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Extraction of Zn (II) and Cu (II) Ions Using PEG (300) - KCl Salt Aqueous Two-Phase Systems

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Abstract

In this paper the process of metal ions extraction (Zn(II) and Cu(II)) was studied in PEG-KCl aqueous two phase system was investigated without using an extracting agent. The experimental runs were performance at constant temperature (25 ^oC), constant mixing time (30 min), and constant PH of the solution (about 3). The effect of KCl salt concentration (from 10% to 25%), volumetric phase ratio of PEG solution to KCl solution (from 0.5 to 2), and the initial metal ion concentration (from 0.25 ml to 2 ml of 1 gm/L solution) were investigated on the percent extraction of Zn(II) and Cu(II). The results indicated that the percent extraction of metal ions increase with increasing of salt concentration and phase ratio, and slightly decrease with increasing of initial metal ion concentration.

Keywords: *Liquid-liquid extraction, aqueous two phase system, metal ions, waste water.*

1. Introduction

Aqueous two-phase systems formed when a water soluble polymer is mixed with a certain inorganic salt (*e.g.* (NH4)2SO4, Na2SO4, Na2CO3, K2HPO4, KCl), may represent an alternative for metal ions extraction processes in industrial separation, as well as environmental remediation applications. (Laura Bulgariu, 2008)

Many different water soluble polymers may be utilized to form aqueous two-phase systems (ATPS), poly ethylene glycol (PEG) is exclusively used because it is non-toxic, non-flammable and non-volatile (Graber, T.A at. el., 2000).

Rogers et al. classified metal ion extractions in the aqueous two-phase` systems into three categories: (1) extraction using a water-soluble extractant; (2) extraction of metal complexes of inorganic anions and (3) extraction by the PEG-rich phase alone without an extractant. Among these three categories, the second type of metal extraction will find wide application to soft metal ions, which form complexes with halide or pseudohalide anions (Rogers, 1993 and Rogers, 1995).

The extraction of a metal ion Mm^+, with a complexing anion, X^-, can be described as (Shibukawa at. el., 2001):

$$M^{m+} + nX^- \Leftrightarrow MX_n{}^{(n-m)-}$$

$$\beta_{MXn} = \frac{[MX_n^{(n-m)-}]}{[M^{m+}][X^-]^n} \quad \ldots(1)$$

$$MX_n{}^{(n-m)-} \Leftrightarrow (MX_n{}^{(n-m)-})_{PEG}$$

$$K_{D;MX_n} = \frac{[MX_n^{(n-m)-}]_{PEG}}{[MX_n^{(n-m)-}]} \quad \ldots(2)$$

Where β and K_D are the stability constant and the distribution coefficient of the metal complex, respectively.

Most of the metal ions studied are extracted as anionic complexes as so that sodium ion or potassium ion may distribute into the top phase as their counter ion. A preliminary experiment showed that the dependence of the distribution of metal ions on the amount of H_2SO_4 added was very small. This result suggests that the co-extraction of hydrogen ion with the anionic complexes can be neglected. Sulphate ion has the ability to form complexes of a number of metal ions so that the complexation reaction of the metal ions with SO_4^{2-} may not be negligible especially in the Na_2SO_4-rich phase:

$$M^{m+} + xSO_4^{2-} \Leftrightarrow M(SO_4)_x^{(2x-m)-}$$

$$\beta_{MSO_4x} = \frac{[M(SO_4)_x^{(2x-m)-}]}{[M^{m+}][SO_4^{2-}]^x} \qquad \ldots(3)$$

$$M(SO_4)_x^{(2x-m)-} \Leftrightarrow (M(SO_4)_x^{(2x-m)-})_{PEG}$$

$$K_{D;M(SO_4)_x} = \frac{[M(SO_4)_x^{(2x-m)-}]_{PEG}}{[M(SO_4)_x^{(2x-m)-}]} \qquad \ldots(4)$$

Consequently the distribution ratio of a metal ion, *D*, defined as the ratio of the metal concentration in the PEG-rich phase to that in the Na_2SO_4 rich phase can be given by

$$D = \frac{\Sigma[MX_n^{(n-m)-}]_{PEG} + \Sigma[M(SO_4)_x^{(2x-m)-}]_{PEG}}{[M^{m+}] + \Sigma[MX_n^{(n-m)-}] + \Sigma[M(SO_4)_x^{(2x-m)-}]} \qquad \ldots(5)$$

It is reasonable to assume that $[M(SO_4)_x^{2x-m}]_{PEG} << [MX_n^{n-m}]_{PEG}$ since the metal ions are scarcely extracted into the PEG-rich phase in the absence of SCN^- or I^-. This may be due to small KD values of the metal sulphate complexes. Therefore, Eq. (2.25) can be rewritten as:

$$D = \frac{\Sigma[MX_n^{(n-m)-}]_{PEG}}{\Sigma[M(SO_4)_x^{(2x-m)-}]} = \frac{\Sigma[K_{ex;MXn}[X^-]^n]_{PEG}}{\Sigma\beta_{MSO_4x}[SO_4^{2-}]^x} \qquad \ldots(6)$$

The extraction of metal ions in presence of inorganic extractants, with aqueous PEG–inorganic salt two-phase systems, can be represented by a succession of equilibriums, schematically presented in Fig. (1). The metal ion, initially present in salt-rich phase as anionic or neutral species (MA_m^{y-}; A –phase-forming anion) will interact with inorganic extractants, most probably at interface, and the formed species (MX_n^{x-}) will be then partitioned into PEG rich phase. The formation of extractable species occurs step by step, until his hydration degree becomes comparable with the hydration environment of PEG-rich phase from extraction system. In function of the stability of metallic species formed with phase-forming anion (β_{MAy-m}) and with inorganic extractant (β_{MXnx-}), the following three situations are possible (Laura Bulgariua, at. el., 2008).

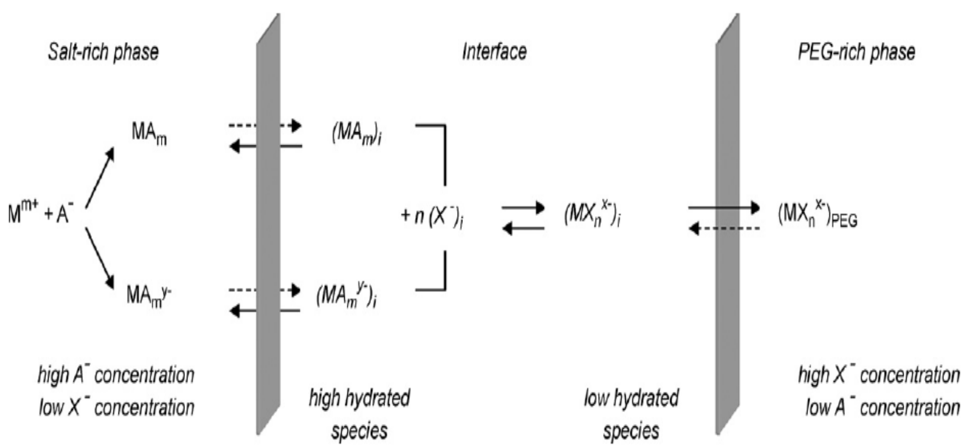

Fig.1. Schematic Representation of Equilibriums Involved in Metal Ions Extraction with Inorganic Extractants, in Aqueous PEG–Inorganic Salt Two-Phase Systems. (A^- –Phase-Forming Anion; X^- – Inorganic Extractant) (Laura Bulgariua, at. el., 2008).

After inorganic extractants addition, the metal ions from this category form, even in salt-rich phase, halide species with the mention that the number of halide ions from metallic species is minimum. These species are marginalized in the salt-rich phase, due to their low hydration, and remitted at interface. Here, they will interact with more halide ion extractants and will form anionic complexes with higher number of halide extractant in molecule. Because the hydration degree of these anionic complexes is lower and compatible with the hydration environment of PEG-rich phase, their partition occurs immediately and this is quantitative one. The anionic species formed at interface, cross like they are into PEG-rich phases, where they will interact predominantly by ionic forces with the other oxygen atoms from PEG molecules. These interactions affect only the bridging water molecules.

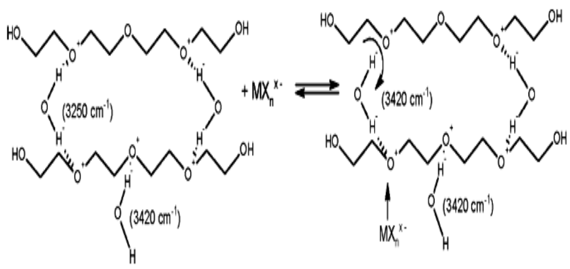

Fig.2. Schematic Representation of Anionic Complexes (MX_n^{x-}) Extraction in Aqueous PEG–Inorganic Salt Two-Phase System (Laura Bulgariua, at. el., 2008).

The breaking of hydrogen bonds between PEG chains and water molecules determined the decrease of polymer chains interaction and the modification of water molecules binding way on polymer macromolecules. The formation of ordinate micro-domains is due to the interaction of anionic extracted species with PEG molecules, which determined a linearization of polymer chains. Probably, a plane square geometry of metal species is preferred due to this reason.

In the same time with the transfer of anionic species into PEG- rich phase, the forming-phase anions (SO_4^{2-}) that have accompanied the formation and the separation of the two aqueous phases are expulsed in salt-rich phase, due to the incompatibility of hydration environment, and the phases are maintained neutral from electrical point of view.

The IR spectra and microscopic images indicate that the extracted species, indifferently by their type (anionic complexes or neutral molecules) cross in PEG-rich phase of extraction system and are "fixed" by characteristic interactions. Thus, in case of anionic species extraction, the IR spectra show that between metal extracted species and PEG molecules strong interactions occur, and the bridging water molecules are used as intermediary. Here, the PEG-rich phases are formed predominantly, from micro-domains with high ordination degree. In case of neutral molecules extraction, the changes observed in IR spectra can be attributed to the formation of some new hydrogen bonds between extracted species and PEG chains. In consequence, the microscopic images show that in the solidified PEG-rich phases of these systems the micro-domains with a lower ordination degree are predominant, which has an organization way and some characteristics similar to the colloidal systems.

A schematic representation of Cd(II) extraction in the presence of halide ions in the considered aqueous two –phase system is presented in fig. (3) according to this, for partition Cd(II), processes which occur at the PEG-rich phases/salt-phase interface are essential: Cd(II) complexation with halide ions and the transformation of cadmium halide species into complex species towards the PEG-rich phase have a higher affinity under the employed conditions (Laura Bulgariua, at. el., 2008).

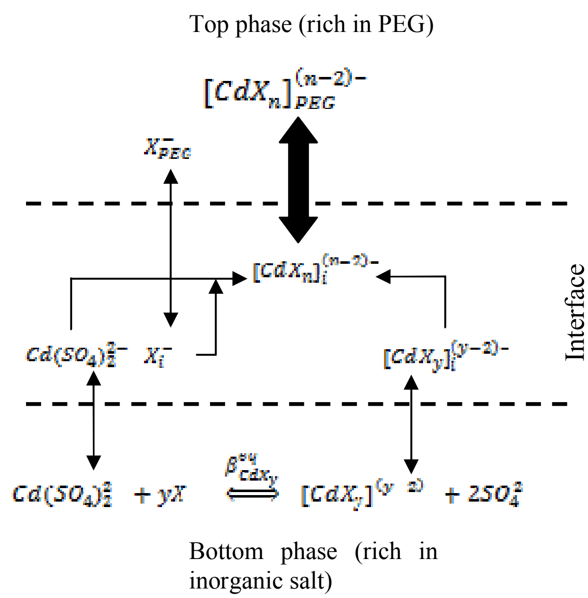

Fig.3. Schematic Representation of the Main Processes Involved in Cd (II) Extraction in the Considered Aqueous Two-Phase System (Laura Bulgariua, at. el., 2008).

The anionic species formed at the interface cross into the PEG-rich phase, where they will interact, predominantly by ionic forces, with the ether oxygen atoms of PEG. An equivalent ionic transfer process ensures the electro neutrality of the two phases. In case of extraction of Cd(II) anionic complexes, the SO_4^{2-} ion which are present in the PEG-rich phase after formation of the aqueous two-phase system are expelled into the salt-rich phase, due to the incompatibility of the hydration environment. Thus, the phases are kept neutral from an electrical point of view and the hydrophobicity of the PEG-rich phase is maintained during of extraction process.

In this study, the extraction of Zn(II) and Cu(II) metal ions in PEG-KCl aqueous two phase system was investigated without using an extractant. The effect of salt concentration, volumetric phase ratio of PEG solution to KCl solution, and initial metal ion concentration on the percent extraction of Zn(II) and Cu(II) were investigated.

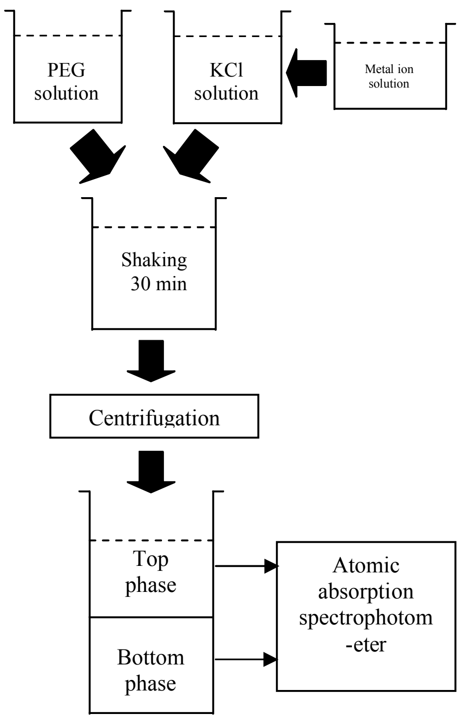

Fig.4. Experimental Procedure Steps

2. Materials and Methods

The PEG used in this study was PEG-3000 (average molecular weight, 3000). Stock solutions of 30% (w/w) PEG were prepared by dissolving of suitable quantity of PEG in deionized water. The stock solutions of inorganic salt at different values (10%, 15%, 20%, and 25% (w/w) KCl) were prepared by dissolving the required amount of salt in deionized water and at constant PH value (about 3) by adding small volumes of acids or bases concentrated solutions. The 1 gm/L solution of metal ions (Zn(II) and Cu(II)) was obtained by metal sulphate salt dissolving in deionized and distillate water, the initial metal ion concentration was varied by taking 0.25, 0.5, 1 and 2 mL of the 1 gm/L metal ion solution prepared.

For each experiment, an aqueous two-phase system was prepared by mixing the prespecified volumetric phase ratio of PEG stock solution – KCl salt stock solution in the range of 0.5, 1, 1.5, and 2

With constant pH of 3 at room temperature (25±2 °C). The (0.25–1.5) mL of 1 gm/L metal ion (Zn(II) and Cu(II)) solutions were added and the system was shaken for 30 minute followed by 15 minute of Centrifugation. Equal volumes (1 ml) for each phase were separated and measured for Zn(II) and Cu(II) ions by means of atomic absorption spectrometer (Type PERKIN – ELMER 5000 in Ibn-Sina State Company, Baghdad). Figure (4) show the experimental procedure steps.

3. Results and Discussion

3.1. Effect of Concentration of KCl

Figure (5) shows the percent extraction of metal ions (Zn(II) and Cu(II)) as a function of concentration of KCl in the stock solution (10%, 15%, 20%, and 25% (w/w) KCl) at phase ratio of 1 and initial metal ion concentration of 0.5 mL of 1 gm/L. It is clear from this figure that the percent extraction of metal ions increase with increasing of KCl concentration in salt phase.

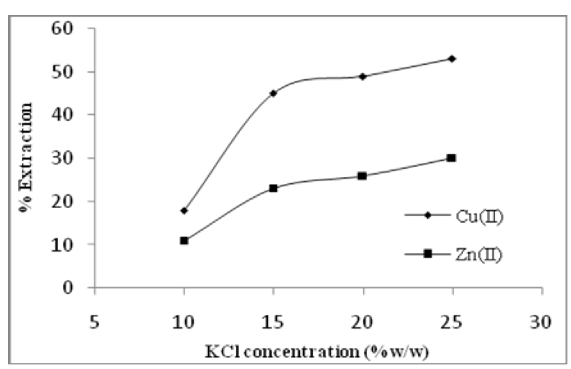

Fig.5. Percent Extraction (%) of Metal Ions as a Function of Concentration of KCl in the Stock Solution % (w/w) at Phase Ratio of 1 and Initial Metal Ion Concentration of 0.5 mL of 1 gm/L.

The formation of aqueous two-phase system of PEG and a certain inorganic salt can be explained on the basis of the competition for hydration between the two components. The addition of an inorganic salt increases the dehydration of the polymer chains, due to the salting-out effect and phase separation (Laura Bulgariu, 2005).

3.2. Effect of the (PEG/KCl) Phase Ratio

Figure (6) shows the percent extraction of metal ions (Zn(II) and Cu(II)) with the volumetric phase ratio of PEG to KCl (0.5, 1, 1.5, and 2) at constant KCl salt concentration in stock solutions of 20% (w/w) and initial metal ion concentration of 0.5 ml of 1 gm/L.

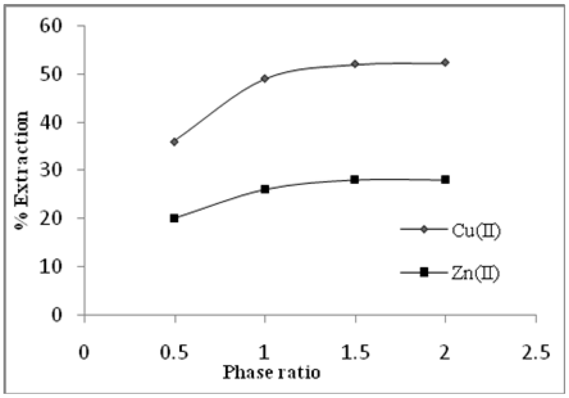

Fig.6. Percent Extraction (%) of Metal Ions as a Function of Phase Ratio at KCl Concentration in Stock Solutions of 20% (w/w) and Initial Metal Ion Concentration of 0.5 mL of 1 gm/L.

The results above indicate that the extraction of the metals above increases with increasing of PEG/KCl volumetric phase ratio. This might be attributed to the increase in the quantity of transferred metal which is related with quantity of the extractant that will furnish the necessary molecules to form the complex to reach the equilibrium state (Graber, T.A., 2007).

3.3. Effect of Initial Metals Concentration

Figure (7) shows the percent extraction of metal ions as a function initial metal concentration in the salt phase at phase ratio of 1 and KCl salt concentration in the stock solution of 20% (w/w). As notices from the results that plotted in Figure (7), increasing the metals concentration in the feed, the percent extraction of metal removed decrease.

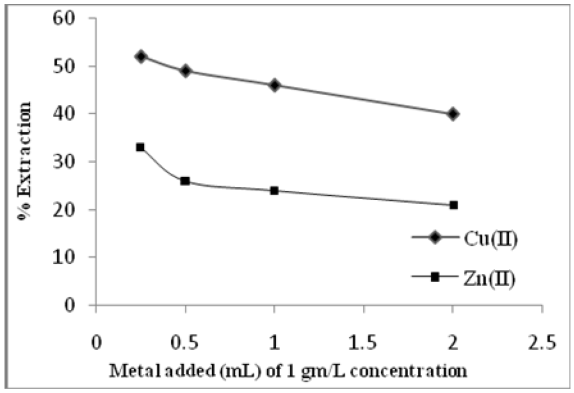

Fig.7. Percent Extraction (%) of Metal Ions as a Function of Initial Metal Ion Concentration at Phase Ratio of 1 and KCl Salt Concentration in the Stock Solution of 20% (w/w).

4. Conclusion

The process of Zn(II) and Cu(II) metal ions extraction was studied using aqueous PEG – KCl salt two phase systems without using an extractant agent. The process variables salt concentration in the salt phase, PEG/KCl volumetric phase ratio, and the initial metal ions concentration were studied on the percent extraction of metal ions. The results indicated that the percent extraction of metal ions increase with increasing of salt concentration and phase ratio, and slightly decrease with increasing of initial metal ion concentration.

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أستخلاص أيونات النحاس والزنك بأستخدام انظمة المحاليل المائية ثنائية الطور المتكونة من بولي اثلين كلايكول (٣٠٠٠) - ملح كلوريد البوتاسيوم

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الخلاصة

تم دراسة عملية أستخلاص أيونات المعادن (النحاس, والزنك) في أنظمة المحاليل المائية ثنائية الطور والمتكونة من بولي اثلين كلايكول وملح كلوريد البوتاسيوم KCl وبدون استخدام عوامل استخلاص (حيث ان ملح كلوريد البوتاسيوم يعمل كعامل أستخلاص بالاضافة لكونه مكون للطور الملحي). تم اجراء التجارب تحت درجة حرارة ثابتة (25 درجة مئوية), زمن الخلط ثابت (30 دقيقة) و PH المحلول ثابت (بحدود 3). تم دراسة المتغيرات التالية على نسبة الاستخلاص:

- تركيز الملح KCl في الطور الملحي من 10% الى 25% وزنا.
- نسبة الطور الحجمية (طور محلول البولي أثيلين كلايكول/ طور محلول ملح كلوريد البوتاسيوم) من 0.5 الى 2.
- التركيز الابتدائي لايونات المعدن ويتراوح بين 0.25 الى 2 مليلتر من تركيز 1غرام / لتر.

اظهرت النتائج أن النسبة المئوية لاستخلاص أيونات المعادن (النحاس والزنك)تزداد بصورة رئيسية بزيادة كل من تركيز ملح KCl في الطور الملحي ونسبة الطور بين البوليمر والملح وتقل مع زيادة التراكيز الابتدائية لأيونات المعادن.