THE INFLUENCE OF PHASE-FORMING SALT ON Cd(II) EXTRACTION IN AQUEOUS PEG-BASED TWO-PHASE SYSTEMS

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The influence of phase-forming salt on Cd(II) extraction in presence of iodide extractants has been studied, in aqueous PEG-based two-phase systems. Na_2SO_4 and $(NH_4)_2SO_4$ were used as phase-forming salts, and the phase diagrams for these two systems were constructed. From the phase diagrams it was found that due to lower salting-out ability of NH_4^+ ions in comparison with Na^+, the minimum $(NH_4)_2SO_4$ concentration required for the two aqueous phases separation is higher than in case of Na_2SO_4. The distribution curves indicate that the aqueous PEG(1550)–Na_2SO_4 two-phase system is more adequate for the extraction of lower Cd(II) concentrations, while the aqueous PEG(1550)–$(NH_4)_2SO_4$ two-phase system can be used in a higher Cd(II) concentration range. The IR spectra of solidified PEG-rich phases separated from considered aqueous two-phase systems showed that the water content from polymeric phases is different, in function of inorganic salt used for the systems preparation.

INTRODUCTION

The aqueous two-phase systems have been used over 40 years for the extraction of biological materials such as cells, enzymes and proteins.[1-4] In the last years they have also been employed for the extraction of organic molecules[5,6] and heavy metal ions.[7-10]

For preparing an aqueous two-phase system, aqueous solutions of a water-soluble polymer and an inorganic salt are required, and the obtained system is composed by two-immiscible phases: a top one (PEG-rich phase) – rich in polymer and a bottom one (salt-rich phase) – with a high content of inorganic salt. The most frequently used water-soluble polymer for the aqueous two-phase systems preparation is polyethylene glycol (PEG). Because PEG is non-toxic, non-flammable, non-volatile and biodegradable, the PEG-based aqueous two-phase systems caused less problems to the environment compared with the traditional solvent extraction systems, where the water immiscible organic solvents are used.[10]

The metal ions extraction in such aqueous two-phase systems depends on numerous factors, which can be included into two categories: (*i*) the metal extracted species properties (stability, electric charge, dimension, hydration degree)[7,9] and (*ii*) the aqueous two-phase systems characteristics, mainly determined by the molecular weight and concentration of PEG[11] and by the type and concentration of inorganic salt.[12,13]

In general, the metal extracted species properties can be adjusted by using a suitable extracting agent, which will improve the selectivity of extraction process. Thus, has been shown that iodide ions can be successfully used for the quantitative Cd(II) extraction, but the values of extraction parameters depend on the characteristics of aqueous two-phase system.[14,15]

The optimum characteristics of aqueous two-phase systems (system stability, time of phase separation, clear interface) can be obtained by a suitable selection of phase-forming components (PEG and inorganic salt). According to the studies from literature,[11,12,16] the higher the molecular weight of PEG is, the easier to obtain the aqueous

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two-phase systems are. But the increase of PEG molecular weight has as result the decrease of number of hydrogen-bonds formed between polymer chains.[17] Thus are obtained the aqueous two-phase systems with a high hydrophobicity of polymer-rich phases (a lower water content), where the metal species cannot be extracted due to the hydration environments incompatibility. This is one of the reasons for which in the most of metal ions extraction studies is used polyethylene glycol with a relative low molecular weight (1200 – 2000). In addition, the concentration of PEG solutions must be selected that the polymer solution to be situated in diluted solution domain, near to critical point.[12]

On the other hand, the concentration of inorganic salt required for the obtaining of aqueous two-phase systems is lower, with the hydration free Gibbs energy is higher and negative.[9] Because, for the utilization of these systems in extraction studies is important that the inorganic phase-forming salt concentration should be smaller (in order to eliminate some of secondary processes), the most effective inorganic salts for the aqueous two-phase systems preparation are phosphates and carbonates. But, in case of heavy metal ions extraction, the use of phosphates or carbonates is not always adequate, because some of these ions can form phosphates or carbonates with lower solubility, which may influence the extraction process. Thus, in case of Cd(II) extraction, for the aqueous two-phase system preparation, sulphates are frequently recommended as salt-forming phase.

In this paper we choose the aqueous PEG(1550)–$(NH_4)_2SO_4$ and PEG(1550)–Na_2SO_4 two-phase systems to investigate the extraction behaviour of Cd(II) in presence of iodide as extracting agent. For each aqueous two-phase system, the phase diagram has been constructed and the system characteristics were calculated. The experiments were done both at different Cd(II) initial concentration and at different iodide concentration added in extraction system. The IR spectra of solidified PEG-rich phases for both aqueous two-phase systems and the IR spectra of solidified PEG aqueous solutions were recorded, and their analysis offer several arguments which sustain the experimental observations presented in this study.

EXPERIMENTAL

Materials

The reagents: PEG (1550) (Serva Feimbiochema Gmb &Co), $(NH_4)_2SO_4$, Na_2SO_4 and NaI (Aldrich) were of analytical degree reagents and were used without further purifications. The PEG stock solutions   (40 % (w/w) and 50 % (w/w)) and the salts stock solutions (40 % (w/w) $(NH_4)_2SO_4$

and 20 % (w/w) Na_2SO_4) were prepared by dissolving an appropriate mass of solid chemicals in distilled water.

The stock solution of 10^{-2} mol/L (~1000 µg Cd(II) /mL) was obtained by cadmium nitrate (Fluka) dissolving in distilled water, followed by solution standardization.[18] The solution of iodide, containing 1 mol NaI/L was prepared by dilution of a known mass of iodide salt to the volume with salt stock solution ($(NH_4)_2SO_4$ or Na_2SO_4). In this way is provided a net decrease of salt forming-phase concentration, after the addition of extractant.

Methods

The phase diagrams were constructed by preparing eight aqueous two-phase systems and determining the concentration of PEG and the salts in the coexisting phases as follow. Aqueous two-phase systems of varied PEG and salts compositions were prepared by mixing exact measured volumes of 40 % (w/w) PEG stock solution, a 40 % (w/w) $(NH_4)_2SO_4$ stock solution and water; or a 50 % (w/w) PEG stock solution, a 20 % (w/w) Na_2SO_4 stock solution and water in a glass centrifuge tube. The water content in PEG (1550) was determined to be 0.48 % (w/w), by drying in air at 70-90°C, and was neglected in calculation of PEG concentration in the stock solutions. The systems were centrifuged for 10 min at 2000 rpm. Immediately before analysis 1 mL of the top and bottom phases were carefully measured out and diluted to 25 ml with distilled water, respectively.

The concentration of PEG from PEG-rich phases was determined from refractive index measurements, using an Abbe refractometer. Since the refractive index of phase sample depends on the PEG and salt concentrations,[19] calibration plots of refractive index versus polymer concentration were prepared for different concentration of $(NH_4)_2SO_4$ and Na_2SO_4 (Fig. 1). The concentration of PEG from salt-rich phases was obtained by difference.

The concentration of inorganic salts ($(NH_4)_2SO_4$ and Na_2SO_4) from salt-rich phases were determined gravimetric, by precipitation with $BaCl_2$,[20] and the salts concentrations from PEG-rich phases were obtained by difference.

The Cd(II) extraction parameters were determined in the following manner. The aqueous two-phase systems were prepared by mixing equal volumes of 40 % (w/w) PEG stock solution and 40 % (w/w) $(NH_4)_2SO_4$ stock solution, or 50 % (w/w) PEG stock solution and 20 % (w/w) Na_2SO_4 stock solution, in a glass centrifuge tube. A (0.1÷0.7) mL of Cd(II) stock solution and (0÷0.7) mL of 1 mol NaI/L were added. The systems were then mechanically shaken for 2 min, followed by 10 min of centrifugation at 2000 rpm.

The phases were then separated using Pasteur pipettes and placed into separated tubes. 1.0 mL from each phase was measured for the Cd(II) spectrophotometric analysis using p, p'-dinitro-diphenyl-carbazide. The absorbance of complex was measured at 630 nm, using a Digital S 104 D Spectrophotometer, in a 1-cm glass cell, against blank solution.[21] The Cd(II) concentration from each phase was determined in duplicate using a prepared calibration plot. The extraction parameters were calculated according with the relations from literature.[14]

For the IR spectra a 1.0÷1.5 mL from each PEG-rich phase, before Cd(II) extraction, was measured and placed on the chemical inert glass slides. 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 - 4000cm^{-1} spectral domain, with a resolution of 4 cm^{-1} and 32 scans, by KBr pellet technique.

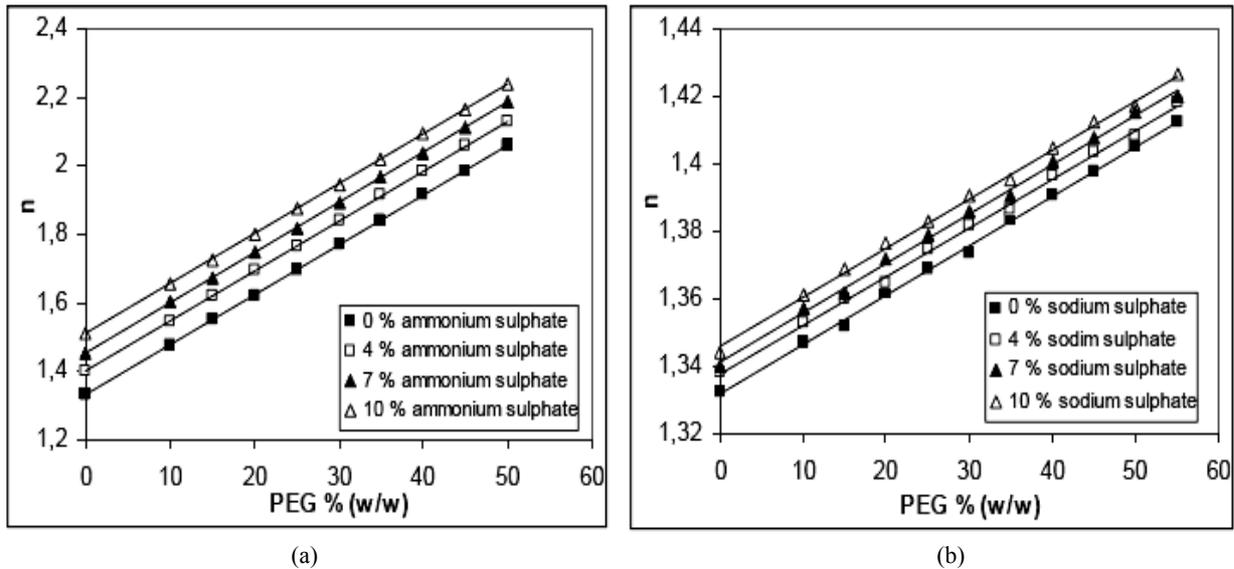(a)   (b)

Fig. 1 – Refractive index calibration curves for (a) PEG(1550)–$(NH_4)_2SO_4$–H_2O; (b) PEG(1550)–Na_2SO_4 – H_2O.

RESULTS AND DISCUSSION

The polyethylene glycol with 1550 average molecular weight was choose for the aqueous two-phase systems preparation, because will be permit the obtaining of PEG-rich phases with a water content higher enough, for the extraction of metal species. On the basis of correlation diagram molecular weight – concentration (Fig. 2), it can be sen that in the concentration range between 40 and 50 % (w/w), the PEG aqueous solutions are situated in the diluted solutions domain, near to the critical point, and can be successfully used for the aqueous two-phase system preparation.

Phase diagrams

The phase diagrams are probable the most simple tools which can be used for the characterization of aqueous two-phase systems. The phase diagram gives such useful information as the relative concentration of forming-phase components needed to maintain a two-phase system, as well as the relative ratios of each component in either phase, variables which influenced the extraction of metal species.[23]

Fig. 3 shows the phase diagrams for the PEG(1550)–$(NH_4)_2SO_4$ and PEG(1550)–Na_2SO_4 systems, where the concentration of PEG and inorganic salts were expressed in weight percents. For each case, the region below the bimodal curve represents a homogenous solution (zone I) and that above, a two-phase region (zone II). Both considered aqueous two-phase systems are easy to obtain, have a clear interface and are stable more than 15 days.
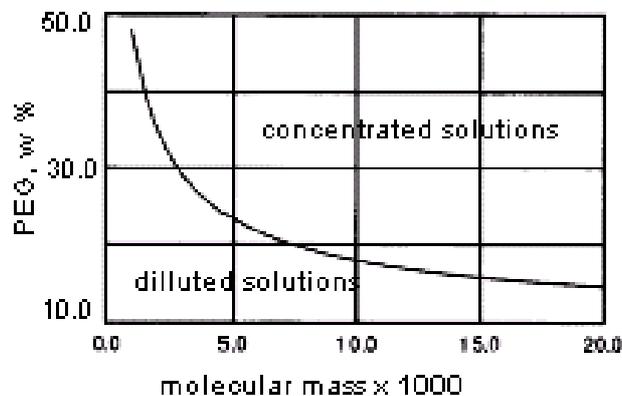

Fig. 2 – The correlation diagram molecular mass-concentration for PEG aqueous solutions.[22]

It can be seeing from Fig. 3, that the effectiveness of salt to form aqueous two-phase systems with PEG depends on their constituent's cations and anions. Several studies[9, 12, 13] shown that the stronger is the hydration degree of ions, the lower is the concentration required to form a two-phase system. It is thus expected, from the Gibbs free energy of hydration values ($\Delta G_{hyd.}$) that Na^+

($\Delta G_{hyd.}$ = -365 kJ/mol)[24] has a salting-out effect on PEG stronger than that of NH_4^+ ($\Delta G_{hyd.}$ = -285 kJ/mol)[24], and thus the Na_2SO_4 concentration required for the separation of the two phases is lower. These observations can be quantitativly sustained on the basis of the systems parameters values obtained from phase diagrams (Table 1).
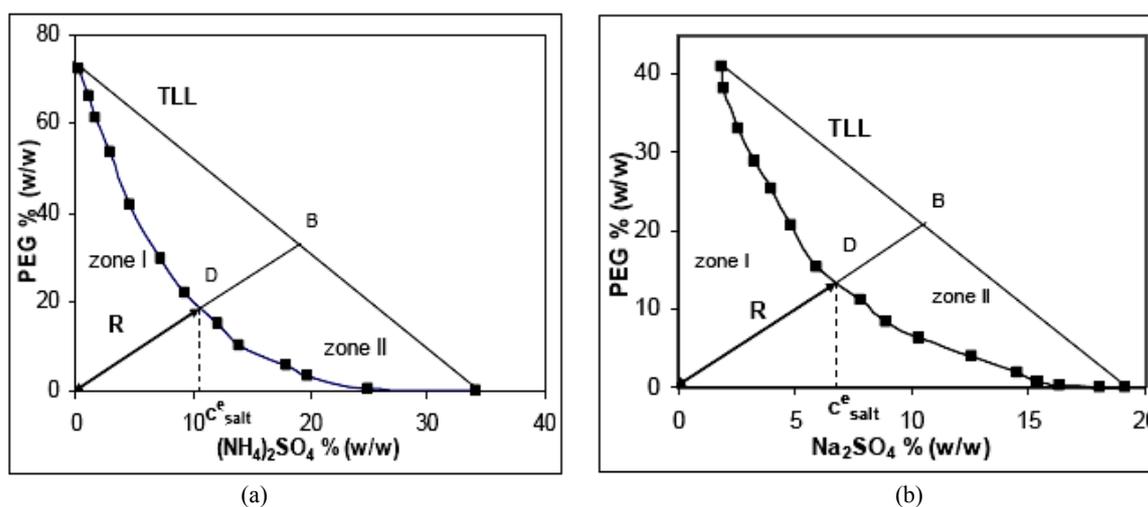

(a)   (b)

Fig. 3 – The phase diagrams for considered aqueous two-phase systems. (a) PEG(1550)–$(NH_4)_2SO_4$; (b) PEG(1550)–Na_2SO_4.

Table 1

The values of systems parameters obtained from phase diagrams for the two considered aqueous two-phase systems

Inorganic salt	c^e_{salt}, % (w/w)	R	TLL	System stability
$(NH_4)_2SO_4$	12.28	17.9673	18.7893	0.9013
Na_2SO_4	7.09	16.0638	18.0315	0.6671

Thus, in case of Na_2SO_4 utilization as salt-forming phase, the separation of the two aqueous phases required a salt concentration by 7.09 % (w/w), while in case of $(NH_4)_2SO_4$ the minimum concentration necessary for the phase separation is higher (12.28 % (w/w)). Even the PEG(1550)–Na_2SO_4 system required a lower salt concentration for the phase separation than in case of PEG(1550)–$(NH_4)_2SO_4$ system, which can represent a real advantage from metal extraction point of view, the lower stability of this indicating a more "fragile" system, comparatively with PEG(1550)–$(NH_4)_2SO_4$ two-phase system.

The Cd(II) extraction in presence of iodide ions

The utilization of Na_2SO_4 and $(NH_4)_2SO_4$ for the aqueous two-phase systems preparation has been tested for Cd(II) extraction in presence of iodide ions, as extracting agent. The experiments have followed both the influence of Cd(II) initial

concentration and the influence of iodide ions concentration, and the results are presented in Fig. 4.

At it can see from Fig. 4a, for a given initial concentration of metal ion, the Cd(II) extraction efficiency increase with increasing of iodide ions concentration and has a similar variation for both considered aqueous two-phase system. This means that both sulphates ($(NH_4)_2SO_4$ and Na_2SO_4) can be successfully used as phase-forming salts for the preparation of aqueous two-phase systems. However, the analysis of distribution curves from Fig. 4b shows that the Na_2SO_4 utilization as salt-forming phase is more adequate for low Cd(II) concentration, until at 35 μg/mL, after that the extraction percent values decrease. In case of using the $(NH_4)_2SO_4$ as salt-forming phase, the Cd(II) extraction efficiency increase progressively with the increase of Cd(II) initial concentration, whitin 10 – 75 μg Cd(II)/mL concentration range, and the decrease of extraction parameters at higher values of metal ion concentration takes place more slowly.

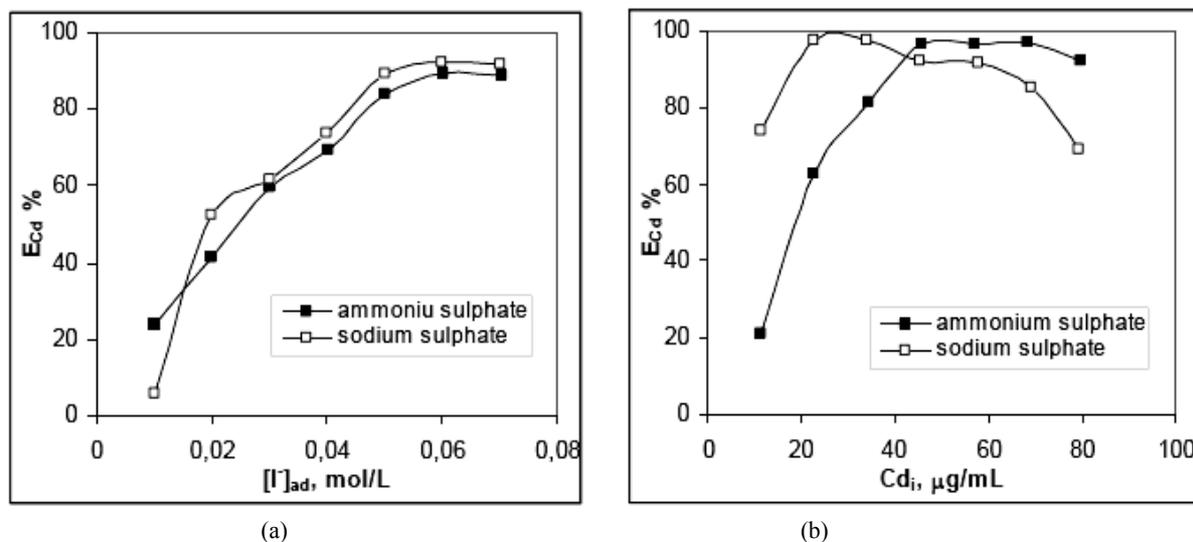(a)   (b)

Fig. 4 – The influence of phase-forming salt on Cd(II) extraction efficiency in presence of iodide ions. (a) $[Cd^{2+}]_{initial} = 34.06$ μg/mL; (b) $[I^-] = 0.06$ mol/L. Temperature 24 °C.

This different behaviour can be attributed, both to the difference of salting-out effect of these salts on PEG (Na_2SO_4 exert a stronger salting-out effect on PEG than $(NH_4)_2SO_4$, which explained the high Cd(II) extraction efficiency at low values of its concentration), and to the larger difference of salts concentration used for two-phase systems preparation (imposed by their solubility).

The IR spectra of solidified PEG-rich phases

To sustain these observations, the IR spectra of solidified PEG (1550) aqueous solution and of solidified PEG-rich phases separated from both aqueous two-phase systems, before Cd(II) extraction, have been recorded and are presented in Fig. 5.

The comparison of these spectra shows that the large and spited band from 3550-3238 cm^{-1} from PEG spectra is more attenuated in the spectra of PEG-rich phases separated from aqueous two-phase systems (1 and 2). This is the spectral region where appears the O–H stretching of water molecules hydrogen-bonded on PEG chains, and describes different ways in which these are bonded o polymer.[25, 26]

The attenuation of the considered band in solidified PEG-rich phase's spectra (1 and 2) showed that at contact between PEG aqueous solution and the inorganic salt solution, the polymer chains dehydration occurs. This observation is in agreement with the hypotheses from literature, which describe the formation of aqueous two-phase systems on the basis of

competition from hydration between organic polymer and inorganic salt.[26]

At it can see from Fig. 5, the intensity of this band is lower (T_{PEG} %/T_1 % = 0.098) and situated at lower wave number in case of $(NH_4)_2SO_4$ use as phase-forming salt, than in case of Na_2SO_4 utilization (T_{PEG} %/T_2 % = 0.1291). This means that in the PEG-rich phases obtained from aqueous PEG(1550)–Na_2SO_4 two-phase system, the water content is higher than in case of PEG-rich phases obtained from aqueous PEG(1550)–$(NH_4)_2SO_4$ two-phase system.

Under these conditions, we can say that even Na_2SO_4 exert a strong salting-out effect on PEG (due to the high hydration free Gibbs energy of Na^+ in comparison with NH_4^+), the high water content of PEG-rich phases is determined by the low concentration of salt solution, limited by they solubility ($S^{25°C} = 19,5$ g/100 g water [27]). These make the aqueous PEG(1550)–Na_2SO_4 two-phase system be more "fragile" from metal extraction point of view, and as a consequence the Cd(II) extraction parameters will decrease at a higher concentration of metal ion.

CONCLUSIONS

The influence of phase-forming salt on the extraction behaviour of Cd(II) in presence of iodide ions as extracting agent, in aqueous PEG-inorganic salt two-phase systems has been studied. Inorganic salts for the aqueous two-phase systems preparation Na_2SO_4 and $(NH_4)_2SO_4$ have been used.
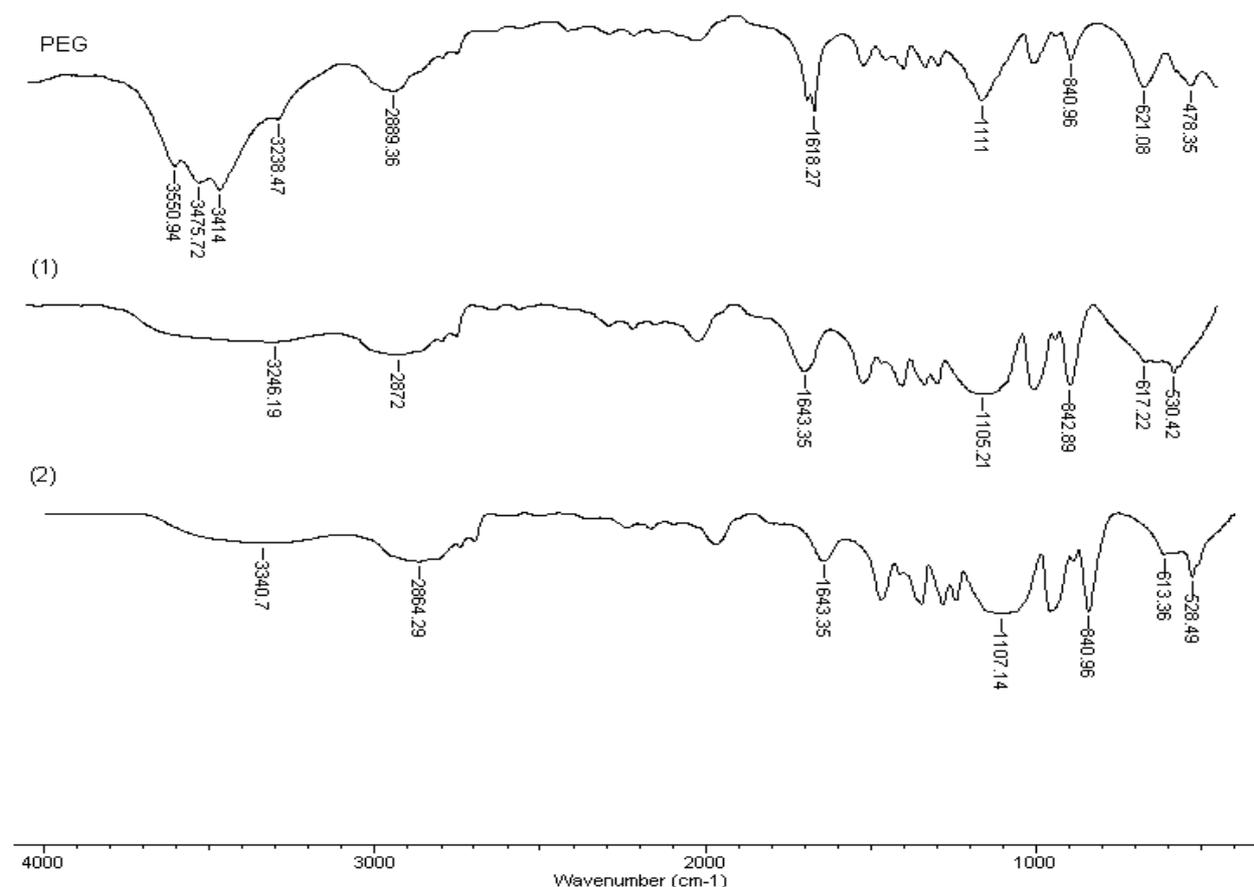
Fig. 5 – The IR spectra of solidified PEG (1550) aqueous solution (PEG) and solidified PEG-rich phases from aqueous PEG(1550) – $(NH_4)_2SO_4$ two-phase system (1) and aqueous PEG(1550)–Na_2SO_4 two-phase system (2).

For both aqueous two-phase systems, the phase diagrams were constructed and the systems parameters were calculated. The analysis of the obtained phase diagrams shows that the minimum salt concentration required for the two phase separation is higher in case of $(NH_4)_2SO_4$ than in case of Na_2SO_4. This can represent an advantage for the utilization of aqueous PEG(1550)–Na_2SO_4 two-phase system in metal ions extraction studies, but the lower stability of this indicates a more "fragile" system, comparatively with PEG(1550)–$(NH_4)_2SO_4$.

The distribution studies indicate that for a given initial concentration of metal ion, the Cd(II) extraction efficiency increases with the increasing of iodide ions concentration, and has a similar variation for both considered aqueous two-phase systems. A different behaviour is obtained by studying the Cd(II) extraction efficiency as a function of initial concentration of metal ion. The experimental results show that the aqueous PEG(1550)–Na_2SO_4 two-phase system is more

adequate for the extraction of low Cd(II) concentration (up to 35 μg Cd(II)/mL), while the aqueous PEG(1550)–$(NH_4)_2SO_4$ two-phase system can be used whitin a larger Cd(II) concentration domain (10 − 75 μg/mL). This different behaviour of these aqueous two-phase systems can be explained on the basis of different salting-out effect of these two inorganic salts (Na_2SO_4 exert a strong salting-out effect on PEG, than $(NH_4)_2SO_4$), and on the other hand on the large difference in salt concentration used for the two-phase systems preparation (imposed by their solubility).

The IR spectra of solidified PEG-rich phases sustain these observations and show that the water content is higher in the polymeric phases separated from aqueous PEG (1550) –Na_2SO_4 two-phase system, than in case of polymeric phases obtained from aqueous PEG (1550) –$(NH_4)_2SO_4$ two-phase system. This means that the aqueous two-phase system obtained by mixing PEG aqueous solution and Na_2SO_4 aqueous solution is more "fragile" from metal extraction point of view.

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