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Journal of the Serbian Chemical Society
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*J. Serb. Chem. Soc. 73* (3) 341–350 (2008)

UDC 546.482+66.061:541.12.012–
–032.2:549.451.1:547.441–036.7

*JSCS–3716*

*Original scientific paper*

# Cd(II) extraction in PEG (1550)–$(NH_4)_2SO_4$ aqueous two-phase systems using halide extractants

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(Received 30 May, revised 30 August 2007)

*Abstract*: The extraction of Cd(II) was studied in an aqueous PEG–$(NH_4)_2SO_4$ two-phase system, formed from a water-soluble polymer (poly(ethylene glycol), PEG) and an inorganic salt ($(NH_4)_2SO_4$), in the presence of halide ions. In the absence of a suitable extracting agent, Cd(II) remains predominantly in the salt-rich phase of the extraction system. By addition of halide ions as extractants, Cd(II) is extracted into the PEG-rich phase due to the formation of cadmium halide species. The efficiency of the extractants increased in the order: $Cl^- < Br^- < I^-$. From the distribution coefficients determined as a function of the concentration of the halide ions, the compositions of the extracted species were assumed and the "conditional" extractions constants calculated. The experimental results indicate that the extractability of Cd(II) in such extraction systems depends on the type of Cd(II) halide species (which is mainly determined by the acidity of salt stock solution) and of their stability.

*Keywords*: aqueous two-phase system; Cd(II) extraction; halide ions; poly(ethylene glycol); $(NH_4)_2SO_4$.

## INTRODUCTION

Traditionally, extraction and recovery of metal ions from aqueous solutions were performed using solvent extraction, where the formation of two immiscible phases involved the mixing of an organic solvent with an aqueous solution.[1,2] However, most of the organic solvents used in the extraction methods are toxic, flammable, volatile and cause many problems to the environment. For this reason, the employment of aqueous two-phase systems for the same purpose has commenced.

The aqueous two-phase systems, formed from a water-soluble organic polymer and a certain inorganic salt, are mild and efficient extraction of metal ions

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doi: 10.2298/JSC0803341B

techniques, which do not use any organic solvents, being thus friendly to the environment.

From a large variety of different water-soluble polymers which may be utilized for the preparation aqueous two-phase systems, poly(ethylene glycol) (PEG) has received the most attention.[3,4] PEG in combination with an inorganic salt, such as $(NH_4)_2SO_4$ determine the separation of two immiscible phases: a top phase – rich in PEG, which plays the role of the organic phase in traditional extraction systems, and a bottom phase – with a high content of inorganic salt.

The utilization of aqueous PEG-based two-phase systems for the extraction of metal ions has several advantages, *i.e.*, they are considered virtually non-toxic and non-flammable and all the components are commercially available. In addition, PEG is biodegradable, which makes the risk of environmental contamination relatively low.[5,6]

Metal ion extraction in such aqueous two-phase systems depends both on the characteristics of the formed aqueous two-phase system (determined by the nature and concentration of the inorganic salt and the molecular mass and concentration of PEG) and on the stability and degree of hydration of the metallic species formed in the extraction system.[7–9] If the optimum characteristics of the aqueous two-phase system (system stability, phase separation time, clear interface) can be obtained by a suitable selection of the phase forming components, the second condition requires the utilization of some extracting agent, which will provide for the selectivity of the extraction process.

Some metal ions (Bi(III), Hg(II), Pb(II), Zn(II), Cu(II), *etc.*) can be extracted into the PEG-rich phase using halide or pseudo-halide ions, by an ion-pair extraction mechanism, similar to the extraction of metal halide complexes with ethers or ketones.[10–16] It has also been shown that in presence of halide ions, Cd(II) partitioning into the PEG-rich phase of aqueous PEG-based two-phase systems occurs and the extracted species were assumed to be $CdX_4^{2-}$, in all cases.[14,17] However, our experimental results have shown that the number of halide ions associated with Cd(II) depends on the acidity of the salt stock solution and on the stability of the extracted cadmium halide species.

In this work, the extraction of Cd(II) in an aqueous PEG (1550)–$(NH_4)_2SO_4$ two-phase system was studied, as a function of the type and concentration of the halide ions extractants. The effect of the acidity of the salt stock solution on the extraction efficiency was also considered. The results are discussed, based on the elementary equilibria involved in extraction process.

## EXPERIMENTAL

The reagents $(NH_4)_2SO_4$, NaI, NaBr, NaCl (from Aldrich) and PEG (1550) (from Serva Feinbiochema GmbH & Co) were of analytical grade and used without purification. The stock solution of 40 % (w/w) PEG (1550) was obtained by dissolving solid PEG in a certain mass of water. The 40 % (w/w) $(NH_4)_2SO_4$ salt stock solution was prepared similarly using water (salt stock solution with pH 4.65) or $10^{-3}$ M $H_2SO_4$ (salt stock solution with pH 3.03). The solution of ≈ 1.0 mg Cd(II) $ml^{-1}$ was prepared by dissolving cadmium nitrate (from Fluka) in distilled water, followed by standardization of the solution.[18] The solutions of the extractants, containing 1 M NaX ($X^- = Cl^-$, $Br^-$ or $I^-$) was obtained by dilution of a know mass of sodium halide salt to volume with the required salt stock solution.

The Cd(II) extraction experiments were performed in the following manner: for each determination, an aqueous two-phase system was prepared by mixing equal volumes of PEG (1550) stock solution and $(NH_4)_2SO_4$ salt stock solutions with the selected pH in a glass centrifuge tube. The pH values of the $(NH_4)_2SO_4$ salt stock solutions were measured with a Radelkis pH/ion-meter OK-271 type, equipped with a combined glass electrode. The Cd(II) stock solution (0.50 ml) and 1 M NaX solution (0.10–0.70 ml) were added. The system was centrifuged for 10 min at 2000 rpm. Centrifugation ensures an energetic mixing of the components of the system, which lowers the time necessary for phase separation. Just before analysis, the phases were carefully separated and placed into separated tubes. Equal volumes (1.0 ml) from each phase were measured spectrophotometrically using *p,p*'-dinitro-sym-diphenylcarbazide (S 104 D Digital Spectrophotometer; $\lambda$ = 630 nm, 1.0 cm glass cell).[19] The Cd(II) content in each phase was determined in duplicate using a prepared calibration graph. The distribution coefficients ($D_{Cd}$) were calculated as the ratio of the Cd(II) concentration in the PEG-rich phase to that in the salt-rich phase. The concentration of halide ions in the PEG-rich phase was determined by conductometric titration with $AgNO_3$, using a Radelkis OK-109 conductometer.

## RESULTS AND DISCUSSION

In a previous studies, it was shown that $(NH_4)_2SO_4$ can be used as the phase forming salt because it exerts a strong salting-out effect on PEG and has a high solubility in water.[20,21] Thus, an efficient extraction system can be prepared in which the differences in the concentration of PEG and the concentration of the inorganic salt concentrations in the two formed phases are large.

In the absence of a suitable extracting agent, the experimental results showed that the cadmium ions remained almost exclusively in the salt-rich phase. The low values of the distribution coefficients ($D_{Cd}$ = 0.281 in case of the salt stock solution with pH 3.03 and $D_{Cd}$ = 0.182 in case of the salt stock solution with pH 4.65) indicate that extraction of Cd(II) does not involve direct chemical interactions between the metal ions and the PEG molecules from the PEG-rich phase of extraction system.

Under the conditions of the prepared aqueous two-phase systems (the $SO_4^{2-}$ concentration in salt-rich phase was 3.45 M), calculations showed that predominant species in the system were $Cd(SO_4)_2^{2-}$ ions (89.2 %), $CdSO_4$ was only 10.7 % and free $Cd^{2+}$ ions were practically non-existent (≈ 0.01 %). The $Cd(SO_4)_2^{2-}$ species formed from a metal ion with a highly negative Gibbs free energy of hydration ($\Delta G_{hydr.} = -1722$ kJ $mol^{-1}$) and an anion with a strong salting-out effect will preferably remain in the salt-rich phase of the extraction system.[22]

Under these conditions, the extraction of Cd(II) can be enhanced by changing the nature of the Cd(II) species using a suitable extracting agent, which should have a lower degree of hydration and form a more stable species with Cd(II) than is $Cd(SO_4)_2^{2-}$.

The halide ions ($Cl^-$, $Br^-$ and $I^-$) were used as inorganic complexing extractants and the extraction of Cd(II) was investigated in dependence of the type of halide ion and the concentration of NaX in the extraction system, for both values of pH of the salt stock solution. Comparatively, the Cd(II) distribution coefficients are given in Figs. 1 and 2.

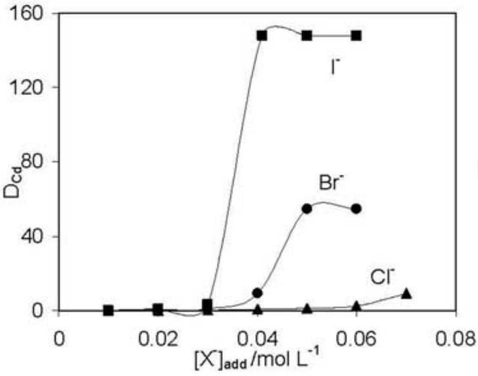

Fig. 1. The $D_{Cd}$ *vs*. $[X^-]_{add}$ dependence for the salt stock solution of pH 3.03. ($Cd_i$ = 57 μg $ml^{-1}$; $t$ = 21 °C).

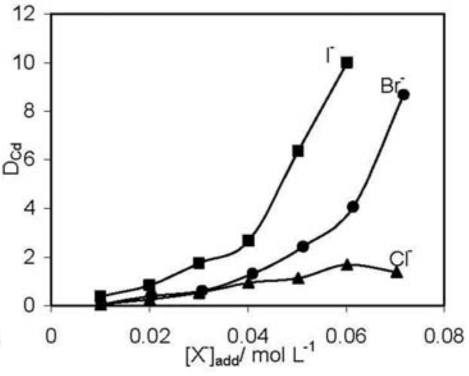

Fig. 2. $D_{Cd}$ vs. $[X^-]_{add}$ dependence for the salt stock solution of pH 4.65. ($Cd_i$ = 57 μg $ml^{-1}$; $t$ = 21 °C).

An increase of Cd(II) extraction into the PEG-rich phase with increasing concentration of halide ions was observed for pH values. The Cd(II) distribution coefficients ($D_{Cd}$) followed the order: $Cl^- < Br^- < I^-$, which is in agreement with data from the literature.[14,17] It can also be observed that, although the $X^- = I^-$, $Br^-$ and $Cl^-$ systems all exhibit similar partitioning behaviour at low concentrations, the Cd(II) distribution coefficients increase earlier for $I^-$ than for $Br^-$ and those for $Br^-$ increase earlier than for $Cl^-$. This order could be simply explained by the increasing stability of the cadmium halide species going from $Cl^-$ to $I^-$; the more polarisable halide ions form stronger complexes with Cd(II).[23]

On the other hand, the presence of $H_2SO_4$ in the extraction system (salt stock solution with pH 3.03) enhanced the efficiency of Cd(II) extraction, and the maximum values of $D_{Cd}$ were obtained at significant lower concentrations of halide ions than was the case of the systems prepared in the absence of $H_2SO_4$ (salt stock solution with pH 4.65). Increasing the acidity of the salt stock solution resulted in an increase of the hydrophobicity of the PEG-rich phase and, consequently, the extracted metal species should have a lower degree hydration and, hence, a larger number of halide ions in their molecules.[24]

The different extraction behaviour of Cd(II) in presence of halide ions for the two different pH values can be attributed to the formation of different cadmium halide species, depending on both the nature of the added halide ion extractant and the acidity of the salt stock solution.

Under these conditions, it can be assumed that the elementary equilibria, summarized in Table I, should be considered in the Cd(II) extraction process using halide ions extractants in the employed two-phase system.

TABLE I. The main elementary equilibriums involved in Cd(II) extraction in the aqueous PEG(1550)–$(NH_4)_2SO_4$–NaX two-phase system

| Elementary equilibrium | Reaction of equilibrium | Constant of equilibrium |
|---|---|---|
| Formation of anionic sulphates | $Cd^{2+} + 2\,SO_4^{2-} \leftrightarrows Cd(SO_4)_2^{2-}$ | $\beta_{Cd(SO_4)_2^{2-}} = \frac{[Cd(SO_4)_2^{2-}]}{[Cd^{2+}]\cdot[SO_4^{2-}]^2}$ |
| Formation of halide species | $Cd^{2+} + nX^- \leftrightarrows CdX_n^{(n-2)-}$ | $\beta_{CdX_n^{(n-2)-}} = \frac{[CdX_n^{(n-2)-}]}{[Cd^{2+}]\cdot[X^-]^n}$ |
| Halide partitioning | $X^- \leftrightarrows (X^-)_{PEG}$ | $D_{X^-} = \frac{[X^-]_{PEG}}{[X^-]}$ |
| Halide species partitioning | $CdX_n^{(n-2)-} \leftrightarrows (CdX_n^{(n-2)-})_{PEG}$ | $D_{CdX_n^{(n-2)-}} = \frac{[CdX_n^{(n-2)-}]_{PEG}}{[CdX_n^{(n-2)-}]}$ |
| Anionic sulphates partitioning | $Cd(SO_4)_2^{2-} \leftrightarrows (Cd(SO_4)_2^{2-})_{PEG}$ | $D_{Cd(SO_4)_2^{2-}} = \frac{[Cd(SO_4)_2^{2-}]_{PEG}}{[Cd(SO_4)_2^{2-}]}$ |

In this table, the chemical species from the PEG-rich phase are denoted by the subscript "PEG", while those in the salt-rich phase are given without a subscript.

The Cd(II) distribution coefficient can be written as:

$$D_{Cd} = \frac{[Cd(SO_4)_2^{2-}]_{PEG} + \sum[CdX_n^{(n-2)-}]_{PEG}}{[Cd(SO_4)_2^{2-}] + \sum[CdX_n^{(n-2)-}]} \tag{1}$$

Under the given experimental conditions, only $CdX_n^{(n-2)-}$ species partition into the PEG-rich phase (the extractants concentration is $10^2$ times larger than that of Cd(II) and the formation of intermediary cadmium halide species can be neglected). In addition, it is reasonable to assume that $[Cd(SO_4)_2^{2-}]_{PEG} << [CdX_n^{(n-2)-}]_{PEG}$, since the number of metal ions extracted into the PEG-rich phase is lower in the absence of extracting agent.

On the other hand, in salt-rich phase, the $SO_4^{2-}$ concentration is more higher than that of the added halide ions and considering the comparable values of the stability constants for $Cd(SO_4)_2^{2-}$ and cadmium halide species, it can be assumed that the predominant Cd(II) species in this phase is $Cd(SO_4)_2^{2-}$.

Based on these observations, Eq. (1) can be rewritten as:

$$D_{Cd} = \frac{[CdX_n^{(n-2)-}]_{PEG}}{[Cd(SO_4)_2^{2-}]} = \\ = \frac{1}{\beta_{Cd(SO_4)_2^{2-}}[SO_4^{2-}]^2} \frac{\beta_{CdX_n^{(n-2)-}} D_{CdX_n^{(n-2)-}}}{(D_{X^-})^n}[X^-]_{PEG}^n \tag{2}$$

where: $n$ is the number of halide ions from the extracted species and $K_{\text{ex}}$ is the extraction constant, which is given by the expression:

$$K_{\text{ex}} = \frac{1}{\beta_{\text{Cd(SO}_4)_2^{2-}}[\text{SO}_4^{2-}]^2} \frac{\beta_{\text{CdX}_n^{(n-2)-}} D_{\text{CdX}_n^{(n-2)-}}}{(D_{\text{X}^-})^n} \tag{3}$$

In the given aqueous two-phase system, where $[\text{SO}_4^{2-}]$ is constant and, for a particular metal ion, the term: $\beta_{\text{Cd(SO}_4)_2^{2-}}[\text{SO}_4^{2-}]^2$ is also constant, the "conditional extraction constant" ($K_{\text{ex}}'$) has the expression:

$$K_{\text{ex}}' = K_{\text{ex}} \beta_{\text{Cd(SO}_4)_2^{2-}}[\text{SO}_4^{2-}]^2 = \frac{\beta_{\text{CdX}_n^{(n-2)-}} D_{\text{CdX}_n^{(n-2)-}}}{(D_{\text{X}^-})^n} \tag{4}$$

Eq. (2) indicates that the slope of a log–log plot of $D_{\text{Cd}}$ against $[\text{X}^-]_{\text{PEG}}$, will give the number of halide ions associated with Cd(II) in the extracted species and the straight line intercept gives the "conditional extraction constant". The dependences of log $D_{\text{Cd}}$ *vs.* log $[\text{X}^-]_{\text{PEG}}$ for the two studied media are presented in Figs. 3 and 4.

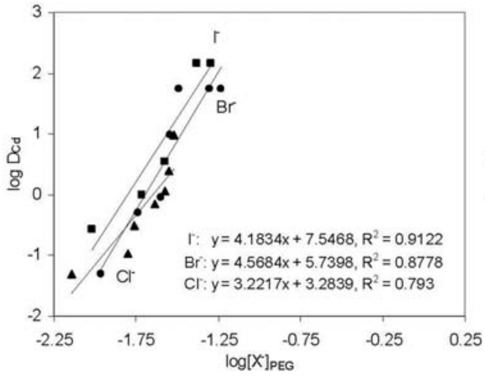

Fig. 3. The log $D_{\text{Cd}}$ *vs.* log $[\text{X}^-]_{\text{PEG}}$ dependence for the salt stock solution of pH 3.03.

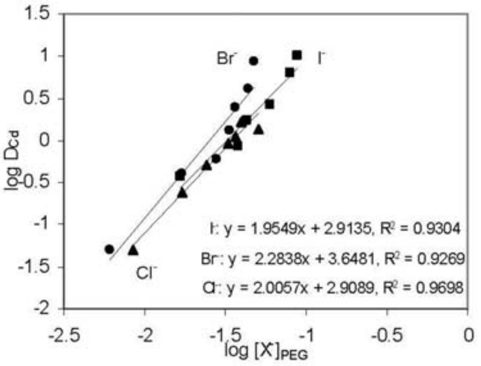

Fig. 4. The log $D_{\text{Cd}}$ *vs.* log $[\text{X}^-]_{\text{PEG}}$ dependence for the salt stock solution of pH 4.65.

It should be observed that the slope of the obtained straight lines depends on the pH value of salt stock solution. Decreasing the pH of salt stock solution resulted in an increase of the number of halide ions in the extracted species from 2 to 4. In the presence of $H_2SO_4$ (pH 3.03), Cd(II) is predominantly extracted as anionic complexes ($\text{CdX}_4^{2-}$), while in the absence of $H_2SO_4$ (the salt stock solution with pH 4.65), the main extracted species are neutral halides ($\text{CdX}_2$). A different behaviour was observed in case of Cd(II) extraction with chloride ions, when at pH 3.03 the probable extracted species is $\text{CdCl}_3^-$ and not $\text{CdCl}_4^{2-}$, as in case of $\text{I}^-$ or $\text{Br}^-$ extractants. This difference is probably due to the higher stability constant of $\text{CdCl}_3^-$ ($\log \beta_{\text{CdCl}_3^-} = 2.4$) than of $\text{CdCl}_4^{2-}$ ($\log \beta_{\text{CdCl}_4^{2-}} = 1.35$).[23]

The extraction of cadmium halide anionic complexes in case of the systems with pH 3.03 (prepared in the presence of $H_2SO_4$), had higher stability and lower hydration, as determined by the accentuated hydrophobicity of the PEG-rich phase of these systems. In case of systems with salt stock solution of pH 4.65 (in the absence of $H_2SO_4$), in which the polymeric phase had a lower hydrophobicity, the formation of such anionic complexes was not necessary, the neutral molecules $CdX_2$ being sufficient.

Using the Cd(II) species found to be extracted, the "conditional extraction constants" were calculated according to Eq. (4). These are compared with those obtained from the straight-line intercept (Figs. 3 and 4) in Table II.

TABLE II. The $\log K_{ex}^{'}$ values in case of Cd(II) extraction in presence of halide ions, in the considered aqueous two-phase system

| Halide ion | Salt stock solution pH | Extracted species | $\log \beta_{\mathrm{CdX}_n^{(n-2)-}}$ [23] | $\log K_{ex}^{'}$ (Graphic, Figs. 3 and 4) | $\log K_{ex}^{'}$ (Calculated, Eq. (4)) |
|---|---|---|---|---|---|
| $I^-$ | 3.12 | $CdI_4^{2-}$ | 6.10 | 7.546 | 7.327 |
|  | 4.53 | $CdI_2$ | 3.04 | 2.913 | 3.097 |
| $Br^-$ | 3.12 | $CdBr_4^{2-}$ | 2.93 | 5.738 | 5.506 |
|  | 4.53 | $CdBr_2$ | 3.92 | 3.648 | 3.621 |
| $Cl^-$ | 3.12 | $CdCl_3^-$ | 2.41 | 3.284 | 3.411 |
|  | 4.53 | $CdCl_2$ | 2.74 | 2.908 | 2.783 |

The agreement of the "conditional extraction constants" obtained graphically and calculation shows that the extraction of Cd(II) in presence of halide ions in the aqueous PEG (1550)–$(NH_4)_2SO_4$ two-phase system can be satisfactory described by the elementary equilibria given in Table I and by the approximations presented above.

The obtained experimental results indicate that the efficiency of Cd(II) extraction in the aqueous PEG (1550)–$(NH_4)_2SO_4$ two-phase system depended on both the acidity of the salt stock solution used for the preparation of the aqueous two-phase system (which influenced the hydrophobicity of the PEG-rich phases[24] and, thus, the nature of the extracted species) and the stability of the chemical species formed between Cd(II) and the halide ions extractants.

The efficiency Cd(II) extraction increased in the order: $Cl^- < Br^- < I^-$, corresponding to the increasing stability of the cadmium halides (Figs. 5 and 6). Although, this dependence cannot be considered a linear one, its existence shows that the formation of extracted species plays an important role in the extraction mechanism.

A schematic representation of Cd(II) extraction in the presence of halide ions in the considered aqueous two-phase system is presented in Fig. 7. According to this, for partition Cd(II), processes which occur at the PEG-rich phase/salt-rich 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.

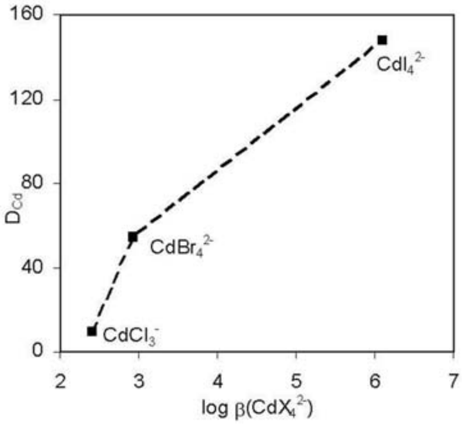

Fig. 5. Cd(II) distribution ratio *vs*. log $\beta$ values[23] for the formation of $CdX_4^{2-}$ at pH 3.03.

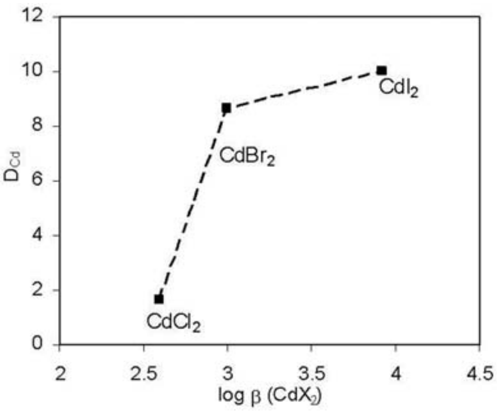

Fig. 6. Cd(II) distribution ratio *vs*. log $\beta$ values[23] for the formation of $CdX_4^{2-}$ at pH 4.65.

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 electroneutrality of the two phases.

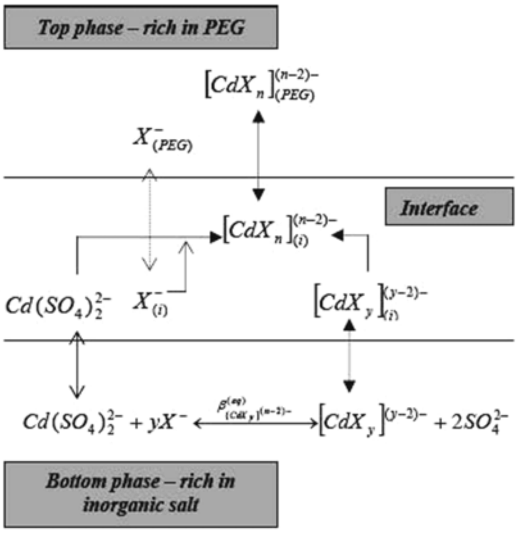

Fig. 7. Schematic representation of the main processes involved in Cd(II) extraction in the considered aqueous two--phase system.

In case of extraction of Cd(II) anionic complexes, the $SO_4^{2-}$ ions 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 environments. 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. The $NH_4^+$ cations can participate in such ionic transfer processes as counterions.

In case of neutral halide extraction, such an ionic transfer process is less important and the extraction occurs until the hydrophobicity of the PEG-rich phase is diminished by the presence of extractible species.

## CONCLUSIONS

The extraction of Cd(II) in aqueous PEG (1550)–$(NH_4)_2SO_4$ two-phase system was investigated as a function of the type and concentration of halide ions extractants, at two different values of pH of the salt stock solution.

In the absence of a suitable extracting agent, the extraction of Cd(II) was insignificant, its preference for the salt-rich phase was determined by the formation of $Cd(SO_4)_2^{2-}$ species, which are stable and with high degree of hydration. The addition of halide ions, as inorganic complexing extractants, resulted in an increase of the extraction of Cd(II) into the PEG-rich phase with increasing halide concentration, due to the formation of metal halide species, more stable than $Cd(SO_4)_2^{2-}$ and with a lower degree of hydration. The efficiency of extractants follows the order: $Cl^- < Br^- < I^-$, which is in agreement with the data from the literature.

On the other hand, the experimental results showed that the extraction of Cd(II) was more effective in the presence of $H_2SO_4$ (salt stock solution of pH 3.03), when the main extracted species were cadmium anionic halide complexes, than in the absence of $H_2SO_4$ (salt stock solution of pH 4.65), when Cd(II) was extracted predominantly as neutral molecules ($CdX_2$).

Based on the experimental results, the nature of the extracted metal species was assumed and the "conditional extraction constants" obtained from the intercepts of straight lines and by calculation were compared. The concordant values of "conditional extraction constants" indicate that the extraction of Cd(II) in the presence of halide ions was mainly determined by two factors: (1) the acidity of the salt stock solution used for the preparation of the aqueous two-phase system and (2) the stability of the extracted species.

## ИЗВОД

## Cd(II) ЕКСТРАКЦИЈА У PEG (1550)–$(NH_4)_2SO_4$ ДВОФАЗНОМ СИСТЕМУ КОРИШЋЕЊЕМ ХАЛОГЕНИДА КАО ЕКСТРАКТАНАТА

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Екстракција Cd(II) је испитивана у воденим двофазним растворима PEG–$(NH_4)_2SO_4$ који настају растварањем полимера (полиетилен гликола, PEG) и неорганске соли ($(NH_4)_2SO_4$), у присуству халогених јона. У одсуству одговарајућег екстракционог агенса, Cd(II) јон заостаје у фази која је богата солима. Додатком халогених јона Cd(II) бива екстрахован у фазу богату PEG формирајући кадмијум-халогениде. Ефикасност екстракције расте на следећи начин: $Cl^- < Br^- < I^-$. Из дистрибуционих коефицијената одређених као функције концентрације халогених јона израчунате су константе екстракције. Експериментални резултати указују на то да екстрактибилност Cd(II) у датом систему зависи од стабилности Cd(II), формираног халогенида и киселости средине.

(Примљено 30. маја, ревидирано 30. августа 2007)

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