Copper Extraction from Aqueous Solution by Pentaerythrityl Tetrabenzylamine

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The extraction of copper(II) from the aqueous phase with pentaerythrityl tetrabenzylamine (PETBA), which was synthesized from pentaerythrityl tetrabromide and benzyl amine, was studied. The influences of ionic strength, extraction time, pH and temperature were evaluated. The extraction results showed that the ionic strength had no effect on extraction efficiency and that the extraction equilibrium was established in a few minutes. The extraction percentage was independent of pH up to pH 7.6 and then decreased gradually to zero at about pH 11.5. The stoichiometry of the compound formed was estimated to be $Cu_2L(NO_3)_4$, where L is PETBA. It was concluded that PETBA can effectively be used in solvent extraction of copper(II) from the aqueous phase to the organic phase.

Key Words: Solvent extraction, copper(II), pentaerythrityl tetrabenzylamine.

Introduction

Copper-bearing raw materials are often subjected to organic solvents with main ligands as their water insoluble amine complexes. In most cases, selective extraction is a more economical and practical method because it requires simple equipment and fewer stages than other methods described in the literature[1−4].

Solvent extraction enjoys a favored position among the separation techniques because of its ease, simplicity, speed and wide scope. Utilizing an apparatus no more complicated than a separatory funnel, requiring several minutes at the most to perform, and applicable both to trace and macro levels of metals, these extraction procedures offer much to the analytical chemist[5]. The development of selective extractants has expanded the use of solvent extraction for metal recovery and purification, replacing, in some situations, pyrometallorgical techniques. The design of a solvent extraction process and its optimization requires a

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proper knowledge of the equilibrium metal distribution in each phase[6]. Reagents such as crown ethers[7], oximes[8], amines and several phosphine oxides[9-10] have been used in extraction studies. The use of amines as extractants for metal ions in solvent extraction has been well established, and there appears to be more published work on the extraction of metal ions[11-16]. The extraction of copper from ammoniacal solution with different 4-acylpyrazol-5-ones was studied by Mickler and Uhlemann[11]. They determined that all curves of the 4-acylpyrazol-5-ones run through a minimum in the pH 6-7 region and the copper extraction is decreased by increasing the ammonia concentration because ammonia works as a competing ligand. The synergic extraction of Cu(II) in the biphasic system 1.0 mol dm^{-3} KNO$_3$ / 1-phenyl-1,3-decanedione (HR), the active component of the commercial extractant LIX 54, and di-n-octylphosphinicacid (HL) in toluene has been studied at 298 K by distribution methods[17]. The equilibrium studies on the solvent extraction of Cu(II) with 5-dodecylsalicylaldoxime, the active component of LIX 860, were carried out at 303 K to clarify the effects of the organic diluent and the aqueous media, together with measurements of the apparent molecular weight and aqueous solubility of the extractant by Yochizuha et al[18]. They found that the title extractant exists as a monomeric species in the organic diluents, i.e., hexane, cyclohexane and toluene, and is sparingly soluble in the aqueous solutions as well as other commercial hydroxyoximes. LIX 64 N[19] and LIX 87 QN[1] were other extraction reagents used. LIX 87 QN diluted with kerosene (mostly aliphatic) was used to co-extract copper and nickel from ammoniacal carbonate solutions[1]. The extraction is improved by synergists such as trioctylphosphine oxide[9], triphenylphosphine oxide[10], crown ethers[20] and methyltrioctyl-ammonium chloride[21].

The pentaerythrityl tetrabenzylamine (PETBA) derivative is a well known chelating ligand coordinating to metal ions with nitrogen atoms as a Lewis base. The derivatives are stable and easily synthesized. Metal ions are extracted from a relatively neutral pH medium. Similar ligands have been used for Lewis acid metal ions with strong affinity[22-24]. PETBA exhibits favorable extraction qualities. However, it is an original extracting agent which has not been used as an extractant in the literature. In this paper, we examine the effects of the extractant and copper concentrations, temperature, pH of the aqueous phase, solvents, A/O ratio and the extraction of copper from the aqueous solution to organic phase.

Experimental

All reagents were of reagent grade. Pentaerythrityl tetra-bromide and benzylamine were obtained from Aldrich Co., and these compounds were purified by distillation in vacuo (10^{-1}torr) or by recrystallization from alcohol. The others were from Merck and were used as supplied without any further purification. The solutions were prepared with bidistilled water and the various chemicals. For the measurement of pH of the aqueous phase after extraction, a Metrohm 691 pH meter with a glass electrode (Metrohm) was used. The copper(II) concentrations were determined by atomic absorption spectrophotometry (Unicam 929 AAS). Its concentration in the organic phase was determined by a mass balance.

Synthesis

The synthesis was performed by the following procedure by the reaction of benzylamine and pentaerythrityl tetrabromide. Benzylamine (0.4 mol) was added to pentaerythrityl tetrabromide (0.05 mol) in a flask (250 ml) without any solvent. The mixture was stirred at 140-160°C under a nitrogen atmosphere for 4 h. The

resulting precipitate after the reaction was dissolved by heating in benzene (100 ml) and then filtered off. The filtrate was extracted with 10% NaOH (200 ml) at five stages and then dried over Na_2SO_4. The product was evaporated and the excess amine was removed under reduced pressure. Then, the obtained product, pentaerythrityl tetrabenzylamine (PETBA), was purified by vacuum distillation at 75°C. Its spectroscopical data, the ^{1}H-NMR and IR-spectra, are presented in Figures 1 and 2. PETBA is characterized by the formula
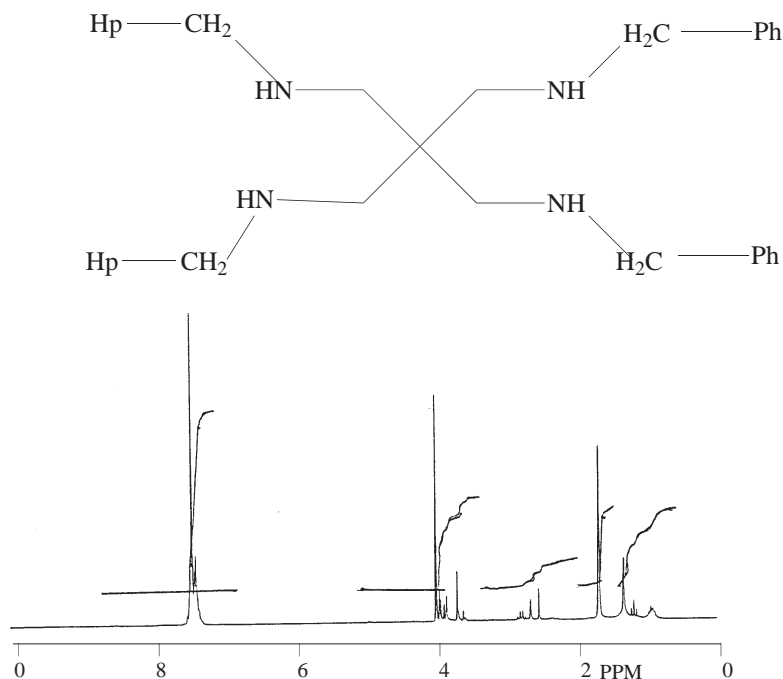
Figure 1. The ^{1}H-NMR spectra of PETBA compound
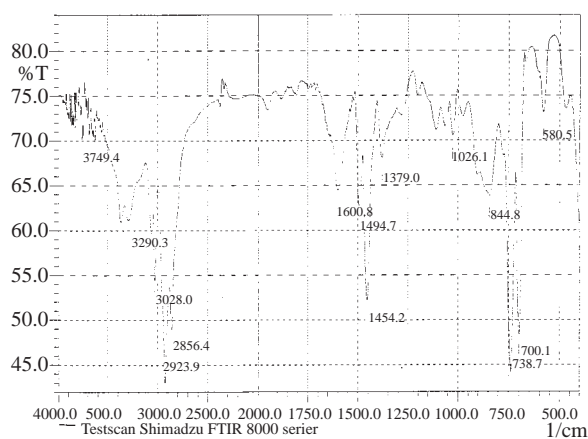
Figure 2. The IR spectra of PETBA compound

Extraction Procedures

Extraction experiments of copper(II) were carried out by shaking the solutions of ligand (10^{-4}-10^{-3}) and aqueous solutions of copper(II) (10^{-2}-10^{-4}) in a conical flask (50 ml) for a period of time at the temperature desired. $CHCl_3$ and CH_2Cl_2 were used as organic solvents. Unless otherwise stated an aqueous/organic phase

ratio (A/O) of 1 was used, the equilibration time was 5 min and temperature was 25^0C. The pH adjustment was done by adding NaOH and HNO_3. The ionic strength of the aqueous phase was kept as I=0.1 M by adding an appropriate amount of potassium nitrate. The pH of the aqueous phase after extraction was measured and then copper(II) concentrations were determined by AAS.

Maximum Loading Curve

The maximum loading capacity of the organic phase containing pentaerythrityl tetrabenzylamine was determined by contacting one sample of the organic phase (10^{-3} M) with fresh aqueous copper(II) nitrate (10^{-3} M) solutions at a constant initial pH. After successive contacts between the organic and the aqueous phase, the organic phase becomes fully loaded with copper(II) under the experimental conditions of pH and temperature (25^0C). The same procedures were repeated at various pHs.

Results and Discussion

The results from contacting equal volumes of PETBA ligand and copper(II) nitrate solution with different equilibrium times (5-120 min) and ionic strengths ($0.1 - 1$ M KNO_3) showed that the extraction efficiency was independent of these parameters in one step extraction processes. The extraction efficiencies were independent of pH up to 7.6, and then decreased gradually to about zero at pH 11.5. Plots of E% *vs.* pH and logD *vs.* pH are shown in Figures 3 and 4. So the subsequent experiments were carried out at the natural pH of the aqueous phase (approx. 6) with 0.1 M KNO_3 ionic strength for 5 min.
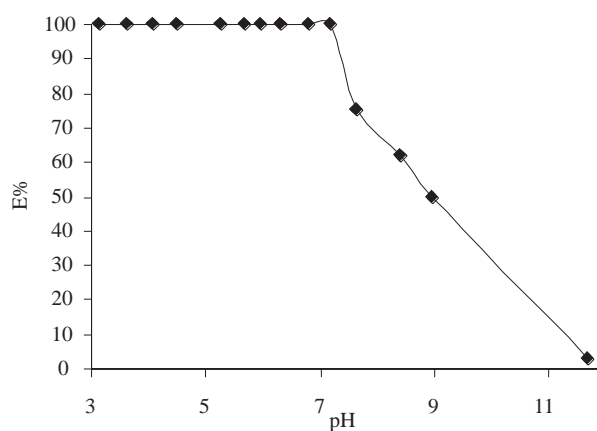

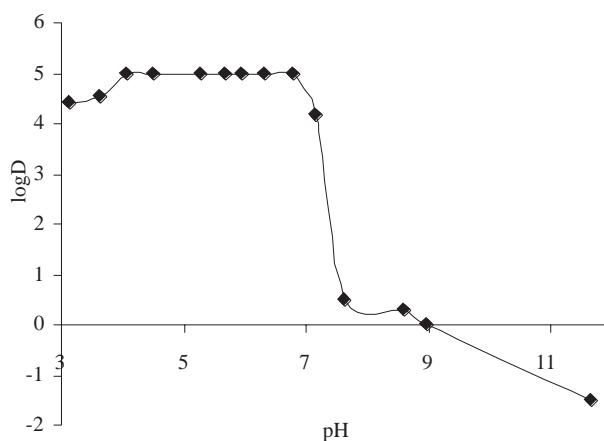**Figure 3.** The plot of E% *vs.* pH

Figure 4. The plot of logD *vs.* pH

Maximum Loading Curve on Extraction

The maximum loading capacity gives the maximum concentration of metal ions which can be extracted from the aqueous phase into the organic phase with PETBA at a constant pH and temperature by using a solution of PETBA in organic solvents. Data on loading characteristics for the system are shown in Figures 5-6. The plot of the concentration of copper(II) in the organic phase *vs.* loading number (Figure 5) shows that the concentration of copper(II) in the organic phase was constant after the 4th loading and increased with increasing initial pH of the aqueous copper(II) solution. The maximum loading of copper(II) in the organic phase after the 5th loading was plotted against initial pH of aqueous copper(II) solution (Figure 6). The maximum loading of copper(II) at pH 6 was more than at other pH values. The maximum loading capacity was found to be 140 ppm at pH 6.0.
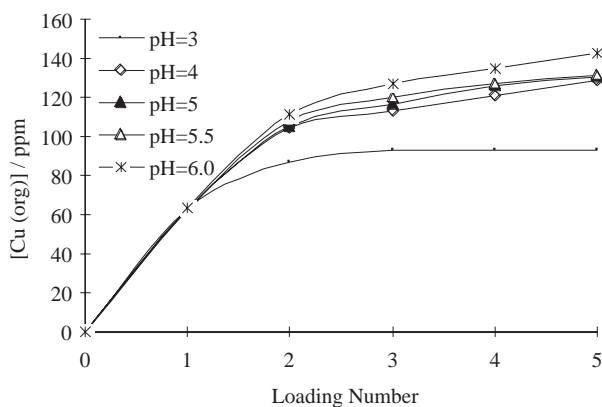

Figure 5. The effect of loading number on the copper(II) concentration of the organic phase in CH_2Cl_2 at various initial pH values
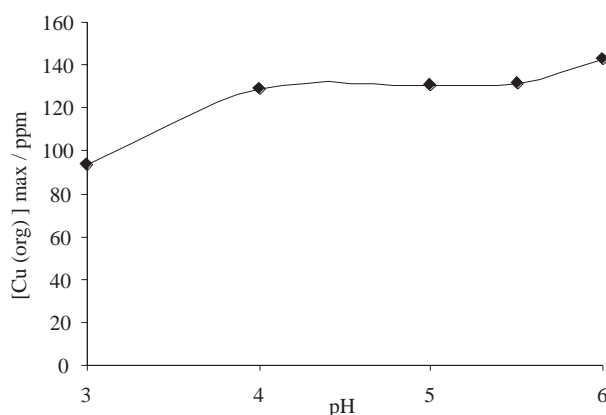
Figure 6. The effect of pH on the maximum loading capacity of organic phase in CH_2Cl_2 containing PETBA at 25°C

Characterization of Copper-Ligand Complex

In order to characterize the copper compound formed with PETBA, studies were carried out using the continuous variation method[25]. The concentrations of copper(II) in the aqueous and PETBA in the organic phase were varied so that their sum was equal to 1×10^{-3} M. The ionic strength was kept constant at I=0.1 M KNO_3. The copper concentration transferred from the aqueous phase to organic phase was plotted against the ligand and copper(II) concentration of these solutions. A maximum point occurs at a concentration ratio C_{Cu}/C_L corresponding to the combining ratio of cation and ligand in the complex. As shown in Figure 7, the maximum copper concentration in the organic phase occurs at a $C_{Cu}/C_L = 2/1$ ratio, confirming that the stoichiometry of the compound is $Cu_2L(NO_3)_4$, by considering the electroneutrality.
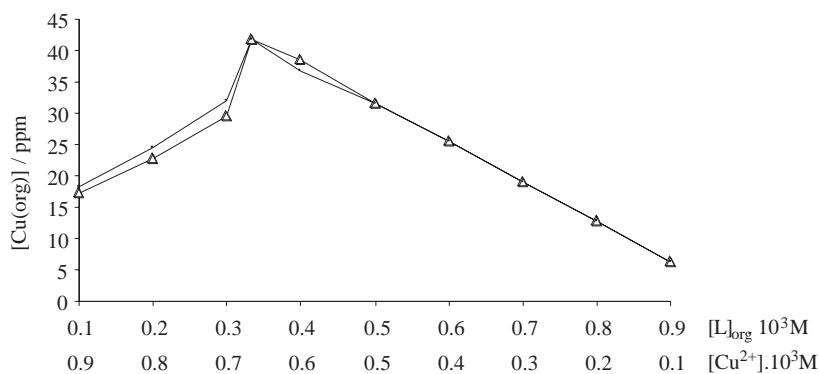

Figure 7. The characterization of the copper(II)-PETBA compound in $CHCl_3$ and CH_2Cl_2 at 25°C

The Effect of Aqueous to Organic Phase Ratio on Extraction Efficiency

The phase ratio (A/O) is one of the factors that affects the extraction efficiency. The extraction efficiency E% can be represented by Equation 1:

$$\%E = \frac{D}{D + (A/O)} \times 100 \tag{1}$$

Where D is the distributing ratio (defined by Eq. 4) and A/O is the volume ratio of aqueous phase/organic phase. Equation 1 indicates that the extraction efficiency decreases with increasing A/O ratio. Figure 8 shows the effect of A/O ratio on percentage extraction which is satisfied by Equation 1.
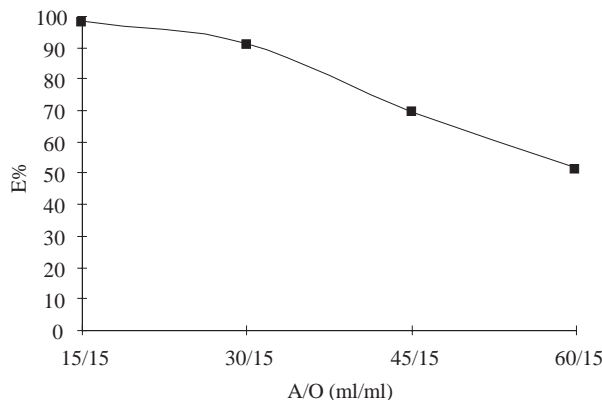

Figure 8. The effect of A/O on the extraction efficiency of copper(II) in CH_2Cl_2 at 25°C

The Effect of Copper(II) and PETBA Concentration on Extraction

Equilibrium data on copper(II) extraction[26] were obtained from shake out tests using copper(II) solutions with concentrations ranging from 5×10^{-4} to 10^{-2} M at an initial pH 6 as the aqueous phase and 10^{-3} M PETBA in CH_2Cl_2 as the organic phase (Figure 9). The extraction of 10^{-3} M copper(II) was carried out with varying concentrations of PETBA in the range 10^{-4}- 10^{-3} M (Figure 10). The percentage extraction of copper(II) increased with increasing PETBA concentration. The data relating to PETBA concentrations above 5×10^{-4} were more than 95% .

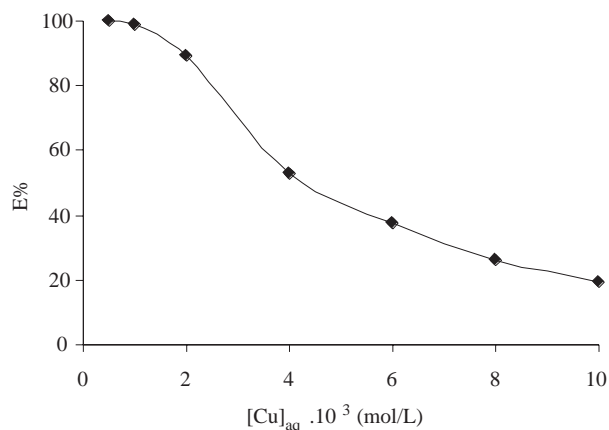**Figure 9.** The effect of copper(II) concentration on the percentage extraction of copper(II) in CH_2Cl_2 at 25°C. Initial PETBA concentration was 10^{-3} M.

The data given in Figure 9 and 10 have been plotted in Figure 11 and 12 as copper(II) extracted *vs.* $[Cu^{2+}]_o$ and $[L]_o$ (initial concentrations) respectively. As seen from these figures, the concentration of $Cu_2L(NO_3)_4$ in the organic phase remains constant after reaching a value that corresponds to a molar ratio Cu/L=2. This result confirms that the stoichiometry of the extraction process can be given as follows:

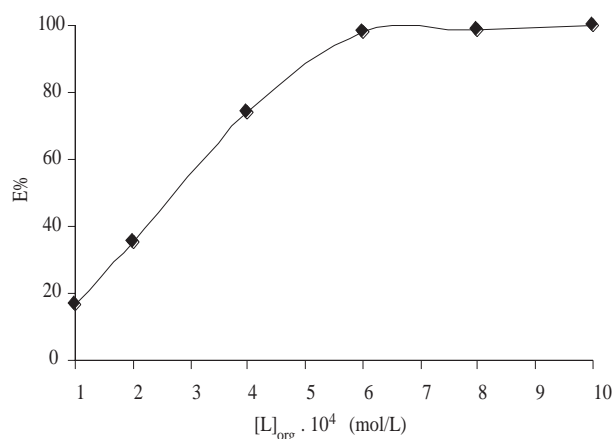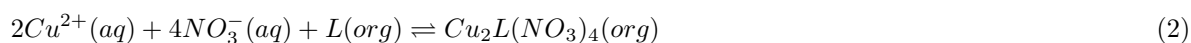**Figure 10.** The effect of PETBA concentration on the percentage extraction of copper(II) in CH_2Cl_2 at $25°C$. Initial Cu^{2+} concentration was 10^{-3} M.

$$2Cu^{2+}(aq) + 4NO_3^-(aq) + L(org) \rightleftharpoons Cu_2L(NO_3)_4(org) \tag{2}$$

$$K_{ex} = \frac{[Cu_2L(NO_3)_4(org)]}{[Cu^{2+}(aq)]^2[NO_3^-(aq)]^4[L(org)]} \tag{3}$$

If the distribution ratio is defined as

$$D = \frac{[Cu^{2+}]_{org}}{[Cu^{2+}]_{aq}} \tag{4}$$

and from the stoichiometric relationship

$$[Cu^{2+}]_{org} = 2[Cu_2L(NO_3)_4]_{org} \tag{5}$$

$$D = \frac{[Cu_2L(NO_3)_4(org)]}{[Cu^{2+}(aq)]} \tag{6}$$

The effect of temperature

The dependence of copper(II) extraction equilibrium on temperature was studied by contacting 15 ml aqueous solutions containing 10^{-3}M Cu(II) (0.1 M KNO_3) with 15 ml CH_2Cl_2 solution containing PETBA (10^{-3}M). The plot of percentage extraction *vs.* temperature given in Figure 13 shows that the extraction efficiency decreases as the temperature increases.
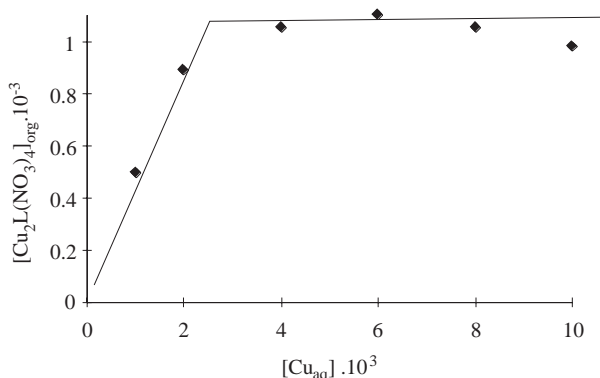
Figure 11. The effect of copper(II) concentration in the aqueous phase against the extracted copper(II) concentration in the organic phase with PETBA in CH₂Cl₂ at 25°C
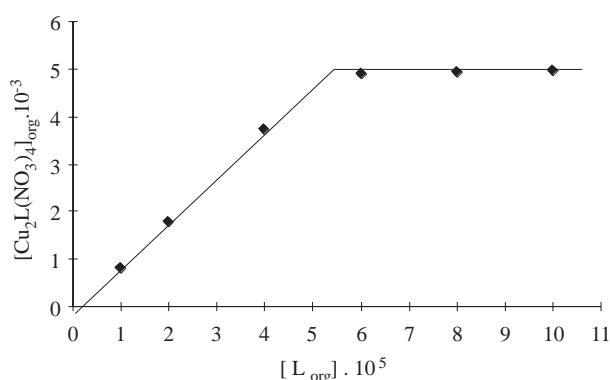

Figure 12. The change in the complex concentration in the organic phase with initial PETBA concentration in CH₂Cl₂ at 25°C. Initial Cu^{2+} concentration was 10^{-3} M.
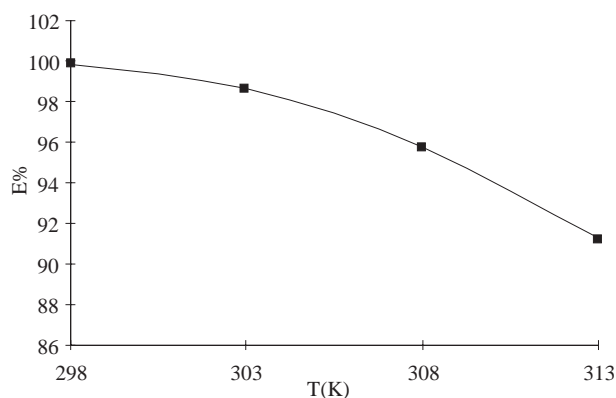

Figure 13. The effect of temperature on the extraction efficiency of PETBA

By assuming that the dependence of K$_{ex}$ on T can be expressed as

$$\frac{R\partial \ln K_{ex}}{\partial(1/T)} = -\Delta H^0 \tag{7}$$

The plot of RlnK$_{ex}$ *vs.* T^{-1} (Figure 14) was found to be linear in this system. The enthalpy change (ΔH^o) and entropy change (ΔS^o) of the extraction process were calculated to be –80.504 kJmol^{-1} and 67.842 Jmol^{-1} K^{-1}, respectively. The fact that the ΔH^{o}has a negative value means that the extraction process is exothermic, and hence the stripping process is enhanced by increasing the temperature. The positive entropy change indicates that copper(II) is transferred from a highly disordered state to one of greater order, although this behavior does not follow the trend of many solvent extraction systems in which the organic solvent is more disordered than the highly ordered water structure[2].
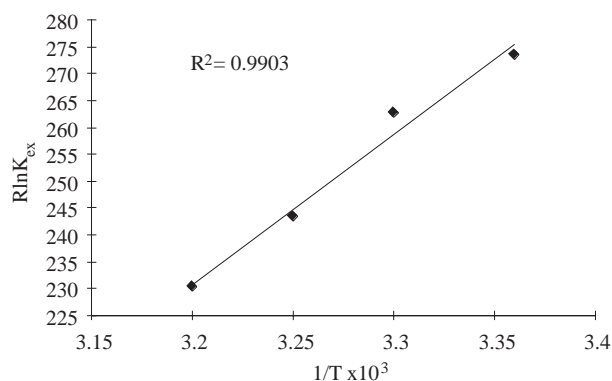
Figure 14. The plot of $RlnK_{ex}$ *vs.* $1/T$

Conclusions

The percentage extraction of copper(II) decreases with increasing temperature. The extraction reaction is exothermic and enthalpy driven. There was no effect of time, ionic strength or pH on copper extraction from aqueous copper(II) solution to organic solution of PETBA. The extraction efficiency of copper(II) decreases with increasing A/O ratio. The experimental results show that the complex extracted in the organic phase can be represented by the general formula Cu_2LA_4, where L represents the pentaerythrityl tetrabenzylamine and A represents nitrate ion. The maximum loading studies show that the copper(II) concentration in the organic phase was constant after the 4th loading and increased with increasing initial pH of the aqueous copper solution; and the maximum loading of copper(II) at pH 6 is higher than that at other pHs. PETBA is recommended as a new type of possible extractant. Because of the expected high hydrophobicity, PETBA was repeatedly chosen as an extractant.

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