DISTRIBUTION OF Co(II) IONS FROM AQUEOUS MEDIA INTO CHCl₃ SOLUTION OF N,N'-ETHYLENEBIS(4-PROPIONYL-2,4-DIHYDRO-5-METHYL-2-PHENYL-3H-PYRAZOL-3-ONE IMINE) (H₂PrEtP)

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Liquid-liquid extraction of cobalt (II) ions have been carried out using 0.05 M solution of N,N'-ethylenebis (4-propionyl-2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-oneimine) (H₂PrEtP) Schiff base in chloroform. Various parameters for the extraction such as effect of pH, concentrations of the extractant, cobalt(II) ion , phase ratio and synergistic effect of 4-propionyl-2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-one (HPrP) have been investigated and optimized. Extraction with single ligand was observed to have a $pH_{1/2}$ of 7.05 with percentage extraction of 53.24 % corresponding to log$D$ value of 0.0563, and optimum pH of 9.25 with percentage extraction of 98.43 %, log$D$ value of 1.7971. The synergistic effect of HPrP on the extraction significantly lowered the $pH_{1/2}$ from pH 7.05 (near neutral) to pH 6.25 (slightly acidic) with percentage extraction of 52.60 % corresponding to log$D$ value of 0.0451. Optimum extraction of 99.30 was observed at pH 8.26 when the mixed ligands, H₂PrEtP and HPrP were used. The extraction of cobalt (II) ions increased rapidly as the concentrations of the ligands H₂PrEtP increased from 2.5×10^{-3} M to 4.0×10^{-2} M and that of HPrP from 2.5×10^{-3} M to to 2.5×10^{-2}. Variation of the metal concentration did not have much effect on the extractions, hence the percentage extraction was relatively high over all the metal concentrations studied.

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Introduction

The extraction of metal ions from aqueous media into chloroform solution of 1-phenyl-3-methyl-4-acylpyrazolone and its derivatives have been extensively reported.[1,2,3,4] Pyrazolones are prominent analytical reagents and potent drugs or pharmaceutical agents.[5,6,7] Presently the bis derivatives of these 4-acylpyrazolones, known as Schiff bases, are being used for the complexation of metal ions from aqueous media. Earlier studies on isolation and characterization of metal complexes of Schiff bases have shown that they form stable metal complexes with Cu(II) and Ni(II) and unstable complexes with Mo(VI), Co(II), Cd(II) and many other transition metals.[1,8] The new Schiff bases such as N,N'-ethylenebis(1-phenyl-3-methyl-4-acylpyrazoloneimine) and its derivatives, N,N'-ethylenebis(4-butanoyl-2,4-dihydro-5-methyl-3H-py-razol-3-oneimine) (H₂BuEtP), N,N'-ethylenebis(1-phenyl-3-methyl-4-acylpyrazoloneimine)-1,2-propane(H₂ADPP) and N,N'-ethylenebis(1-phenyl-3-methyl-4-propionylpyrazolo-neimine) (H₂PrEtP) have been successfully synthesized and characterized using ultraviolet, infrared, ¹H and ¹³C NMR spectroscopy. [9,11,12,13] The synthesis provides an opportunity for a N=C-C-OH bonding moiety and extends the scope of coordination to involve quadridentate ligands from initial bidentate 4-acylpyrazolone.[8,10,11,12,13]

In continuation of our work on the synthesis and characterization of 1-phenyl-3-methyl-4-acylpyrazolone-5 derivatives and their application in the extraction of transition metal ion such as Ni(II), [8] we report the use of the Schiff base N,N'-ethylenbis(4-propionyl-2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-oneimine) as a potential extractant for cobalt(II) ions.

In studying the solvent extraction of cobalt(II) ions from aqueous media using N,N'-ethylenbis(4-propionyl-2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-one   imine) (H₂PrEtP) as an organic extractant the synergistic effect of 4-propionyl-2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-one (HPrP), effect of pH of buffered media, variation in phase ratio and concentrations of both ligands and cobalt(II) ions were studied and optimized.

Materials and Methods

All reagents were of analytical grade. H₂PrEtP (Schiff base) was synthesized by the method reported elsewhere.[9,11] The ligand's purity after recrystallization from aqueous ethanol was established by elemental analysis for C, H and N; analysis of IR and NMR spectral data at Institute for Inorganic Chemistry Technology, University of Dresden Germany.[9,11]

All other reagents were used as purchased from Aldrich and BDH.

Doubly distilled deionised water was used in all dilutions. Stock solution of 0.05 M H₂PrEtP was prepared by dissolving the required amount of the ligand in chloroform. 0.05 M solution of HPrP was similarly prepared in chloroform. Stock solution of 1.697×10^{-2} M of Co(II) was also prepared similarly by dissolving cobalt(II) chloride hexahydrate in 0.1 ml of 10 M HNO₃ and making up to mark in a 50 ml volumetric flask with deionized water. Buffer solutions of pH range 1 to 10 were prepared with; 0.1 M HCl/0.1 M NaCl (pH 1.0 to 2.9), 0.1 M CH₃COOH/0.1 M NaCl (pH 3.0 to 3.5), 0.1 M CH₃COOH/0.1 M CH₃COONa (pH 3.6 to 5.6), 0.1 M KH₂PO₄/0.1 M NaOH (pH 5.7 to 10.0). The pH of the buffered solutions were measured using a digital labtech pH meter.

Extraction procedure

A buffered solution (2 ml) containing 8.48×10^{-4} M of Co(II) ions at the required pH was prepared in a 10 ml extraction bottle. Equal volume (2 ml) of 0.05 M solution of H₂PrEtP in chloroform was added. For the mixed ligand extractions a mixture of 0.05 M H₂PrEtP and 0.05 M HPrP solution in chloroform was mixed in the ratio of 9:1 by volume. The mixture was mechanically agitated for 30 minutes at room temperature, 30 °C, to enable the attainment of equilibrium. The phase (aqueous and organic) were allowed to settle and separated with the aid of a micropipette. Concentration of Co(II) ions in the aqueous phase was determined with a Buck Scientific Atomic Absorption Spectrophotometer (AAS) at 240.7 nm. The concentration of Co(II) ion extracted into the organic phase was determined by the difference between the concentration of Co(II) ion in the aqueous phase before and after the extraction. The distribution ratio D can be expressed as c_{org}/c_{aq} where c_{org} and c_{aq} are the concentrations of cobalt(II) in the chloroform and the aqueous phase, respectively.

Results and Discussion

Effect of buffer solutions.

Distribution of Co(II) from aqueous phase into chloroform phase having the Schiff base H₂PrEtP can be represented by the Eqn. (1)

$$Co^{2+}_{(aq)} + H_2PrEtP_{(org)} \leftrightarrow Co(PrEtP)_{(org)} + 2H^+_{(org)} \quad (1)$$
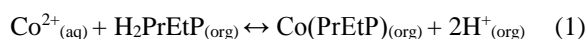
The Eqn. (1) is based on the assumption that the Co(II) from aqueous phase is extracted into chloroform by the Schiff base by forming a complex with the Co(II) ion in the 1:1 mole ratio. Thus the extraction constant K_{ext} can be expressed by the Eqn. (2).

$$K_{ext} = \frac{\left[Co(PrEtP)_{(org)}\right]\left[H^+\right]^2}{\left[Co^{2+}_{(aq)}\right]\left[H_2PrEtP_{(org)}\right]} \quad (2)$$
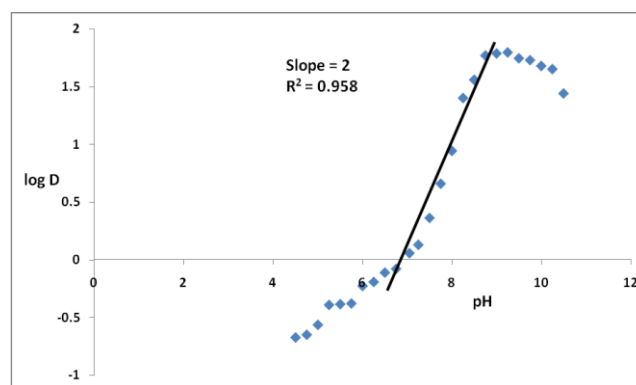

Figure 1. Graph of log D against pH for the extraction of 8.48×10^{-4} M Co(II) ions from buffered aqueous solution into chloroform solution of 0.05 M H₂PrEtP.

The plot in Fig. 1 shows the effect of pH of aqueous solution on the distribution of Co(II) into chloroform solution of H₂PrEtP and a slope of two was obtained from the graph indicated that 2 mole of hydrogen ions were displaced. This confirms that there were ligand–metal interaction through the oxygen atoms of the hydroxyl functional groups of ligand according to the Eqn. 1.

The distribution ratio of the metal ions between the two liquid phases becomes

$$D = \frac{\left[Co(PrEtP)_{(org)}\right]}{\left[Co^{2+}_{(aq)}\right]} \quad (3)$$

and substituting D into equation 2 after arrangement gives

$$\log D = \log K_{ext} + \log\left[H2PrEtP\right] + 2pH \quad (4)$$

The above mentioned result shows that the extraction of cobalt(II) ions into chloroform solution of H₂PrEtP increased with increase in pH of aqueous solution and reached a peak at pH 9.25 where an extraction of 98.43% was achieved. Thereafter, further increase in pH resulted into a decrease in percentage extraction of the metal. The partition coefficient, log$D$ was determined statistically from the plot and found to be 1.78±0.02. The pH₁/₂ was found to be 7.05. Statistical analysis of the data for all the extraction processes are recorded in Table 1, where pH*opt* and %E_{opt} means optimum pH and percentage extraction at optimum pH, respectively.

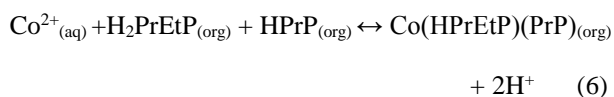**Effect of addition of HPrP (synergist) on the distribution of Co(II).**

On addition of HPrP, quantitative extraction of 99.30 % was obtained at pH 8.26. The pH₁/₂ was significantly lowered from pH 7.05 (near neutral) to a slightly acidic pH of 6.25.

Table 1. Analysis of extraction data for the effect of pH of aqueous phase on the distribution of 8.48×10^{-4}M of Co(II) into 0.05M chloroform solution of H₂PrEtP.

Organic phase	pH½	% E at pH½	pH$_{opt}$	% E at optimal pH	Log D	LogK_{ex}	Species extracted
0.05 M H₂PrEtP	7.05	53.24 %	9.25	98.43 %	1.78±0.02	-14.12±0.4	Co(PrEtP)
9:1, 0.05 M H₂PrEtP and 0.05 M HPrP	6.25	52.60	8.26	99.30	2.06±0.10	-11.8±0.33	Co(HPrEtP)(PrP)
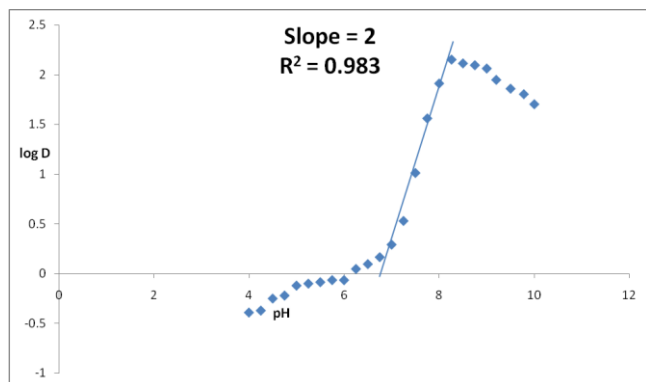
Figure 2. Graph of LogD against pH for the extraction of 8.48×10^{-4} M Co(II) ions from buffered aqueous solution into chloroform solution of 0.05 M 9:1 H₂PrEtP and HPrP

Figure 3. Plot of LogD against Log [Co(II)] for the extraction of Co(II) from buffer solution into chloroform solution of 0.05 M H₂PrEtP.

The partition coefficient was found to be 2.06 ± 0.10 and was determined statistically from the plot shown in Fig. 2. Plot of Log*D* against pH in the mixed ligands system in Fig. 2 gave a slope of 2 indicating that 2 moles of hydrogen ions were displaced during the extraction process thus the possible reaction equation for the extraction may be written as:
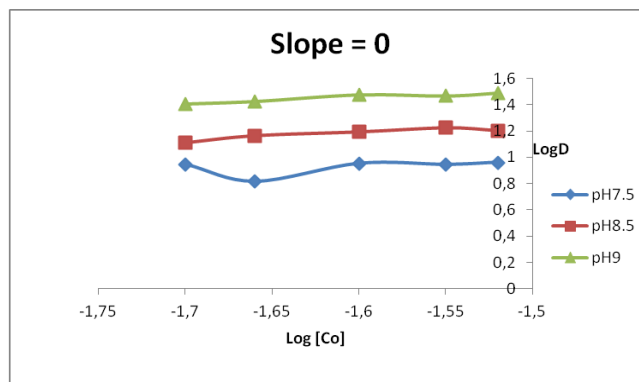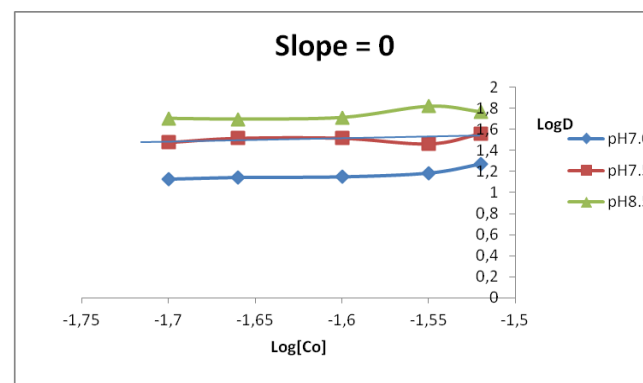
$$Co^{2+}_{(aq)} + H_2PrEtP_{(org)} + HPrP_{(org)} \leftrightarrow Co(HPrEtP)(PrP)_{(org)} + 2H^+ \quad (6)$$

Hence,

$$K_{ext} = \frac{\left[Co(HPrEtP)(PrP)_{(org)}\right]\left[H^+\right]^2}{\left[Co^{2+}_{(aq)}\right]\left[H_2PrEtP_{(org)}\right]\left[HPrP_{(org)}\right]} \quad (7)$$

Statistical analysis of the data for all the extraction processes is recorded in Table 1.

Effects of metal ions (Co²⁺) concentrations.

Variation of the metal ion concentration did not have much effect on the distribution pattern of the cobalt into chloroform solution of H₂PrEtP. Very high percentage extractions were achieved at all concentrations of the metal ions, studied both in the presence and absence of (synergist) HPrP, as shown in Fig. 3 and Fig. 4.

Figure 4. Plot of LogD against Log [Co(II)] for the extraction of Co(II) from buffer solution into chloroform solution of 0.05 M H₂PrEtP and 0.05 M HPrP in 9:1 ratio.

Extraction plots for the variation of metal concentrations gave a zero slope indicating that the extraction is independent of the concentrations of the metal ions. Data obtained from the extraction processes shows that Co²⁺ distributes better into chloroform solution of H₂PrEtP in the presence of HPrP as synergist at pH 7.0, 7.5 and 8.5. In absence of the synergist, the maximum extraction of Co²⁺ ions occurred at 3.0×10^{-2} M Co(II) concentration at pH 9.0 where an extraction of 96.85 % was obtained. The least percentage extraction was observed at metal concentration of 2.2×10^{-2} M, pH 7.5 which gave a % *E* of 86.85 %. In the presence of HPrP as synergist the maximum extraction was achieved at 2.8×10^{-2} M metal ion concentration and pH 8.5 corresponding to 98.52 % extraction.

Effect of ligand (H$_2$PrEtP) and synergist (HPrP) concentrations.

All extraction processes studied showed that the extraction of Co^{2+} into chloroform solution of H$_2$PrEtP and HPrP increases as the ligands concentrations increased. The extractions follow similar trends on variation of the concentrations of the ligand either in the presence or absence of synergist as shown in Figs. 5, 6 and 7.
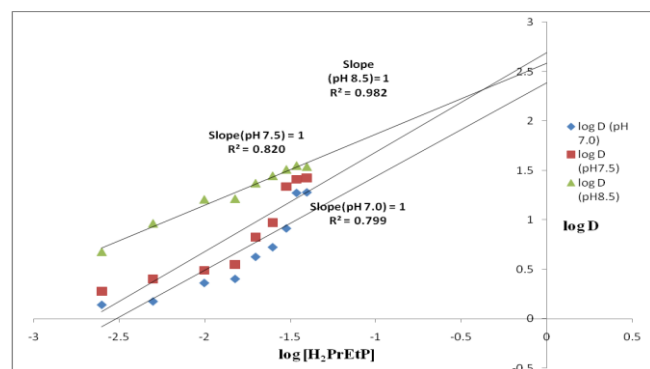

Figure 5. Plot of logD against log[H$_2$PrEtP] for the extraction of 8.48×10^{-4} M of Co(II) from aqueous solutions into chloroform solution of H$_2$PrEtP with HPrP kept constant.
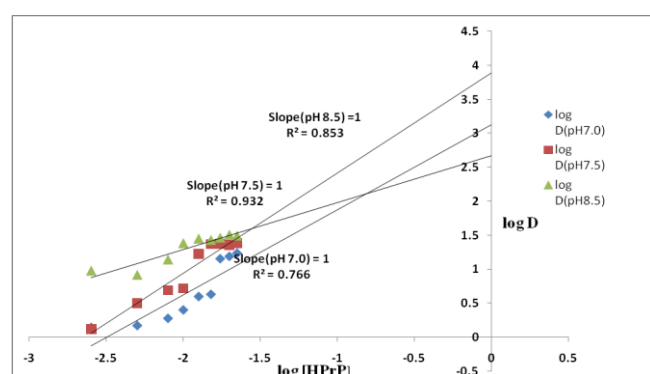

Figure 6. Plot of logD against log[HPrP] for the extraction of 8.48×10^{-4} M of Co(II) from aqueous solutions into chloroform solution of H$_2$PrEtP with H$_2$PrEtP kept constant.
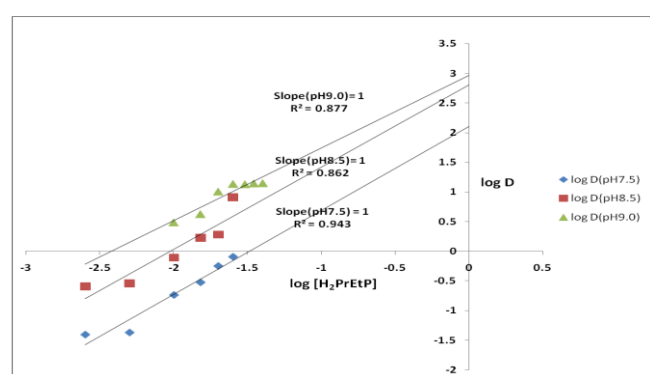

Figure 7. Plot of logD against log [H$_2$PrEtP] for the extraction of 8.48×10^{-4} M of Co(II) from aqueous solutions into chloroform solution of H$_2$PrEtP in the absence of synergist at constant pH of 7.5, 8.5 and 9.0.

Based on the results presented in Figures 5, 6 and 7, the conclusion is that the extraction of Co(II) ions is dependent on both pH of the aqueous medium and the concentration of the ligand. The studied ligand gives a better extraction of cobalt in a moderately alkaline pH.

Conclusion

On studying the distribution of Co(II) in buffered aqueous medium with a chloroform solution of H$_2$PrEtP alone a pH$_{1/2}$ of 7.05 was observed. The synergistic effect HPrP shifted the pH$_{1/2}$ from 7.05 (near neutral) to 6.25 (slightly acidic). The partition coefficients were; H$_2$PrEtP alone D_1 1.78±0.02 and H$_2$PrEtP/HPrP mixture D_2 2.06±0.10, indicating that there is a slight difference in the distribution of Co(II) ions into chloroform solution of H$_2$PrEtP as Co(PrEtP)$_{(org)}$ and into mixture of H$_2$PrEtP/HPrP as Co(HPrEtP)(PrP)$_{(org)}$. The extraction constant $K_{ext}Co_1$ for H$_2$PrEtP is -14.12±0.40 and is less than $K_{ext}Co_2$ -11.8±0.33 for H$_2$PrEtP/HPrP. Hence Co^{2+} distributes better into the mixed ligand system from the buffered media. From all the observation, we concluded that the extraction of Co(II) ions in buffered media with H$_2$PrEtP or its mixture with HPrP is more efficient in slightly alkaline medium.

Acknowledgement

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