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Hg (II) extraction in a PEG-based aqueous two-phase system in the presence of halide ions. I. Liquid phase analysis

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Abstract: The partition behaviour of Hg (II) was studied in an aqueous polyethylene glycol (PEG) – $(NH_4)_2SO_4$ two-phase system as a function of halide, halide concentration, and pH. For a system prepared by mixing equal volumes of 40 % (w/w) PEG (1550) with 40 % (w/w) $(NH_4)_2SO_4$, Hg(II) remains almost exclusively in the salt-rich phase. The addition of NaX (X = Cl^-, Br^-, I^-) enhances Hg (II) partition into the PEG-rich phase due to the formation of halide complexes. The efficiency of halide extractants increases in the order: $Cl^- < Br^- < I^-$. Mercury extraction is improved at lower halide ion concentration by higher stock salt solution acidity. From the distribution coefficients determined as a function of halide ion concentration, the extracted species were identified. The Hg (II) extractability is determined by the type and stability of the Hg (II) halide species, and depends on the stock salt solution acidity. The observed behaviour is discussed and a possible extraction mechanism is proposed.

Keywords: Extraction, aqueous two-phase system, polyethylene glycol, mercury, halide ions

1 Introduction

Solvent extraction is one of the techniques for separation and selective recovery of metal ions most widely applied in industry [1]. In general, metal ions are extracted from aqueous solutions into organic solvents (water-immiscible) by using a suitable extracting agent

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[2–4]. However, most of the solvents employed are toxic, inflammable, volatile and have caused environmental problems.

In recent years, aqueous two-phase systems have proved efficient extractants for metal ion separations and other applications [5]. These systems are formed by mixing a water-soluble polymer (*i.e.* polyethylene glycol, PEG) and an inorganic salt (*i.e.* Na_2SO_4, $(NH_4)_2SO_4$, K_2HPO_3, Na_2CO_3) in specified concentrations [6, 7]. The resulting systems are composed of two immiscible aqueous phases: an upper one rich in PEG, which fills the role of the organic phase in traditional extraction systems, and a lower one rich in inorganic salt.

These extraction systems offer several unique advantages over traditional systems including: (1) polyethylene glycol is non-toxic, non-inflammable, non-volatile, inexpensive, commercially available, and biodegradable; (2) no organic solvent is necessary for phase separation; and (1) extraction selectivity can be ensured by using water-soluble extractants such as halide ions. Thus, aqueous two-phase systems are considered a "green" extraction technique [7, 8].

In aqueous PEG-based two-phase systems, metal partitions between two aqueous phases. Extraction is determined by the different physicochemical properties of the phases, manifested as different hydration environments [9]. Thus, for a metal species to partition from the salt-rich phase (having a well ordered hydration environment due to the strong hydrogen bonds) into a PEG-rich phase (with a less ordered hydration environment) it must not interact strongly with water.

Some soft metal ions (Cd(II), Tl(I), Bi(III), Zn(II), Cu(II), Fe(III), etc.) can be extracted into a 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 [5, 10–14]. However, few studies have clarified the extracted metal species and the elementary processes involved [11, 12].

In this paper, we investigate the partition behaviour of Hg (II) ions in an aqueous PEG (1550) – $(NH_4)_2SO_4$ two-phase system in the presence of halide ions (Cl^-, Br^-, I^-). Hg (II) partition was studied as a function of type and concentration of halide extractant at three different values of salt stock solution pH. The results are discussed in terms of the elementary equilibria involved.

2 Experimental

2.1 Materials

The polyethylene glycol used in this study was PEG (1550), purchased from Serva Feinbiochema Gmb. & Co. All inorganic salts: $(NH_4)_2SO_4$, NaI, NaBr, NaCl (from Aldrich) were of analytical-reagent grade and used without purification. Stock 40% PEG was prepared by the addition of the appropriate mass of water. Stock 40% $(NH_4)_2SO_4$ was prepared similarly, and the three different pH values (3.12; 4.53 and 7.12) were obtained by adding small volumes of concentrated H_2SO_4 or NH_3 (Reactivul Bucharest), which

were taken into account in the total solution mass. The halide solution, containing 1M NaX (X^- = Cl^-, Br^- or I^-) was obtained by dilution of sodium halide to volume with stock salt solution. This approach gives a systematic decrease in the concentration of phase-forming salt as the halide concentration increases. The 1300 μg Hg(II)/mL solution was prepared by dissolving mercury (II) nitrate (Fluka) in distilled water followed by standardization [15].

2.2 Methods

The pH of the $(NH_4)_2SO_4$ stock solution was measured with a Radelkis OK-271 pH/ionmeter equipped with a combined glass electrode.

The Hg (II) distribution coefficients were determined in the following manner: for each experiment an aqueous two-phase system was prepared by mixing equal volumes of PEG stock solution and $(NH_4)_2SO_4$ stock solution (with selected pH) in a glass centrifuge tube. Hg (II) stock solution (0.5 mL) and 1M NaX solution (0.1-0.7 mL) were added. The system was mechanically shaken for 2 min., followed by 10 min. of centrifugation at 2000 rpm. Just before analysis, the phases were carefully separated using Pasteur pipettes and placed in separate tubes. Equal volumes (1.0 mL) from each phase were taken for Hg(II) spectrophotometric analysis using methylene blue - thymol. The absorbance of the green complex was measured at 610 nm using a Digital S 104 D spectrophotometer in a 1-cm glass cell against a distilled water reference [16]. The Hg (II) content in each phase was determined in duplicate, using a prepared calibration graph. The halide (Cl^-, Br^- or I^-) concentration in the PEG-rich phase was determined by conductometric titration with $AgNO_3$, using a Radelkis OK-109 conductivity meter.

3 Results and discussion

Using the phase equilibrium studies of PEG-inorganic salt systems [17, 18], the concentrations for the PEG (1550) – $(NH_4)_2SO_4$ aqueous two-phase system have been selected so that the system will remain biphasic. Ammonium sulphate was chosen because it exerts a strong salting-out effect on PEG, it has high solubility in water ($S^{20^\circ C}$ = 75.4 g/100 g water) [19], the phases separate rapidly, and the phase interface is clear. Thus we can prepare an efficient extraction system.

In a previous paper [20], we have shown that in the absence of suitable extracting agents, Hg (II) remains principally in the salt-rich phase, regardless of the stock salt solution acidity. The low values of the distribution coefficients (0.483; 0.372; 0.392 for pH = 3.12; 4.53 and 7.12 respectively) suggest that Hg (II) extraction does not involve complexation between metal and PEG. In the aqueous two-phase system, where the SO_4^{2-} concentration is 3.45 mol/L, calculation shows that the predominant species is $Hg(SO_4)_2^{2-}$. It is obvious that the $Hg(SO_4)_2^{2-}$ species, formed from a metal ion with a highly negative Gibbs free energy of hydration ($\Delta G_{hydr.}$ = −1495 kJ/mol) [21] and an anion with a strong salting-out effect, will prefer the highly hydrating environment of

the salt-rich phase. Thus, Hg (II) extraction efficiency can be enhanced by changing the hydration properties of the mercury using a suitable extracting agent. This should have a lower hydration energy and form a more stable species with Hg (II) than $Hg(SO_4)_2^{2-}$.

Halide ions (Cl^-, Br^- or I^-) can be used as extracting agents because they have high solubility in water but lower Gibbs free energy of hydration. They partition into the PEG-rich phase significantly for all pH values of stock salt solution (Table 1), even in the absence of metal ions.

Table 1 Halide extraction percentage (E_X^- %) in the PEG (1550) – $(NH_4)_2SO_4$ aqueous two-phase system in the absence of metal ions.

Salt stock solution pH	E_X^- %		
	Cl^-	Br^-	I^-
3.12	49.53	52.53	60.55
4.53	45.23	52.36	76.70
7.12	43.52	51.53	70.21

Hg (II) ions are known to form very stable anionic complexes with halide ions, so the enhanced Hg (II) extractability with halide addition can be attributed to the formation of such extractible species.

The use of halide ions (Cl^-, Br^- or I^-) as extracting agents was investigated by studying the Hg (II) partitioning behavior as a function of several experimental parameters: initial concentration of Hg (II), stock salt solution acidity, and the type and concentration of halide.

The influence of Hg (II) initial concentration was studied over the range 30 - 70 μg Hg(II) /mL (Fig. 1). As shown in Fig. 1, the Hg (II) extracted into the PEG-rich phase at constant iodide concentration (0.06 mol/L) increases with increasing initial metal ion concentration.

On the basis of this observation and taking into account the limits of the spectrophotometric method used for Hg (II) analysis, an initial concentration of 52 μg Hg(II)/mL was selected for the distribution studies.

Within the pH range 2 – 7, the phase forming components (PEG, NH_4^+, SO_4^{2-}) are essentially uninvolved in secondary processes [22], indicating that stock salt solution pH has little effect on phase formation and separation.

Experimental results (Fig. 2) show that Hg (II) extraction efficiency is very little affected by variation in stock salt solution pH; the extraction percentages are high (95-99 %) for all pH values.

In general, a decrease in pH increases the PEG-rich phase hydrophobicity and enhances metal ion extraction [23]. However, for Hg (II) extraction this tendency is not evident, due to the high stability of the mercury-halide species formed. Thus, the extraction efficiency does not increase in systems with higher acidity. In addition, the high Hg (II) extraction efficiency at pH = 7.12 (prepared by NH_3 addition) suggests that

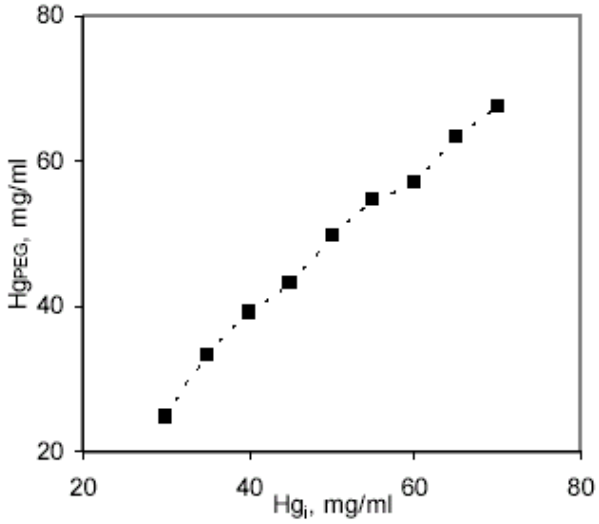

Fig. 1 The effect of initial Hg (II) concentration on extraction in the presence of iodide ions [I^-]= 0.06 mol/L; stock salt solution pH=4.53, temperature: 22 °C.

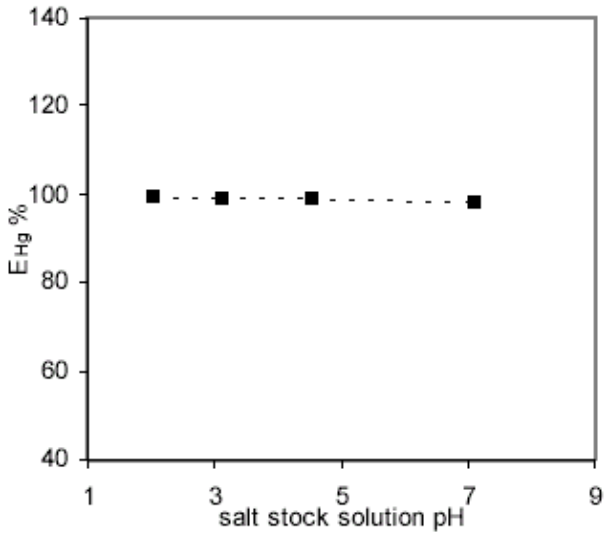

Fig. 2 The effect of stock salt solution pH on Hg (II) extraction in the presence of halide ions. The Hg (II) initial concentration was 52 μg Hg(II)/mL. [X^-] = 0.06 mol/L. Temperature: 22 °C.

protonation of PEG ether oxygen atoms is not necessary.

Fig. 3 shows the variation of Hg (II) distribution coefficient (the ratio of the Hg (II) concentration in the PEG-rich phase to that in the salt-rich phase) with NaX concentration for all three pH values. An increase in Hg (II) extraction into the PEG-rich phase with increasing halide concentration was observed for all cases.

The Hg (II) distribution coefficients follow the order: $Cl^- < Br^- < I^-$, similar to the partition behaviour of halide extractants in the absence of metal ions. This suggests that the partition equilibria of the extractants should be considered.

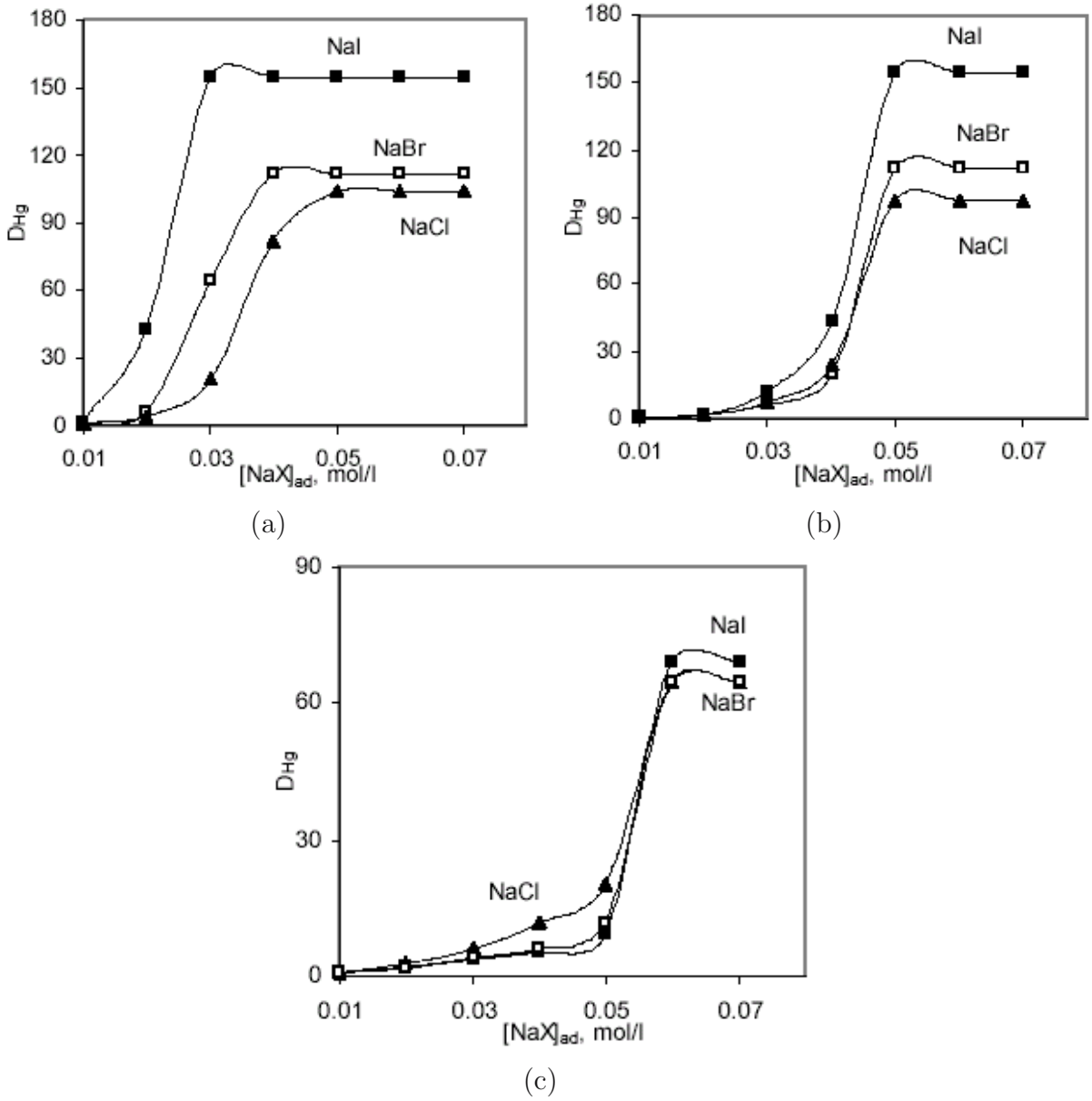

Fig. 3 Hg (II) distribution coefficient with varying halide concentration, at stock salt solution pH values: (a) 3.12; (b) 4.53; (c) 7.12. The initial Hg (II) concentration was 52 μg Hg(II)/mL. Temperature: 22 °C.

As shown in Fig. 3, in these systems Hg (II) is quantitatively extracted for all three pH values. Maximum extraction occurs at lower halide concentration when the acidity is high (Fig. 4); the order $Cl^- < Br^- < I^-$ remains the same.

Thus, with addition of H_2SO_4 (pH=3.12), maximum extraction is obtained at 0.03-0.05 mol X^-/L; for pH=4.53 (without added H_2SO_4), the halide necessary is 0.05-0.06 mol X^-/L; and for the systems with pH=7.12 (with NH_3) it is higher yet (0.06 mol X^-/L). This behavior is attributed to the increased PEG-rich phase hydrophobicity with decreased pH, which suggests that equilibria forming mercury halide species are involved.

On the basis of these experimental observations we assume that the elementary equi-

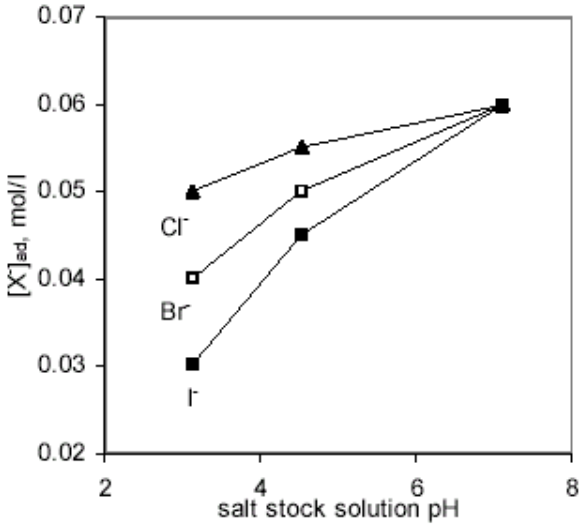

Fig. 4 Halide concentration necessary to obtain maximum extraction.

libria are those summarized in Table 2.

Under these assumptions, the Hg (II) distribution coefficient can be written:

$$D_{Hg} = \frac{[Hg(SO_4)_2^{2-}]_{PEG} + \sum [HgX_i^{(i-2)-}]_{PEG}}{[Hg^{2+}] + [HgSO_4] + [Hg(SO_4)_2^{2-}] + \sum [HgX_j^{(j-2)-}]} \quad (1)$$

Table 2 Elementary equilibria involved in Hg (II) extraction with halide ions in a PEG (1550) – $(NH_4)_2SO_4$ aqueous two-phase system.

Type of equilibrium	Reaction of equilibrium	Constant of equilibrium
Formation of Hg(II) anionic sulphates	$Hg^{2+} + 2SO_4^{2-} \leftrightarrows Hg(SO_4)_2^{2-}$	$\beta_{Hg(SO_4)_2^{2-}} = \frac{[Hg(SO_4)_2^{2-}]}{[Hg^{2+}]\cdot[SO_4^{2-}]^2}$
Formation of Hg(II) halides	$Hg^{2+} + nX^- \leftrightarrows HgX_n^{(n-2)-}$	$\beta_{HgI_n^{(n-2)-}} = \frac{[HgX_n^{(n-2)-}]}{[Hg^{2+}]\cdot[X^-]^n}$
Halide partition	$X^- \leftrightarrows (X^-)_{PEG}$	$D_{X^-} = \frac{[X^-]_{PEG}}{[X^-]}$
Hg(II) halides partition	$HgX_n^{(n-2)-} \leftrightarrows (HgX_n^{(n-2)-})_{PEG}$	$D_{HgI_n^{(n-2)-}} = \frac{[HgX_n^{(n-2)-}]_{PEG}}{[HgX_n^{(n-2)-}]}$
Hg(II) anionic sulphates partition	$Hg(SO_4)_2^{2-} \leftrightarrows (Hg(SO_4)_2^{2-})_{PEG}$	$D_{Hg(SO_4)_2^{2-}} = \frac{[Hg(SO_4)_2^{2-}]_{PEG}}{[Hg(SO_4)_2^{2-}]}$

In this table, the chemical species in the PEG-rich phase is denoted by the "PEG" subscript, while that in the salt-rich phase is given without any subscript.

Under the experimental conditions only $HgX_n^{(n-2)-}$ species partition into the PEG-rich phase (the extractant concentration is 10^2 times larger than that of Hg(II) and the formation of intermediate mercury halides can be neglected). In addition, it is reasonable to assume that: $[HgX_n^{(n-2)-}]_{PEG} \ll [Hg(SO_4)_2^{2-}]_{PEG}$, since the metal ion is poorly extracted into the PEG-rich phase in the absence of halide ions.

On the other hand, in the salt-rich phase mercury ions exist as $Hg(SO_4)_2^{2-}$. When halide ions are added HgX_2 molecules are probably formed in this phase. These are more stable than $Hg(SO_4)_2^{2-}$ and are hydrated well enough to exist in the salt-rich phase.

Therefore, eq. (1) can be rewritten as:

$$D_{Hg} = \frac{[HgX_n^{(n-2)-}]_{PEG}}{[HgX_2]} = \frac{\beta_{HgX_n^{(n-2)-}}}{\beta_{HgX_2}} \cdot \frac{D_{HgX_n^{(n-2)-}}}{(D_{X^-})^n} \cdot [X^-]_{PEG}^n = K_{ex} \cdot [X^-]_{PEG}^n \quad (2)$$

where: K_{ex}= extraction constant, given by the expression:

$$K_{ex} = \frac{\beta_{HgX_n^{(n-2)-}}}{\beta_{HgX_2}} \cdot \frac{D_{HgX_n^{(n-2)-}}}{(D_{X^-})^n} \quad (3)$$

n = total number of halide ions in the extracted species.

Eq. (2) indicates that the slope of a log-log plot of D_{Hg} against $[X^-]_{PEG}$ will give the number of halide ions associated with Hg(II) in the extracted species, and the straight line intercept (log K_{ex}) gives the extraction constant.

Fig. 5 shows the log D_{Hg} vs log $[X^-]_{PEG}$ dependences for all three pH values. For systems with pH=4.53 and 7.12, the main extracted species are the HgX_3^- anionic complex. In the presence of H_2SO_4 (pH=3.12), Hg (II) is extracted by I^- and Br^- predominantly as HgX_4^{2-}. A different behavior is observed in Hg (II) extraction with Cl^- at pH=3.12. The extracted species is $HgCl_3^-$ and not $HgCl_4^{2-}$, as with I^- or Br^- extractants. This is probably due to the lower difference of stability of the two species ($\log\beta_{HgCl_3^-}$= 14.07; $\log\beta_{HgCl_4^{2-}}$=15.07) [24].

For pH=3.12, the increased PEG-rich phase hydrophobicity ensures the extraction of HgX_4^{2-}species, which have high stability and lower hydration. Where pH=4.53 and 7.12, the polymeric phases are less hydrophobic and the formation of HgX_4^{2-} complexes is not necessary, as HgX_3^- is extractible enough. This behaviour can be explained in two ways: (1) the HgX_4^{2-} complexes are too poorly hydrated and are incompatible with the PEG-rich phase, or (2) the formation of extractible species at the interface occurs step by step, until the metal ion dehydrates enough (due to complexation with halide) for the metal halide species to transfer immediately into the PEG-rich phase.

Using the Hg (II) species found to be extracted, the extraction constants were calculated according to eq. (1). These are compared with those obtained from the straight line intercept (Fig. 5) in Table 3.

The agreement of the extraction constants obtained graphically and by calculation shows that Hg (II) extraction in the presence of halide ions in the PEG (1550) – $(NH_4)_2SO_4$ aqueous two-phase system can be satisfactory described by the elementary equilibria in Table 2 using the working approximations mentioned above.

Fig. 6 shows a model of Hg (II) extraction in the presence of halide ions in the aqueous two-phase system. Anionic species formed at the interface cross into the PEG-rich phase, where they will interact, predominantly by ionic forces, with PEG ether oxygen atoms. Electroneutrality of the two aqueous phases is ensured by ionic transfer (Fig. 7). Thus,

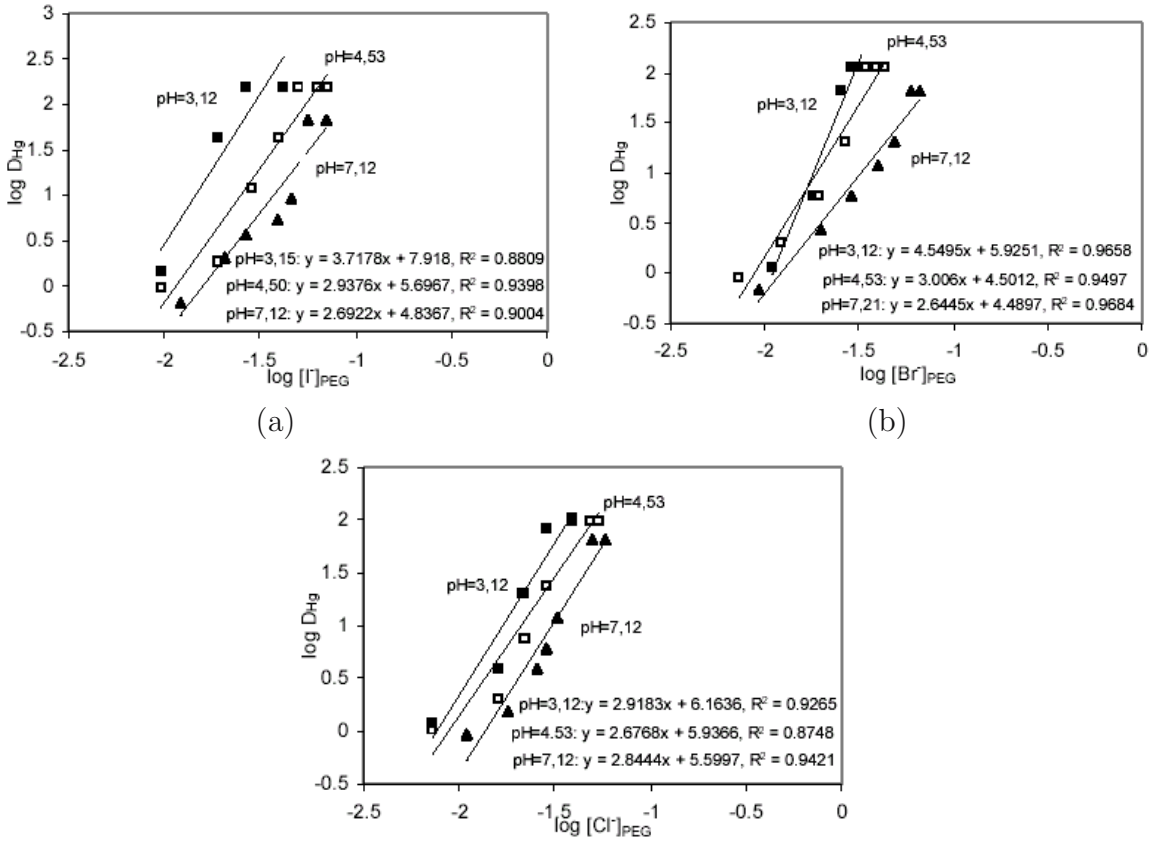

Fig. 5 Plots of log D_{Hg} vs. log $[X^-]_{PEG}$for the three stock salt solution pH values in the presence of: (a) I^-; (b) Br^-; (c) Cl^-. The Hg (II) initial concentration was 52 μg Hg(II)/mL. Temperature: 22 °C.

during extraction of Hg (II) anionic complexes, the SO_4^{2-} ions which accompanied phase separation are expelled into the salt-rich phase and the phases are kept electrically neutral.

The interaction of the extracted Hg (II) species with the PEG-rich phase will be the subject of another study using solid phase analysis.

4 Conclusions

The extraction behaviour of Hg (II) in an aqueous PEG (1550) – $(NH_4)_2SO_4$ two-phase system was investigated as a function of initial Hg (II) concentration, stock salt solution pH, and type and concentration of halide ions.

In the absence of a suitable extracting agent, Hg (II) extraction is insignificant; its preference for the salt-rich phase is due to the formation of highly hydrated $Hg(SO_4)_2^{2-}$ The addition of halide ions as inorganic complexing extractants increased Hg (II) partition into the PEG-rich phase, due to the formation of stable and less hydrated metal halide complexes. Under these conditions, for a given initial concentration of Hg (II) (52 μg Hg(II)/mL), the extraction efficiency increases with increasing halide concentration and

Table 3 Log K_{ex} values for Hg (II) extraction in the presence of halide ions.

Halide ion	Salt stock solution pH	Extracted species	log $\beta_{HgX_n^{(n-2)-}}$ [24]	log K_{ex} (graphic – Fig. 5)	log K_{ex} (calculation – eq. 3)
I^-	3.12	HgI_4^{2-}	29.83	7.918	7.806
	4.53	HgI_3^-	27.60	5.696	5.436
	7.12	HgI_3^-	27.60	4.836	5.126
Br^-	3.12	$HgBr_4^{2-}$	21.00	5.925	5.636
	4.53	$HgBr_3^-$	19.74	4.501	4.484
	7.12	$HgBr_3^-$	19.74	4.489	4.256
Cl^-	3.12	$HgCl_3^-$	14.07	6.163	6.018
	4.53	$HgCl_3^-$	14.07	5.936	5.897
	7.12	$HgCl_3^-$	14.07	5.599	5.661

$\log\beta_{HgI_2}$=23.84; $\log\beta_{HgBr_2}$=17.33; $\log\beta_{HgCl_2}$=10.12 [24].

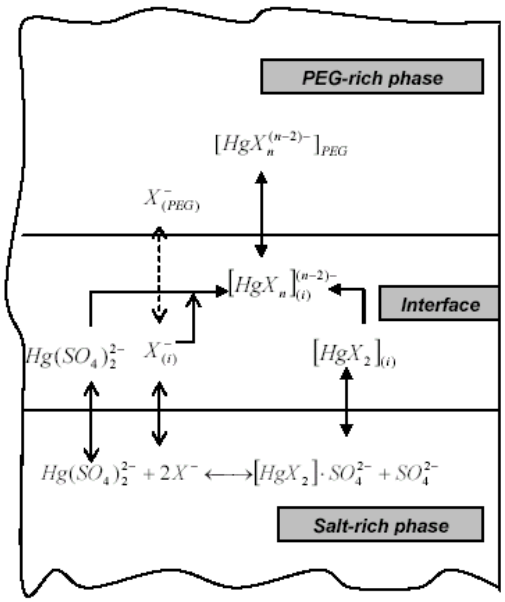

Fig. 6 Schematic representation of the main processes involved in Hg (II) partitioning in an aqueous two-phase system.

follows the order: $Cl^- < Br^- < I^-$.

The Hg (II) extractability depends on the stock salt solution pH. The higher the acidity, the lower the halide concentration that is necessary to obtain maximum extraction. The high Hg (II) extraction parameters for systems prepared by NH_3 addition (pH=7.12) suggest that protonation of PEG ether oxygen atoms is not necessary.

On the basis of experimental results the metal species extracted were determined. The extraction constants obtained from the straight line intercept and by calculation

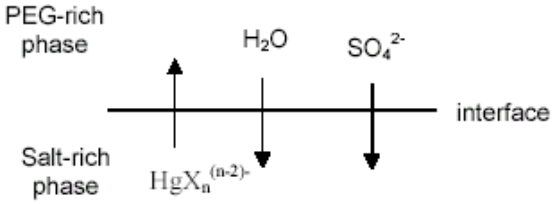

Fig. 7 Ion transfer across the interface between the two aqueous phases.

were compared. Their agreement indicates that Hg (II) extraction in the presence of halide ions, in this aqueous two-phase system, can be described to good approximation by the elementary equilibria in Table 2 and the working approximations above.

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