the extracted complexes and explain the low value of $\log K_{ex}$. The *para*-nitro group strongly attracts the negative charge of the ring and depletes it by both inductive and resonance effects. Therefore, it is not surprising that the nitro derivative has the lowest $\log K_{ex}$ in the series.

4. Conclusion

Copper(II) is extracted with SAN from sulfate media as mixed chelate complex, CuL_2HL. In the presence of substituents, copper(II) is extracted as simple chelates of the type CuL_2. After determining the extraction constants, the extraction efficiencies follow the order $SAN > pCH_3 > pOCH_3 > pBr > pNO_2$, expected in the light of their acidity constant, and steric, resonance, and inductive effects of substituents on the phenyl ring of the amine component. The factor that governs these differences is the distribution constant of the ligands. The stoichiometry is close to that obtained by Barkat [14]. However, it is evident that the values of $\log K_{ex}$ change with the composition of organic diluents. The present findings are somewhat different from those obtained previously [15], in which the system is limited by many of the problems associated with D2EHPA solvent extraction including dimerization, phase separation, solvent loss, and emulsion formation.

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