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USE AQUEOUS PEG-INORGANIC SALT TWO-PHASE SYSTEMS FOR Bi(III) EXTRACTION IN THE PRESENCE OF INORGANIC EXTRACTANTS

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ABSTRACT. The Bi(III) extraction behaviour was studied in aqueous polyethylene glycol (PEG) – $(NH_4)_2SO_4$ two-phase system, using inorganic anions (I^-, Br^-, Cl^- and SCN^-), as extractants. The aqueous two-phase systems were prepared using aqueous solutions of phase-forming components (PEG and $(NH_4)_2SO_4$) in water or in 1N H_2SO_4. The experimental results show that more adequate for Bi(III) extraction is the aqueous two-phase systems, where the aqueous solutions of phase-forming components are prepared in 1N H_2SO_4. Under these conditions, the addition of inorganic extractants determined the partitioning of Bi(III) into PEG-rich phase, easy observable at extractants concentration higher than 0.06 mol/dm^3. The efficiency of extractants follows the order: $I^- \gg Br^- > Cl^- \gg SCN^-$. Using the Bi(III) distribution coefficients calculated as a function of inorganic extractants concentration, the extracted species were assumed.

Keywords: aqueous PEG-based two-phase system, Bi(III) extraction, inorganic extractants

INTRODUCTION

Various conventional liquid-liquid extraction methods have been proposed for the recovery of bismuth ions, through years [1]. Its utilization at the manufacture of semiconductors, alloys and metallurgical additives, etc., are few cases where the solvent extraction can be used in order to solve environmental problems [2]. Several solvent extractions systems are mentioned for the extraction of bismuth as neutral complexes or ion-pairs, using different organic extractants [3-5]. But, the utilization of conventional extraction methods requires large volumes of organic solvents, which may cause environmental pollution, and thus are not appreciated.

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In recent years, the aqueous PEG-based two-phase systems have been suggested for several applications in metal ion recovery, particularly those formed by polyethylene glycol (PEG) and inorganic salts, as an alternative to the conventional extraction systems. These systems are formed by mixing an aqueous solution of PEG with an aqueous solution of certain inorganic salt (for example: $(NH_4)_2SO_4$, Na_2SO_4, K_2HPO_4, etc.) [6-8] and are composed by two immiscible phases, a superior one – rich in PEG, which has the role of organic phases from conventional extraction systems, and an inferior one – rich in inorganic salt. One of the main advantages of these systems is that the metal species partitioning occurs between two aqueous phases, which is an evident environmental benefit. In addition, the aqueous PEG- inorganic salt two-phase systems permit the utilization of cheaper inorganic anions (such as halide and pseudo-halide ions) as extractants, for the efficient extraction of several soft metal ions. For example, Cu(II), Co(II), Zn(II) and Fe(III) are extracted in presence of SCN^- ions at high acidity of salt stock solution [9-11]. Also, iodide ions can be successfully used for the quantitative extraction of Cd(II) and Hg(II) [12-15].

All these metal ions forms in presence of halide and pseudo-halide ions, anionic complexes and their extraction efficiency is mainly determined both by the properties of chemical species formed in extraction system (stability, hydration degree, electric charge), and by the characteristics of aqueous two-phase systems (nature and concentration of inorganic salt, molecular mass and concentration of PEG, acidity of phase-forming component solutions) [16, 17].

Starting from these observations, we believe that such aqueous PEG-inorganic salt two-phase systems can be used for efficient extraction of Bi(III) in presence of inorganic anions, as extractants. In the case of Bi(III), the stability of its chemical species with inorganic anions, such as I^-, Br^-, Cl^- and SCN^-, increases from SCN^- to I^-, and increase with the increasing of the inorganic anions number from molecule, following the order: $BiX^{2+} < BiX_2^+ < BiX_3 < BiX_4^- < BiX_5^{2-} < BiX_6^{3-}$ [18]. Under these conditions, at high acidity of phase-forming components solutions, a quantitative extraction of Bi(III) is expected to be obtained, and the extraction species should have a maximum number of inorganic anions (most probable 6) associated to metal ion.

In this study we have investigated the extraction behaviour of Bi(III) in aqueous PEG(1500) – $(NH_4)_2SO_4$, in order to establish the optimum experimental conditions for its efficient extraction. The experimental parameters considered in this study have been: initial concentration of metal ions, the type and concentration of inorganic extractants (I^-, Br^-, Cl^- and SCN^-) and the acidity of phase-forming components solutions. The aqueous two-phase systems were prepared using aqueous solutions of PEG and $(NH_4)_2SO_4$ in water and in 1 N H_2SO_4. The differences between these two ways of aqueous two-phase systems preparation have been evidenced using IR spectra of solidified PEG-rich phases. The extracted species were assumed on the basis of experimental distribution coefficients calculated in function of inorganic extractants concentration.

RESULTS AND DISCUSSION

The optimum conditions for Bi(III) extraction were established by varying several experimental parameters, such as: the pH of phase-forming components stock solutions, Bi(III) initial concentration, type and concentration of inorganic extractants.

In the study of Bi(III) extraction in aqueous PEG(1500) – $(NH_4)_2SO_4$ two-phase system, a first experimental parameter which should considered is the acidity of phase-forming components stock solutions. According with the distribution diagram of bismuth species [19], in aqueous solutions the free Bi^{3+} ions are present only in 0 – 0.8 pH range. Over this value the predominant species are BiO^+, which are more stable [18], but have a lower reactivity towards halide and pseudo-halide extractants, in comparison with Bi^{3+} ions.

On the basis of these observations, the influence of salt stock solution acidity on bismuth extraction in presence of 0.10 mol/dm^3 iodide extractants, have been studied in 0.20 – 3.50 pH range. The experimental results (Figure 1) indicate that the extraction efficiency increase with the increasing of salt stock solution acidity, but the maximum value of extraction percent is not higher than 50 %, even the salt stock solution pH is close to 0.

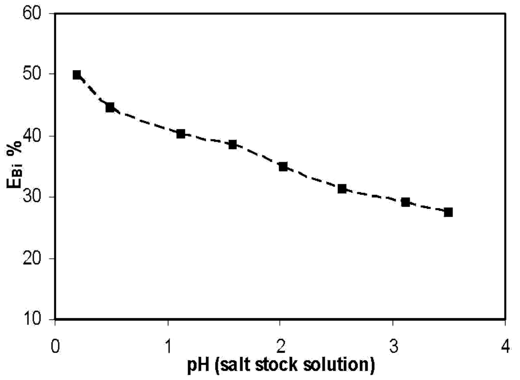

Figure 1. E_{Bi}% vs. salt stock solution pH. (Bi_i = 62.75 μg/cm^3, $[I^-]_{add}$ = 0.10 mol/dm^3; temperature = 24 °C).

This is due to the fact that the 40% (w/w) PEG aqueous stock solution has a higher pH value (6.2), and from this reason at interface, the apparition of a yellow precipitate can be observed, and the extraction process is stopped.

For to eliminated this inconvenient, both PEG and $(NH_4)_2SO_4$ stock solutions have been prepared using 1N H_2SO_4, instead of water. Under these conditions, in extraction systems bismuth is predominant as Bi^{3+} in both phases, and in presence of 0.10 mol I^-/dm^3, the obtained value of extraction percent is 99.65%. Thus, the extraction process could be considered a quantitative one, and this system was used for further Bi(III) extraction experiments.

But, the utilization of phase-forming components prepared in 1N H_2SO_4 instead of water, will change the characteristics of obtained aqueous two-phase system. For to underline the differences between the aqueous two-phase systems prepared using water and 1N H_2SO_4, the IR spectra of polymer-rich phases have been recorded.

In Figures 2 and 3 are presented the IR spectra obtained for solidified 40% (w/w) PEG(1500) solution (PEG) and blank PEG-rich phases (M), in water and 1N H_2SO_4.

It can be observed that the most significant changes are in the spectral region where appears the O–H stretching for water molecules hydrogen bonded by polymer chains [20, 21].

Thus, in the case of PEG solution in water, the large and splitter band from 3550-3238 cm^{-1} from PEG 1 spectra (Figure 2) is more attenuated in the spectra of blank PEG-rich phase (M 1) and moved to low wave number (3296 cm^{-1}). This is due to the fact that at the contact of PEG solution in water and salt stock solution with high acidity (in this case $(NH_4)_2SO_4$ solution with pH= 0.5), the dehydration of polymer chains occurs and the obtained PEG-rich phases are more hydrophobic [21]. This characteristic, plays an important role in extraction process of metal ions with inorganic extractants, and can be directly correlated with the number of extractants from extracted species molecules [10, 12, 14].

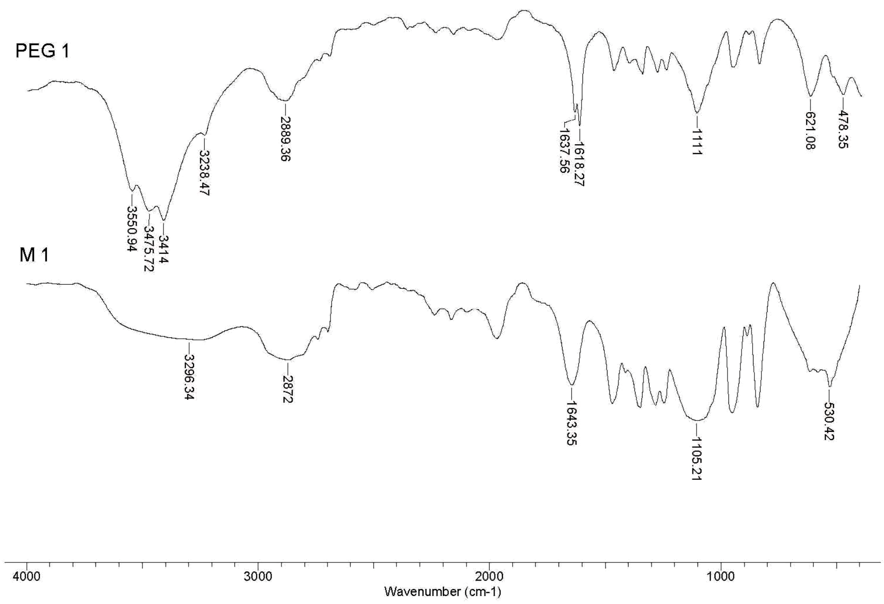

Figure 2. The IR spectra of solidified 40% (w/w) polyethylene glycol solution (PEG 1) and blank phase (M 1), in water.

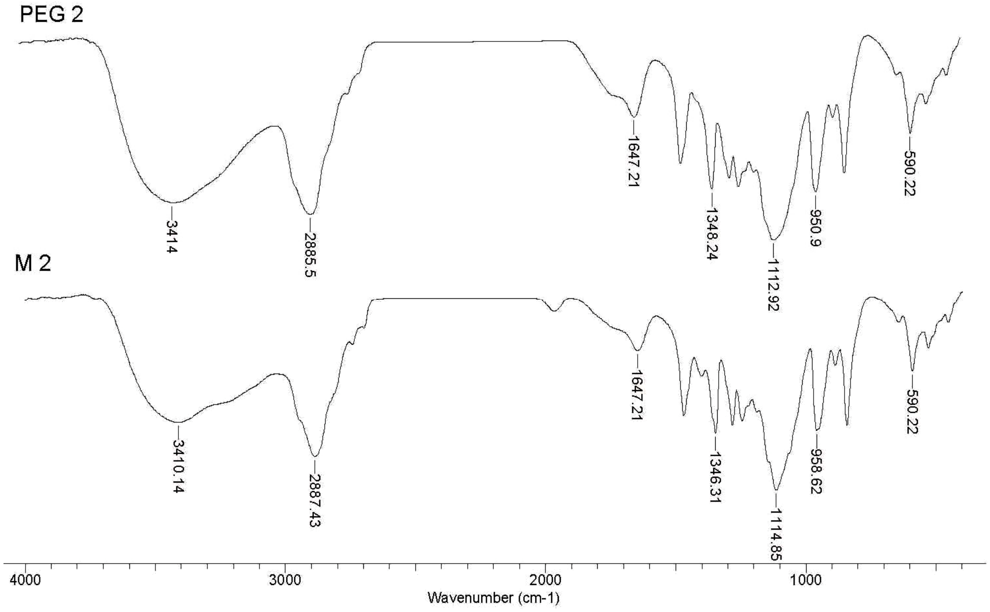

Figure 3. The IR spectra of solidified 40% (w/w) polyethylene glycol solution (PEG 2) and blank phase (M 2), in 1N H_2SO_4.

In case of PEG solution prepared in 1N H_2SO_4 (Figure 3), the maximum absorption band of water molecules is situated at 3414 cm^{-1} in solidified PEG solution (PEG 2) and remains almost unchanged after the formation of aqueous two-phase system (M 2). Thus, by using PEG solution prepared in 1N H_2SO_4, the dehydration degree of polymer chains is not significant changed after aqueous two-phase system formation, and the obtained PEG-rich phases have a lower hydrophobicity. In these conditions, is expected that in the extracted species molecules, the number of extractants associated to metal ion to be lower than maximum (6 in case of Bi(III)).

The influence of Bi(III) initial concentration was studied in the metal concentration range between 21 and 74 μg/cm^3. At it can seen from Figure 4, the Bi(III) concentration extracted into PEG-rich phase at constant concentration of iodide extractant (0.10 mol/dm^3) in considered aqueous two-phase system, increase with the increasing of initial concentration of metal ion.

On the basis of this observation and considering the limits of spectrophotometrically method used for Bi(III) analysis, in further distribution studies, an initial concentration of 62.75 μg/dm^3 was selected.

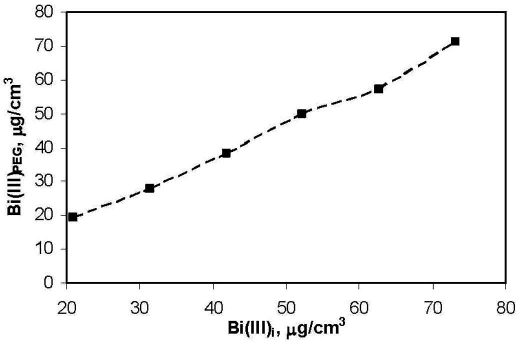

Figure 4. The influence of initial metal ion concentration on bismuth extraction in presence of iodide extractants, in considered aqueous two-phase system. ($[I^-]_{add}$ = 0.10 mol/dm^3; temperature = 24 °C).

The Bi(III) extraction behaviour was also investigated in function of type and concentration of inorganic extractants (I^-, Br^-, Cl^- and SCN^-) added in aqueous two-phase system. Comparatively, the variation of extraction parameters (D_{Bi} and E_{Bi} %) in function of NH_4X concentration added in extraction system are given in Figures 5a and 5b. An increasing of Bi(III) extraction into PEG-rich phase with increasing of inorganic extractants concentration was observed, for all cases. The values of extraction parameters follow the order: I^- >> Br^- > Cl^- >> SCN^-, which is in agreement with the results presented in other studies from literature [22, 23]. As it can seen from Figures 5a and 5b, the Bi(III) extraction parameters have higher values for I^- than Br^-, those for Br^- increase at lower concentrations that for Cl^-, and all of them are higher than the values of extraction parameters obtained in the case of SCN^-. This order could be explained by the increasing of bismuth extracted species stability from SCN^- to I^- [18]. The softness and most polarizable iodide ions have the smallest hydration Gibbs energy (ΔGhydr. = - 220 kJ mol^{-1}) [24] and form stronger complexes with bismuth, which are easy extracted into PEG-rich phase.

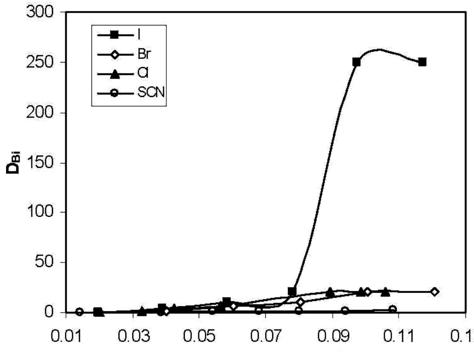

Figure 5a. The variation of Bi(III) distribution coefficient in function of extractants concentration. (Bi_i = 62.75 µg/cm^3, temperature = 24 °C).

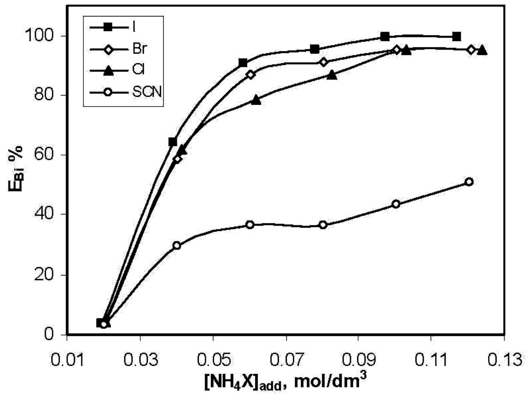

Figure 5b. The variation of Bi(III) extraction percent in function of extractants concentration. (Bi_i = 62.75 μg/cm^3, temperature = 24 °C).

The nature of the extracted species was deduced from log-log plots of distribution coefficients (D_{Bi}) versus the inorganic extractants concentrations in PEG-rich phases (in mentioned experimental conditions). The obtained dependences gave a straight line (Figure 6) with slopes 4 for halide extractants and 2 for SCN^- system, respectively. This indicate that in considered aqueous two-phase system in presence of halide extractants, Bi(III) is extracted predominant as anionic complexes (BiX_4^-), while in case of SCN^- extractant, the main extracted species have a molar ratio Bi : SCN^- = 1 : 2.

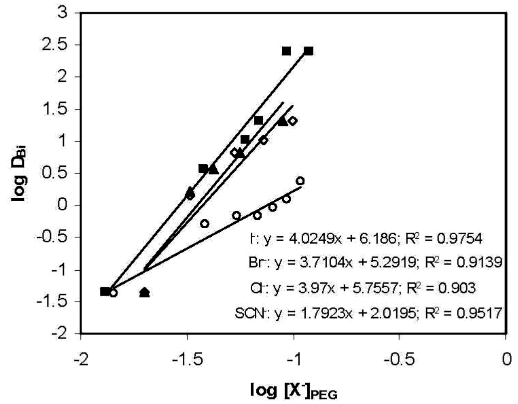

Figure 6. The log D_{Bi} against log $[X^-]_{PEG}$ dependences (Bi_i = 62.75 μg/cm^3, temperature = 24 °C).

The extraction of BiX_4^- species in case of halide extractants (instead of BiX_6^{3-}, which are more stable [18]), is mainly determined by the relative high water content of PEG-rich phases of this aqueous two-phase system (see

Figure 3). Because the hydrophobicity of these phases is lower, the formation of BiX_6^{3-} species (with a too lower hydration degree), is not necessary. In case of SCN^- extractant, the probable extraction of a mixed $Bi(SCN)_2NO_3$ species is a consequence of the appropriate stability of thiocyanate and nitrate bismuth species. This leads to the situation that during the extraction process, the exchange of NO_3^- ions with SCN^- ions, to be mainly determined by kinetics factors.

On the basis of obtained experimental results, the bismuth extraction process in presence of inorganic extractants (I^-, Br^-, Cl^- and SCN^-), in considered aqueous two-phase system can be schematic represented as in Figure 7.

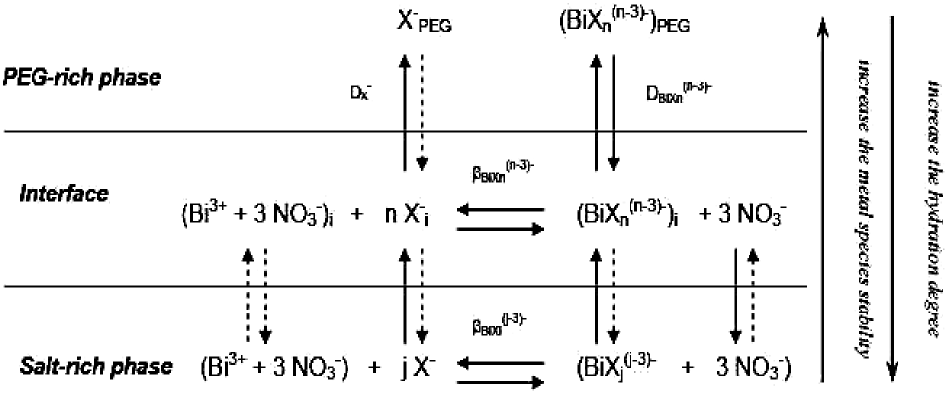

Figure 7. The schematic representation of the main elementary processes involved in Bi(III) extraction in presence of inorganic extractants, in the considered aqueous two-phase system.

According with this representation, the extraction process occurs step by step, until the hydration degree of metal ion become lowered enough (due to its complexation with extractants), and when this state is reached the metal species are immediately transferred into PEG-rich phase. After extractants addition, even in salt-rich phase, intermediary species $BiX_j(NO_3)_{3-j}$ (j = 1, 2 or 3) are probable formed, which are more stable than $Bi(NO_3)_3$, but have a hydration degree large enough for to maintain these species at the interface of this phase. At interface, these species will interact with other extractants, and in consequence the hydration degree of metal species will decrease. When, the metal species have a hydration degree compatible with those of PEG-rich phase, the partition of these occurs immediately.

The compatibility between metal species and PEG-rich phase hydration degree is a necessary condition, but not a sufficient one. According with the experimental results, an efficient extraction is obtained only when the metal ion react with inorganic extractants and form species with high stability. Thus, when in extraction system are formed a stable metallic species, these will cross the interface with salt-rich phase, and will be efficient partitioned into PEG-rich phase (case of Bi(III) extraction in presence of halide extractants: I^-, Br^-, Cl^-). When, the formed metallic species formed in extraction system have a lower stability, the extraction process to occur until an “equilibrium state” is attained, depends on the hydrophobicity of the two aqueous phases (case of Bi(III) extraction in presence of SCN^- extractants).

CONCLUSIONS

The Bi(III) extraction behaviour in aqueous PEG(1500)–$(NH_4)_2SO_4$ two-phase system was investigated as a function of several experimental parameters: acidity of stock solutions of phase-forming components, initial concentration of Bi(III) in extraction system, type and concentration of inorganic extractants (I^-, Br^-, Cl^- and SCN^-).

The aqueous two-phase systems were prepared using aqueous solutions of phase-forming components in water and in 1N H_2SO_4. The experimental results have indicate that a quantitative extraction of Bi(III) is obtained only when both PEG and $(NH_4)_2SO_4$ stock solutions are prepared in 1N H_2SO_4, and such systems were chosen for the extraction experiments.

The addition of inorganic extractants determined an increasing of Bi(III) partition into PEG-rich phase, due to the formation of bismuth halide complexes, stable and with lower hydration degree. Under these conditions, for a given initial concentration of Bi(III) in extraction system (62.75 $\mu g/dm^3$), the extraction efficiency increase with the increasing of inorganic extractants concentration, and follow the order: $I^- \gg Br^- > Cl^- \gg SCN^-$. The nature of extracted species was assumed using the experimental distribution coefficients. The obtained results have indicate that in considered aqueous two-phase system in presence of halide extractants, Bi(III) is extracted predominant as BiX_4^-, while in case of SCN^- extractant, the main extracted species have a molar ratio Bi : SCN^- = 1 : 2.

On the basis of experimental results it can say that the Bi(III) extraction in presence of inorganic extractants (I^-, Br^-, Cl^- and SCN^-) occurs step by step, until the hydration degree of metal ion decrease enough (due to his complexation with extractants), and when this state is reach, the metal species are transferred into PEG-rich phase. Even the compatibility between metal species and PEG-rich phase hydration degree is a necessary condition this is not a sufficient one. An efficient extraction is obtained only when the metal species formed between Bi(III) and extractants, have a high stability.

EXPERIMENTAL SECTION

$(NH_4)_2SO_4$ (from Reactivul Bucharest) and NH_4X (X^- = I^-, Br^-, Cl^- and SCN^-) purchased from Aldrich, were analytical reagent degree and used without further purifications. Polyethylene glycol (PEG) with molecular mass

1500 (from Aldrich) was used as received. All aqueous solutions were prepared using double distilled water, obtained from a commercial distillation system.

Stock solutions of 40% (w/w) PEG(1500) were prepared by dissolving of an appropriate mass of solid polyethylene glycol in double distilled water or H_2SO_4 (Reactivul Bucharest) of known concentration. The 40% (w/w) of $(NH_4)_2SO_4$ stock solution was obtained similarly. The solution of ~ 2000 μg Bi(III)/cm^3 (10^{-2} mol/dm^3) was prepared by bismuth nitrate (from Fluka) dissolving in 20 cm^3 of HNO_3 concentrated solution (Reactivul Bucharest) and dilution to volume with double distilled water. After preparation, the exact concentration of Bi(III) was determined by standardization [25]. The solutions of inorganic extractants, containing 1 mol/dm^3 NH_4X (X^- = I^-, Br^-, Cl^- and SCN^-) were obtained by dilution of a known mass of inorganic salt to the volume with appropriate $(NH_4)_2SO_4$ stock solution. This approach provide a sever decreasing of salt forming-phase concentration after the addition of extractants.

For each experiment an aqueous two-phase system was prepared by mixing equal volumes (5 cm^3) of PEG(1500) and $(NH_4)_2SO_4$ stock solutions with different pH (measured with a Radelkis pH/ion-meter OK-281 equipped with a combined glass electrode), in a glass centrifuge tube. The systems were pre-equilibrated by centrifugation for 2 min at 2000 rpm. A 0.1 ÷ 0.5 cm^3 of Bi(III) stock solution and (0.1 ÷ 0.12) cm^3 of 1 mol/dm^3 NH_4X (X^- = I^-, Br^-, Cl^- and SCN^-) were added. The systems were again centrifuged 10 min at 2000 rpm. The centrifugation time was experimentally determined to be sufficient for these systems to reach equilibrium. Before analysis, the phases were separated using Pasteur pipettes and placed in separated tubes. 1.0 cm^3 from each phase were measured for spectrophotometrically Bi(III) analysis with KI (Digital S 104 D Spectrophotometer, 1 cm glass cell, λ= 460 nm, against a blank solution) [26]. Each Bi(III) concentration was determined in duplicate using a prepared calibration graph, and the extraction parameters (distribution coefficient (D_{Bi}) and the extraction percent (E_{Bi} %)) were calculated according to their definitions. The inorganic extractants concentration in PEG-rich phase was determined by conductometric titration with $AgNO_3$, using a Radelkis OK-109 conductometer.

For the IR experiments 1.0 ÷ 1.5 cm^3 from PEG stock solutions and blank PEG-rich phases separated from extraction systems (before the addition of metal ion and extractants), were measured and placed on the glass slides (chemical inert). The samples were solidified at room temperature (24 ± 0.5 °C). The IR spectra have been recorded using a FTIR Bio-Rad Spectrometer, in a 400 – 4000 cm^{-1} spectral domain with a resolution of 4 cm^{-1}, by KBr pellet technique.

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