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The Partition Behavior of Zn(II) using Halide Ions Extractants in Aqueous Peg-Based Two-Phase Systems

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Abstract: The partition behavior of Zn(II) has been studied in aqueous polyethylene glycol PEG(1550) – $(NH_4)_2SO_4$ two-phase system using halide ions (Cl^-, Br^- and I^-) as extracting agents, at two different values of salt stock solution pH. The efficiency of extractants increase in this order: $Cl^- > Br^- > I^-$. The extracted species were estimated from the distribution coefficients' values determined as a function of halide ions concentration, and the "conditional extraction constants" were calculated. The experimental results suggest that the Zn(II) partition in presence of halide ions in such systems is the result of two competitive processes. The IR spectra of solidified PEG-rich phases show that the passing of metal species into PEG-rich phases bring a supplementary water contribution, which makes the extraction process to occurs until it reaches an "equilibrium state", dependent on the hydrophobicity of these phases and not on the type of extracted metal species.

Keywords: Aqueous two-phase system, Zn(II) partition, halide ions, polyethylene glycol, $(NH_4)_2SO_4$

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INTRODUCTION

Nowadays there is a growing interest in the use of aqueous two-phase systems as a powerful but mild extraction technique for biomolecules (1–3), organic colorants (4), and toxic metal ions (5–7).

Aqueous two-phase systems consist of two immiscible aqueous phases, formed when certain water-soluble polymer (frequently polyethylene glycol, PEG) is combined with another one (dextran, ficoll) or with certain inorganic salt (i.e. Na_2SO_4, $(NH_4)_2SO_4$, Na_2CO_3, K_2HPO_4) in a specific concentration (8, 9).

In such an extraction system the metallic species partitions between the two immiscible aqueous phases easily with the hydration degree is lower. For this reason, at metal ions extraction the complexing extracting agents are required, because in the absence of extractants, the distribution coefficients are often all very low (10).

Rogers et al. (11) classifies metal ions extraction in aqueous PEG-based two-phase systems into three categories:

1. extraction by PEG-rich phase without an extracting agent
2. extraction of metal ions using inorganic anions as extractants, and
3. extraction using water-soluble organic extractants.

From these three categories, the second type of metal extraction is widely used in case of soft metal ions, which form anionic complex species with halide or pseudo-halide anions.

The use of halide ions as extracting agents in such aqueous two-phase systems is possible due both to the high solubility in water of alkaline halide salts (12) and to the lower negative hydration free Gibbs energy (13), which makes these anions to be significantly extracted into PEG-rich phases in the absence of metal ions. In addition, halide ions are not so expensive and commercially available.

According to studies from literature, in aqueous PEG -MSO_4 two-phase systems ($M = Na^+$ or NH_4^+), some metal ions (i.e. Hg(II), Cd(II), Bi(III), Pb(II)) (14–19), can be quantitatively extracted into PEG-rich phase by adding halide ions, and the extraction efficiency depends both on the PEG-rich phases' hydrophobicity and the stability of metal halide species formed in extraction systems. But, all these metal ions form in the presence of halide, chemical species which are more stable than the complex metal sulphates (20), and the higher the number of halide ions from molecules is, the more stable they become.

In case of Zn(II), the stability of this halide chemical species is lower than the complex zinc sulphate, and it decreases with the increasing number of halide ions, in this order: $ZnX^+ > ZnX_2 > ZnX_3^- > ZnX_4^{2-}$ (20). Under these conditions, the study of Zn(II) partition in the presence of halide ions, in aqueous PEG-based two-phase systems will emphasize the importance of extracted metal species stability on the extraction process and so give useful information for the design of such extraction systems for the metal ions extraction.

In this paper we have studied the partition behavior of Zn(II) in aqueous PEG(1550) – $(NH_4)_2SO_4$ two-phase system as a function of type and concentration of halide ions used as extractants. The experiments were made at two different values of salt stock solution pH, and the effect of salt stock solution acidity on the Zn(II) extraction efficiency was also discussed. The decrease of salt stock solution pH makes the PEG-rich phases of extraction systems to be more hydrophobic, and the extraction of metal species to be improved. The results have been discussed on the basis of the elementary equilibriums involved in the extraction process. The analysis of IR spectra of solidified PEG-rich phases obtained before and after metal species extraction sustains the observations from distribution studies.

EXPERIMENTAL

Materials

Polyethylene glycol PEG (1550) was purchased from Serva Fembiochema Gmb & Co and was used as received. $(NH_4)_2SO_4$, NaI, NaBr, NaCl (from Aldrich) were reagents of analytical degree and were used without further purification. The 40% (w/w) of PEG (1550) and $(NH_4)_2SO_4$ aqueous stock solutions were obtained by dissolving an appropriate mass of solid chemicals in distilled water. The different pH values (3.12 and 4.53) of $(NH_4)_2SO_4$ stock solution were obtained by adding small volumes of H_2SO_4 concentrated solution (Reactivul Bucharest), which was considered in the total solution mass.

The stock solution of 695 μg Zn(II)/cm^3 ($\sim 10^{-2}$ mol/dm^3) was prepared by the dissolving of zinc sulphate (from Aldrich) in distilled water, followed by the solution's standardization (21).

The stock solutions of extractants, containing 1 mol/dm^3 NaX ($X^- = Cl^-$, Br^- and I^-) were prepared by dissolving halide salts and diluting the known mass of halide salt to the volume with $(NH_4)_2SO_4$ salt stock solution. This approach prevents the sudden decrease of phase forming salt concentration after adding the extractants in extraction system.

Methods

For each experiment 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 different pH (3.12 and 4.53), in a glass centrifuge tube. The pH values of $(NH_4)_2SO_4$ salt stock solutions were measured with a Radelkis pH/ion-meter OK-271, equipped with a combined glass electrode. Then, 0.7 cm^3 of Zn(II) stock solution and (0.1 ÷ 0.7 cm^3) of 1 mol/dm^3 NaX ($X^- = Cl^-$, Br^- and I^-) were added. The phases were disengaged by 10 min of centrifugation at 2000 rpm and were carefully separated. Equal volumes from each phase were measured for the spectrophotometric analysis of Zn(II) with xylenol orange (22). The Zn(II) concentration (Digital S 104 D Spectrophotometer, $\lambda = 570$ nm, 1-cm glass cell) was determined in duplicate using a prepared calibration graph, and the Zn(II) distribution coefficients (D_{Zn}) were calculated as the ratio between Zn(II) concentration in PEG-rich phase to that in salt-rich phase.

The halide ions concentration from the PEG-rich phase was determined by conductometric titration (Radelkis OK-109 conductometer) using silver nitrate.

For the IR experiments, a $1.0 \div 1.5$ cm^3 from each PEG-rich phase was measured and placed on the glass slides (chemically inert). The samples were solidified at room temperature ($23 \pm 0.5°C$). The solidified blank phases, for each pH value of the salt stock solution, were obtained in the same way, except that in these systems the metal ion and extractants solutions in the aqueous two-phase systems were not added.

The IR spectra have been recording using a FTIR Bio-Rad Spectrometer, in a 400–4000 cm^{-1} spectral domain, with a resolution of 4 cm^{-1} and 32 scans, by KBr pellet technique. For the IR spectra recording, from solidified PEG-rich phases, under microscope, the portions which contain the metal extracted species were cut up. Only the spectral bands which are modified after metal ion extraction were taken into consideration.

RESULTS AND DISCUSSIONS

Although it is not considered a metal ion with a highly toxic potential, the study of Zn(II) partition in the presence of halide ions in aqueous PEG (1550) – $(NH_4)_2SO_4$ two phase system emphasizes very useful aspects in the design of such extraction systems for metal ions extraction.

As we see in a previous paper (23), in the absence of an extracting agent, the zinc ions remain predominantly in the lower salt-rich phase of the extraction system. The Zn(II) distribution coefficient obtained in this case was only 0.34 and the variation of the salt stock solution pH giving similar D_{Zn} values.

Under these conditions, the enhancement of Zn(II) extraction efficiency can be achieved by using suitable extractants, like halide ions. Comparatively, the Zn(II) distribution coefficients as a function of halide ions concentration added in extraction systems, for the two considered media are presented in Figs. 1 and 2.

As you can see from Figs. 1 and 2, in the presence of halide ions, the Zn(II) are not quantitatively extracted in halide concentration range between 0.01 and 0.07 mol/dm^3. However, the experimental results indicate the existence of a distribution maximum corresponding to 0.05 mol/dm^3 halide ions concentration, and that the D_{Zn} values are higher in case of systems with salt stock solution $pH = 3.12$ (prepared in presence of H_2SO_4), than in the case of systems with salt stock solution $pH = 4.53$

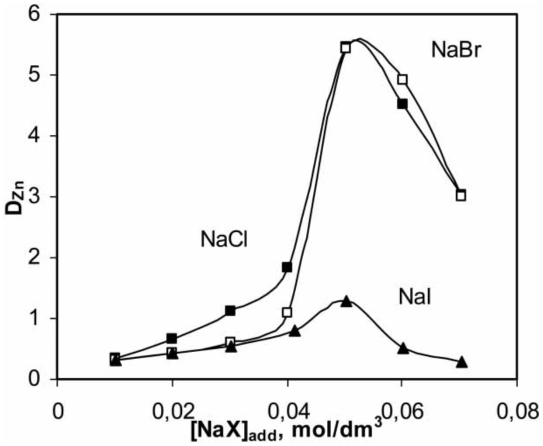

Figure 1. D_{Zn} vs. $[NaX]_{add}$, at salt stock solution pH = 3.12. The Zn(II) concentration from extraction system was 49 μg/cm^3. Temperature: 23°C.

(prepared in absence of H_2SO_4). In both cases, the Zn(II) distribution coefficients follow the order: $Cl^- > Br^- > I^-$.

The increase of halide ions concentration over 0.05 mol/dm^3 determined a decrease of Zn(II) extraction efficiency which is more pronounced in case of systems that were prepared in the absence of H_2SO_4 (salt stock solution pH = 4.53), than in the case of systems that were prepared in the presence of H_2SO_4 (salt stock solution pH = 3.12).

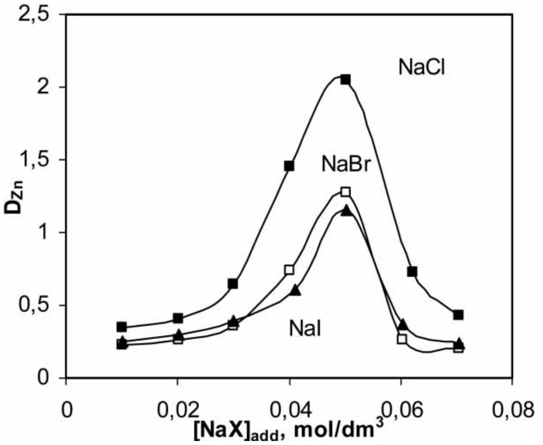

Figure 2. D_{Zn} vs. $[NaX]_{add}$, at salt stock solution pH = 4.53. The Zn(II) concentration from extraction system was 49 μg/cm^3. Temperature: 23°C.

The shape of experimental curves, presented in Figs. 1 and 2, suggest that Zn(II) extraction in PEG-rich phase is the result of two competitive processes:

1. the formation in the extraction system of easy extractible species with a lower hydration degree, obtained by Zn(II) interaction with halide ions, and
2. the formation in extraction system of the most stable chemical species, where the formation complex zinc sulphate has a important role.

Thus, if within the halide concentration range between 0.01 and 0.05 mol/dm^3, the formation of halide species process is predominant, at higher halide ions concentration this is limited by the low stability of these species. The much slower decrease of extraction parameters values at halide ions concentration higher than 0.05 mol/dm^3, in case of systems with salt stock solution pH = 3.12, compared to the systems with pH = 4.53, is probably due to some kinetics factors, determined by the distinct hydrophobicity of the PEG-rich phases.

On the basis of these experimental observations, the extraction of Zn(II) with complexing halide ions X$^-$, can be described as:

$$\mathrm{Zn^{2+} + nX^- \leftrightarrows ZnX_n^{(n-2)-}}; \quad \beta_{ZnX_n^{(n-2)-}} = \frac{[\mathrm{ZnX_n^{(n-2)-}}]}{[\mathrm{Zn^{2+}}]\cdot[\mathrm{X^-}]^{n}} \tag{1}$$

$$\mathrm{ZnX_n^{(n-2)-} \leftrightarrows (ZnX_n^{(n-2)-})_{PEG}}; \quad \mathrm{D}_{\mathrm{ZnX_n^{(n-2)-}}} = \frac{[\mathrm{ZnX_n^{(n-2)-}}]_{\mathrm{PEG}}}{[\mathrm{ZnX_n^{(n-2)-}}]} \tag{2}$$

where: $\beta_{\mathrm{ZnX_n^{(n-2)-}}}$ and $\mathrm{D}_{\mathrm{ZnX_n^{(n-2)-}}}$ represent the stability constant and the distribution coefficient on zinc extracted species. Here, the chemical species in the PEG-rich phase are denoted by the subscript "PEG", while that in the salt-rich phase is given without subscript.

On the other hand, the $\mathrm{SO_4^{2-}}$ ions can form complex species with $\mathrm{Zn^{2+}}$ and these species cannot be neglected, especially in the salt-rich phase:

$$\mathrm{Zn^{2+} + 2\,SO_4^{2-} \leftrightarrows Zn(SO_4)_2^{2-}}; \quad \beta_{Zn(SO_4)_2^{2-}} = \frac{[Zn(SO_4)_2^{2-}]}{[Zn^{2+}]\cdot[SO_4^{2-}]^2} \tag{3}$$

$$\mathrm{Zn(SO_4)_2^{2-} \leftrightarrows (Zn(SO_4)_2^{2-})_{PEG}}; \quad \mathrm{D}_{\mathrm{Zn(SO_4)_2^{2-}}} = \frac{[\mathrm{Zn(SO_4)_2^{2-}}]_{\mathrm{PEG}}}{[\mathrm{Zn(SO_4)_2^{2-}}]} \tag{4}$$

Under these conditions, the Zn(II) distribution coefficient, defined as the ratio of Zn(II) concentration in the PEG-rich phase to that in the $\mathrm{(NH_4)_2SO_4}$-rich phase, is given by the relation:

$$\mathrm{D_Zn} = \frac{[\mathrm{Zn(SO_4)_2^{2-}}]_{\mathrm{PEG}} + \sum[\mathrm{ZnX_i^{(i-2)-}}]_{\mathrm{PEG}}}{[\mathrm{Zn^{2+}}] + [\mathrm{Zn(SO_4)_2^{2-}}] + \sum[\mathrm{ZnX_j^{(j-2)-}}]} \tag{5}$$

In the conditions of extraction system preparation, where the SO_4^{2-} concentration is higher (3.5 mol/dm^3) than the added halide ions concentration (maximum 0.07 mol/dm^3), by comparing the stability constants for complex zinc sulphate and zinc halide species (20), we can say that in the salt-rich phase, the $Zn(SO_4)_2^{2-}$ species are predominant.

On the other hand, due to the relatively low values of distribution coefficients obtained experimental in the case of Zn(II) extraction with halide ions, in the PEG-rich phase of extraction system besides the $ZnX_n^{(n-2)-}$ species (the formation of intermediary zinc halide species can be neglected due to high excess of added extracting agent: $\sum [ZnX_i^{(i-2)-}]_{PEG} = [ZnX_n^{(n-2)-}]_{PEG}$), the presence of $Zn(SO_4)_2^{2-}$ species must be considered too; even their weight is smaller due to the hydration properties of complex zinc sulphate.

On the basis of these work approximations, Eq. (5) can be rewritten:

$$D_{Zn} = \frac{[Zn(SO_4)_2^{2-}]_{PEG} + [ZnX_n^{(n-2)-}]_{PEG}}{[Zn(SO_4)_2^{2-}]}$$

$$= K_{ex} \cdot \frac{1}{\beta_{Zn(SO_4)_2^{2-}} \cdot [SO_4^{2-}]^2} \cdot [X^-]^n_{PEG} \tag{6}$$

where: K_{ex} represents the extraction constant.

For a given metal ion, in considered aqueous two-phase systems, where the SO_4^{2-} concentration is not modified, and the term: $\beta_{Zn(SO_4)_2^{2-}} \cdot [SO_4^{2-}]^2 =$ constant and Eq. (6) becomes:

$$D_{Zn} = K'_{ex}[X^-]^n_{PEG} \tag{7}$$

where:

$$K'_{ex} = K_{ex}/\beta_{Zn(SO_4)_2^{2-}} \cdot [SO_4^{2-}]^2 \tag{8}$$

and it represents the "conditional extraction constant," which includes the constants of elementary equilibriums involved in Zn(II) extraction process.

The logarithmic form of the "conditional extraction constant" is given by:

$$\log K'_{ex} = \log\ \beta_{Zn(SO_4)_2^{2-}} + \log \frac{D_{ZnX_n^{(n-2)-}} \cdot \beta_{ZnX_n^{(n-2)-}}}{(D_{X^-})^n} \tag{9}$$

The D_X^- represents the distribution coefficient of the halide, in the absence of metal ion, between the two aqueous phases.

Equation (7) indicates that the slope of the logarithmic dependency between D_{Zn} and $[X^-]_{PEG}$ will indicate the number of X^- ions per metal ion from extracted species and the straight line intercept will make it possible to determine the "conditional extraction constant", in each case. In Figs. 3 and 4, are presented the dependences between log D_{Zn} and log $[X^-]_{PEG}$ for the two considered values of salt stock solution pH.

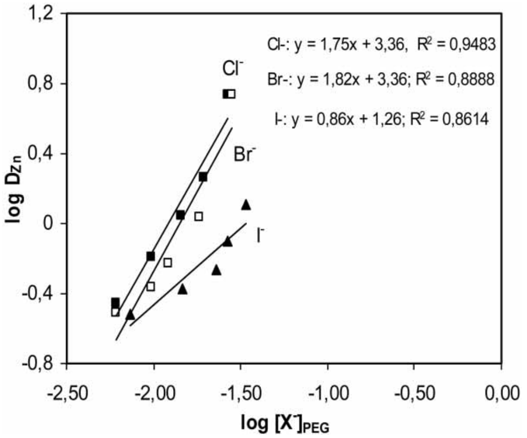

Figure 3. The log D_{Zn} vs. log $[X^-]_{PEG}$ dependency, at salt stock solution pH = 3.12.

It can be seen that the decrease of salt stock solution pH determined an increase of halide ions number from extracted species. Thus, in case of systems prepared by H_2SO_4 addition (salt stock solution pH = 3.12), the main extracted species are neutral molecules (ZnX_2), while in case of systems with salt stock solution pH = 4.53 (in absence of H_2SO_4), zinc ions are extracted, predominantly as cationic species (ZnX^+).

Even if the PEG-rich phase of extraction system has a more pronounced hydrophobicity (in case of systems with salt stock solution pH = 3.12), the low stability of zinc anionic species (ZnX_3^- or ZnX_4^{2-}) (20) makes that in these phases, only the neutral molecules (ZnX_2) which are more stable, are extracted. In addition, due to the low number of halide ions from extracted

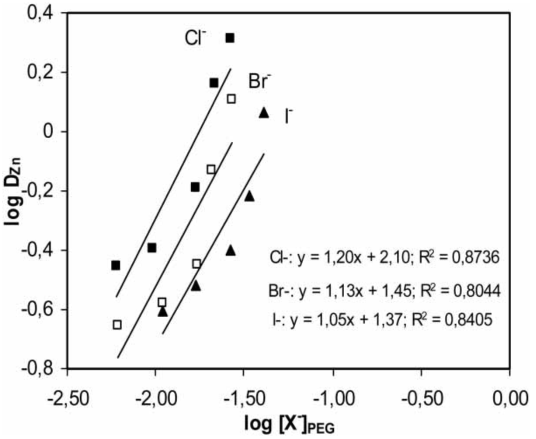

Figure 4. The log D_{Zn} vs. log $[X^-]_{PEG}$ dependency, at salt stock solution pH = 4.53.

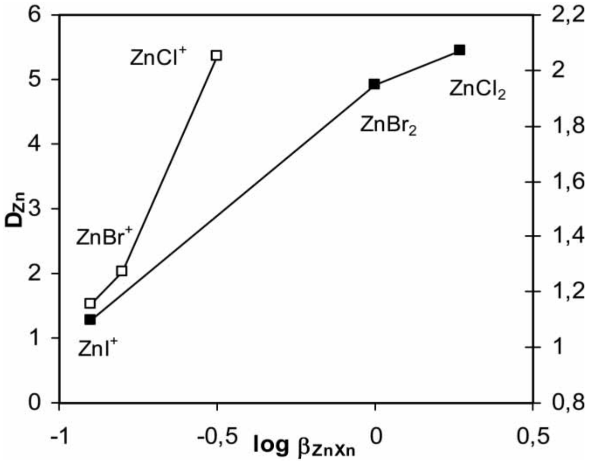

Figure 5. The Zn(II) distribution coefficient vs. log β values (19), of extracted metal species.

species, the hydration degree of these species is relatively high and the obtained values of extraction are not very high. These observations are evident in case of Zn(II) extraction with iodide ions, when for both pH values of the salt stock solution, the extracted species are the same ZnI^+, and the D_{Zn} values are close.

Under these conditions, it is obvious that the Zn(II) partitioning in the presence of halide ions takes place in the following order: $Cl^- > Br^- > I^-$, similarly to the decrease of stability of zinc halide species (Fig. 5).

Using estimated extracted species of zinc for each case, the "conditional extraction constants" have been calculated with Eq. (9). Comparatively, the values of "conditional extraction constants" obtained by calculation and graphically from straight line intercept (Figs. 3 and 4) are summarized in Table 1.

Table 1. The log K'_{ex} values in case of Zn(II) extraction in presence of halide ions, in considered aqueous two-phase system

Halide ion	Salt stock solution pH	Extracted species	log $\beta_{CdX_n^{(n-2)-}}$(19)	log K'_{ex} (graphic-Fig. 3 and 4)	log K'_{ex} (calcul-Eq. 9)
I^-	3.12	ZnI^+	−0.90	1.26	1.59
	4.53	ZnI^+	−0.90	1.37	1.22
Br^-	3.12	$ZnBr_2$	0.00	3.36	3.22
	4.53	$ZnBr^+$	−0.80	1.45	1.49
Cl^-	3.12	$ZnCl_2$	0.27	3.36	3.60
	4.53	$ZnCl^+$	−0.16	2.10	2.09

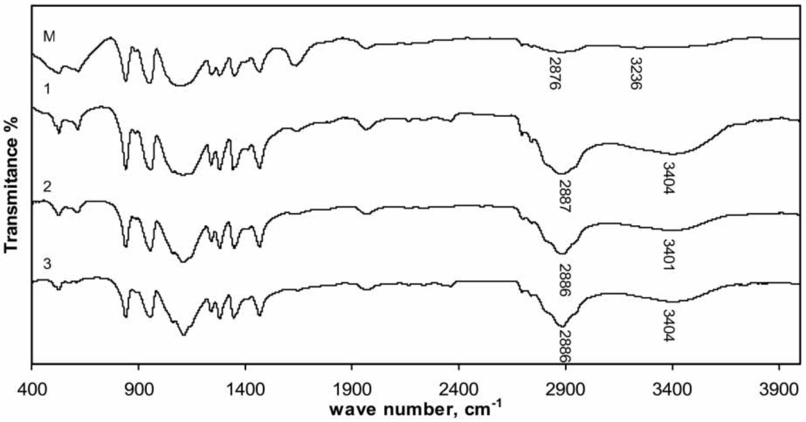

Figure 6. The IR spectra of solidified PEG-rich phases before (M) and after Zn(II) extraction with chloride ions (1); bromide ions (2) and iodide ions (3), at pH = 3.12. ($Zn_i = 49\ \mu g/cm^3$, $[I^-]_{add} = 0.06\ mol/dm^3$).

The concordant values of the "conditional extraction constant" obtained in these two ways indicate that Zn(II) extraction in the presence of halide ions in aqueous PEG(1550)–$(NH_4)_2SO_4$ two-phase system can be satisfactorily described using elementary equilibriums and the work approximations which were presented above.

The Zn(II) extraction in the presence of halide ions in considered aqueous two-phase systems is mainly governed by the difference of hydrophobicity

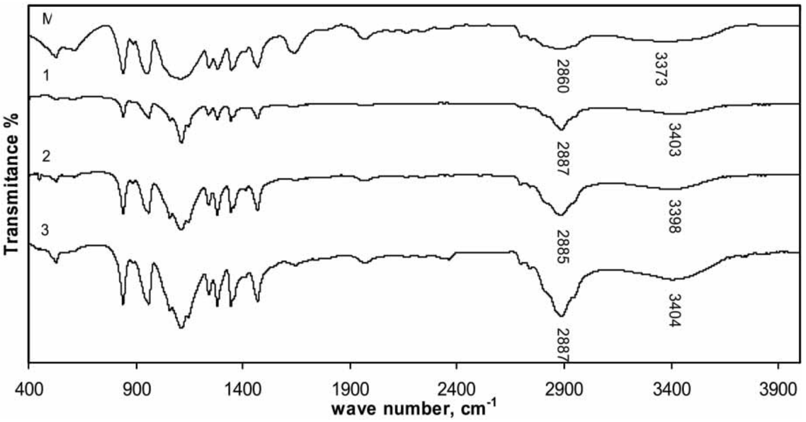

Figure 7. The IR spectra of solidified PEG-rich phases before (M) and after Zn(II) extraction with chloride ions (1); bromide ions (2) and iodide ions (3), at pH = 4.53. ($Zn_i = 49\ \mu g/cm^3$, $[I^-]_{add} = 0.06\ mol/dm^3$).

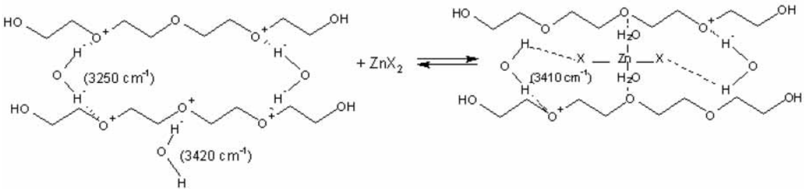

Figure 8. The "fixation" way of zinc extracted species in PEG-rich phases, according with the IR spectra.

between the two immiscible phases, and lesser by the type of metal species formed in extraction system.

These observations are sustained and by IR spectra of solidified PEG-rich phases before and after zinc extraction (Figs. 6 and 7). The comparison of these spectra show that after metal ion extraction, no supplementary bands appear, for none of the salt stock solution pH, which means that in Zn(II) extraction process, the complexation equilibriums between metal species and PEG molecules are not involved.

The most important changes in IR spectra are situated in the high wave number region, where the O-H stretching associated with the water molecules hydrogen-bonded on the polymer chains and the C-H stretching from ethylene radicals appears.

The analysis of IR spectra show that, even if in the blank phases (M) these bands are situated at a different wave number in function of the salt stock solution pH, after metal species extraction, they are moved to a high wave number, almost the same, for both considered media.

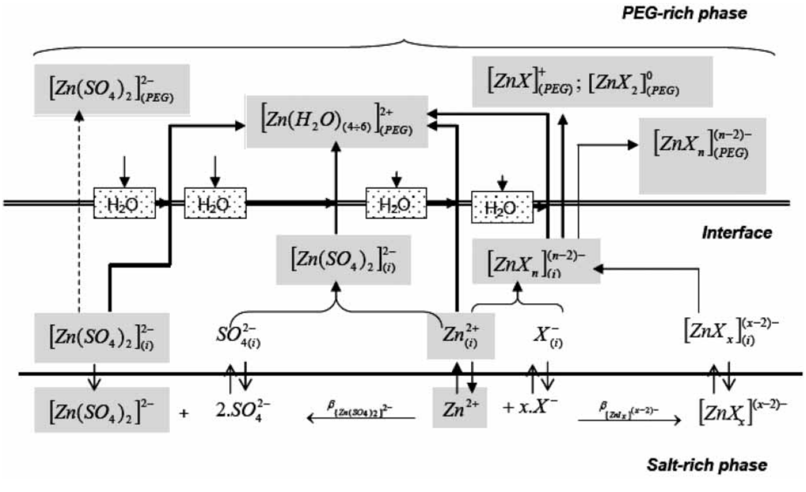

Figure 9. The schematic representation of the main processes involved in Zn(II) extraction with halide ions, in the considered aqueous two-phase system.

These changes from IR spectra suggest that in case of metal species extraction in PEG-rich phase, a supplementary water contribution in this phase is brought (due both to the high negative hydration free Gibbs energy of zinc ions and low stability of zinc halide species formed in extraction system). As a consequence, the change of water molecules binding way (24) takes place and the "relaxation" of the interactions between polymer chains occurs (Fig. 8).

Figure 9 represents a schematic model, based on the main processes involved in Zn(II) extraction with halide ions, in considered aqueous two-phase system. The passing of metal species into PEG-rich phase of extraction system bring a supplementary water contribution, which make that the extraction process to occur until a "equilibrium state" is attained, which depends on the hydrophobicity of the two aqueous phases and not on the type of extracted metal species.

CONCLUSIONS

Although it is not considered a metal ion with high toxicity, the study of Zn(II) partitioning in aqueous PEG(1550) – $(NH_4)_2SO_4$ two-phase system using halide ions as extracting agents evidenced some useful aspects in the design of such extraction systems for metal ions extraction.

The experiments took place at two different pH values of salt stock solution, in a halide concentration range between 0.01 and 0.07 mol/dm^3. In the presence of halide ions as extracting agents, the Zn(II) is not quantitatively extracted in the considered aqueous two-phase system. However, the experimental results indicate the existence of distribution maximum corresponding to 0.05 mol/dm^3, and that D_{Zn} values are higher in case of systems with salt stock solution $pH = 3.12$, than in the case of systems with salt stock solution $pH = 4.53$. The efficiency of extractants follows the order: $Cl^- > Br^- > I^-$.

The increase of halide ions' concentration over 0.05 mol/dm^3 determined a decrease of Zn(II) extraction efficiency, more pronounced in case of systems with salt stock solution $pH = 4.53$, than in the case of systems with salt stock solution $pH = 3.12$.

The shape of distribution curves suggests that the Zn(II) extraction into PEG-rich phase in presence of halide ions is the result of two competitive processes:

1. the formation in extraction system of zinc halide species, easy extractible due to the low hydration degrees, and
2. the formation within the extraction systems of the most stable zinc chemical species, where the formation of complex zinc sulphate plays an important role.

On the basis of experimental results the metal extracted species were estimated and the "conditional extraction constants," obtained from straight line intercepts and by calculation, were compared for each case.

The IR spectra of solidified PEG-rich phases obtained before and after Zn(II) extraction with halide ions, indicate that the passing of extracted species into PEG-rich phase bring a supplementary water contribution which makes the extraction process to occurs until a "equilibrium state," which depends on the hydrophobicity of the two phases and not on the type of the extracted species.

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