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**Fate of metal ions in PEG-400/Na<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O aqueous biphasic system:  
from eviction to extraction towards the upper polymer-rich phase**

**Eris Sinoimeri<sup>a,b</sup>, Anne-Claire Pescheux<sup>a,b</sup>, Ismaël Guillotte<sup>b</sup>, Jérôme Cognard<sup>a,b</sup>, Lenka Svecova<sup>a</sup>, Isabelle Billard<sup>a\*</sup>**

<sup>a</sup>Univ. Grenoble Alpes, Univ. Savoie Mont Blanc, CNRS, Grenoble INP (Institute of Engineering and Management Univ. Grenoble Alpes), LEPMI, 38000 Grenoble, France

<sup>b</sup>Aperam Research Center, Rue Roger Salengro, Isbergues, France

\*Corresponding author, e-mail: [isabelle.billard@grenoble-inp.fr](mailto:isabelle.billard@grenoble-inp.fr);

Lepmi, 1130 rue de la Piscine, 38402 Saint Martin d'Hères, France.

**Abstract:** The fate of eight metal ions, Co(II), Cr(III), Cr(VI), Cu(II), Fe(III), Mn(II), Mo(VI) and Ni(II), introduced as minor components in the well-known aqueous biphasic system PEG-400/Na<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O was investigated at T = 25°C and as a function of the increasing PEG-400 amount in the system. Among this list, the six cations Co(II), Cr(III), Cu(II), Fe(III), Mn(II) and Ni(II) tend to be excluded from the upper PEG-rich phase as the PEG amount is increased, a behavior which is similar to that of Na(I), a major component of the system and the binodal curve (shape and position) is not modified by their presence. By contrast, the two oxoanions Cr(VI) and Mo(VI) accumulate in the upper PEG-rich phase (up to ca. 100%) as PEG amount in the system is increased, which is similar to a traditional extraction phenomenon, assimilating PEG to the (organic) extracting phase. The extraction mechanism, ascribed to the PEG crown-ether open chain properties, is supported by experiments where the PEG structure is slightly modified.

**Keywords:** Cr(VI), aqueous biphasic systems, extraction, crown-ether like properties of polyethylene glycol (PEG)

## 1. Introduction

Aqueous Biphasic Systems (ABS) can be defined as mixtures of three different chemical compounds, one being water, and the other two inducing either a monophasic or a biphasic state of the sample, depending on the temperature and on their proportions. In the followings, these latter two compounds will be called ABS inducers, because both of them are needed to get a biphasic liquid/liquid state. The chemical nature of these two compounds has dramatically evolved in the published literature, reflecting a shift in the interest of the scientific community towards constantly new challenges. Common compositions used to involve two polymers, such as polyethylene glycol, polypropylene glycol or dextran [1–3]. These were followed by mixtures of a polymer as above and an inorganic salt such as NaNO<sub>3</sub>, Na<sub>2</sub>SO<sub>4</sub>, etc. [4,5]. More recently, ionic liquids (ILs, here defined as salts with a melting temperature below 100 °C) have offered a “boost” to the field [6–8] either associated to polymers [9,10], inorganic salts as above [11,12] or mineral acids [13,14]. Even two “simple” salts can form ABS with water [15,16].

Apart from fundamental studies involving the determination of the binodal data (as a function of polymer molecular weight, IL chemical nature or temperature for example), ABS have also been used to perform liquid/liquid extraction of molecular compounds or biological entities [17–19]. The introduction of ILs together with mineral acids in ABS composition allowed efficient metal ion extraction, even in the absence of any extracting additional compounds [20–23]. Although this ILs/mineral acid combination may be considered as a breakthrough in the field, in view of more environmentally-friendly process, it does not totally avoid toxic compounds, because the deleterious impact of ILs on environment is now assessed [24] and because **releases of mineral acids have also some environmental concerns [25,26].**

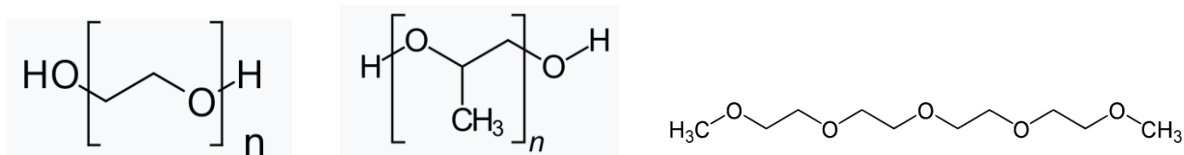
In order to lower the environmental impacts of extraction, it would be interesting to investigate other compositions, **avoiding as much as possible mineral acids and ILs.** Therefore, this work aims at deriving general rules regarding metal ion behaviour in ABS comprising  $\text{Na}_2\text{SO}_4$  and a non-toxic, very cheap material, polyethylene glycol (PEG). Emphasis was put on the fate of several transition metal ions: Co(II), Cr(III), Cr(VI), Cu(II), Fe(III), Mn(II), Mo(VI) and Ni(II). Insights into the extraction mechanism of the only two oxoanions of this list, Cr(VI) and Mo(VI), are obtained.

**This work is of fundamental nature but it has some potential applied aspects. In this respect, the concentrations of the different metal ions and of the  $\text{Na}_2\text{SO}_4$  salt were fixed as a compromise between different criteria. In view of the fundamental aim of this work, we had to cope with the different salt solubilities, the need for a rather high  $\text{Na}_2\text{SO}_4$  concentration, in order to obtain the biphasic state, but nevertheless avoiding immediate crystallization [27]. On an applied perspective, many industrial wastes are based on aqueous sulfate media and contain several ions of interest to this study. For example, deadly chromium sulfate salts are used in the tanning industry [28,29], while Co, Fe, Mn and Ni, among other elements, are found in the leachate of NiMH batteries obtained by use of sulfuric acid [30]. Fe, Cu, Co, Cr, Mn, and Ni are present together with sulfate ions in pickle liquors of the steel [31] and copper industry [32]. In this last example, the  $\text{Na}_2\text{SO}_4$  concentration is in the range of 135 g/L and the concentration ratios of  $\text{Na}_2\text{SO}_4$  to the metal ions vary from ca. 4 to more than 100. We therefore chose to test the robustness of the system PEG-400/ $\text{Na}_2\text{SO}_4$ / $\text{H}_2\text{O}$  by setting a single individual concentration of all the metal ions and a  $\text{Na}_2\text{SO}_4$  concentration close to the value of 135 g/L cited above.**

## 2. Materials and Methods

### 2.1 Chemicals

Polyethylene glycol with an average molecular weight of 400 (abbreviated as PEG-400) was acquired from Chem-lab with a purity of 99% while polypropylene glycol with an average molecular weight of 400 (abbreviated as PPG-400) and tetraethylene glycol dimethyl ether (abbreviated as TEG-DE) were acquired from Sigma-Aldrich. The chemical structures of these organic compounds are displayed in scheme 1.



Scheme 1: Chemical structure of (left to right): PEG, PPG and TEG-DE (source: Wikipedia).

Sulfuric acid  $\text{H}_2\text{SO}_4$  (96% in water) was provided by Carl Roth while  $\text{Na}_2\text{SO}_4$  was purchased from Fisher Chemicals. The metal salts used in this work are  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$  (Fluka, pur. >99 %),  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (Alfa Aesar, pur. 98-99%),  $\text{Cr}_2(\text{SO}_4)_3$  (Alfa Aesar, pur. 98-99%),  $\text{Na}_2\text{CrO}_4 \cdot 4\text{H}_2\text{O}$  (Prolabo, pur. 99%),  $\text{Fe}_2(\text{SO}_4)_3$  (Fluka, pur. 98-99%),  $\text{MnSO}_4 \cdot \text{H}_2\text{O}$  (Carl Roth, pur. 98%),  $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$  (Prolabo, pur. 98-99%) and  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  (Acros, pur. 98-99%). All these chemicals were used as received. The water used in all experiments was passed through a purification system Milli-Q apparatus commercialized by Merck (18 M $\Omega$ ).

### 2.2 Stock solution preparation

First, for studies in the absence of metal salts, an aqueous solution of  $\text{Na}_2\text{SO}_4$  was prepared at 145 g/L (1.02 M) and its pH was adjusted between 1.9 and 2.2 with  $\text{H}_2\text{SO}_4$ , which closely corresponds to the second  $\text{pK}_a$  value of  $\text{H}_2\text{SO}_4$ .

Second, single metal stock solutions in  $\text{Na}_2\text{SO}_4/\text{H}_2\text{O}$  as described above were prepared to investigate the influence of metal ions onto the binodal curve in the system PEG-400/ $\text{Na}_2\text{SO}_4/\text{H}_2\text{O}$ . The metal ions considered are: Cr(III), Cr(VI), Fe(III), Mo(VI) and Ni(II). The samples were stirred overnight to allow the total dissolution of the salt. Concentrations equal to 5.0 g/L of salt have been prepared, except for Cr(III) for solubility limit reasons. The AAS analysis performed lead to a concentration of 2.3 g/L for Cr(III) saturated solution. Considering the preparation protocol, the ratio (in g) of  $\text{Na}_2\text{SO}_4$  to the metal ion is equal to 29 (except for Cr(III)). For one particular experiment, a concentration of 20 g/L of Cr(VI) salt was also prepared, following the same procedure. These metal stock solutions were used only for the binodal determinations.

Third, single metal stock solutions in  $\text{Na}_2\text{SO}_4/\text{H}_2\text{O}$  as described above were prepared to investigate the extraction of Co(II) and of the above mentioned metal ions : Cr(III), Cr(VI), Cu(II), Fe(III), Mn(II), Mo(VI) and Ni(II).

### 2.3 Phase diagrams by turbidity method

The binodal curves were determined using the classical turbidity method [6], starting with a known amount of PEG-400 (which is in liquid state at room temperature). Dropwise additions of an aqueous stock solution of  $\text{Na}_2\text{SO}_4$  at 145 g/L (without or with metal salt, accordingly) and, alternatively, ultrapure water, allows to change the state of the system from monophasic to biphasic and vice versa. The weights of added water and  $\text{Na}_2\text{SO}_4$  stock solutions were measured using a balance (Precisa gravimeters AG  $\pm 0.0001$  g). The solution was kept under constant agitation using a magnet (400 rpm) and was thermoregulated at  $T = 25$  °C or  $T = 40$  °C by the use of a water heating/cooling system. In the following, in line with our previous work [13], we will note the ABS as PEG-400/[ $\text{Na}_2\text{SO}_4 + \text{Me}(x)$ ]/ $\text{H}_2\text{O}$ , where Me(x) stands for the metal ion and its oxidation state, in order to pinpoint the preparation protocol.

With this procedure, the total amount of water in any ABS sample is the sum of the ultra-pure water added and the water from the  $\text{Na}_2\text{SO}_4$  acid aqueous solution (without or with metal ions). This has been duly considered in the calculations.

The binodal curves thus obtained are plotted in an orthogonal 2D plot, where the x axis corresponds to the weight percentage (wt%) of the  $\text{Na}_2\text{SO}_4$  salt, while the y-axis corresponds to the weight percentage (wt%) of PEG-400. The remaining wt% corresponds to the contribution of water and metal salt, if any, to the total mass of the sample. For example, a concentration of 5 g/L of Ni(II) for a total weight percent of

$\text{Na}_2\text{SO}_4$  of ca. 10 % corresponds to 0.86 wt% of Ni(II) sulphate salt in the sample. At maximum, a concentration of 20 g/L of Cr(VI) for a total weight percent of  $\text{Na}_2\text{SO}_4$  equal to ~10 % corresponds to ca. 5 wt% of Cr(VI) sulphate salt in the sample.

#### 2.4 Experimental protocol, phase characterisation and quantifications

Experiments were performed at  $T = 25\text{ }^\circ\text{C}$ , using a thermostatic bath. Before mixing, densities of the various aqueous phases have been recorded at the working temperature. The PEG-400 density is equal to 1.11 ( $T = 25\text{ }^\circ\text{C}$ ). Then, a known mass of PEG-400 was contacted with a known mass of the aqueous [ $\text{Na}_2\text{SO}_4 + \text{Me}(x)$ ] stock solution in order to test the mixtures 20/80, 30/70, 40/60 wt% of PEG-400 and aqueous solution, respectively. The masses of the PEG and aqueous solutions were chosen in order to obtain a lower phase with a volume above 10 mL (typical example for 20 wt% of PEG-400: 10 g of PEG-400 plus 40 g of aqueous solution). There was no ultra-pure water added. Metal ions were Co(II), Cr(III), Cr(VI), Cu(II), Fe(III), Mn(II), Mo(VI) and Ni(II). Samples were shaken by hand for a few seconds only, which was proved enough to reach equilibrium. All the mixtures studied were in the biphasic state, while the mixture 10/90 wt% of PEG-400/[ $\text{Na}_2\text{SO}_4 + \text{Me}(x)$ ] was monophasic, whatever the nature of the metal ion. Photos of some of the samples with Cr(III) and Cr(VI) are presented in Fig. 1, while samples with Co(II) and without added metal ions can be found in the ESI (Fig. S0). Once samples were equilibrated at  $T = 25\text{ }^\circ\text{C}$ , the volumes of the upper and lower phases were recorded and then the two phases were carefully separated. As compared to the situation before mixing, important changes in the volumes of the two phases could be observed. It should be highlighted that pipetting the total upper phase is almost impossible without pollution from the lower phase, which would be deleterious to the analytical characterisations. It was thus decided to pipette as much as possible of the upper phase, then to discard the interface to finally attain the lower phase without pollution. Subsequently, densities and pH were measured for the upper and lower phases. The experimental uncertainty on volume determination of the upper and lower phases is equal to 0.1 mL. Global mass balance was checked as mass of upper phase plus mass of lower phase compared to the total initial mass and was within the 98-107% range.

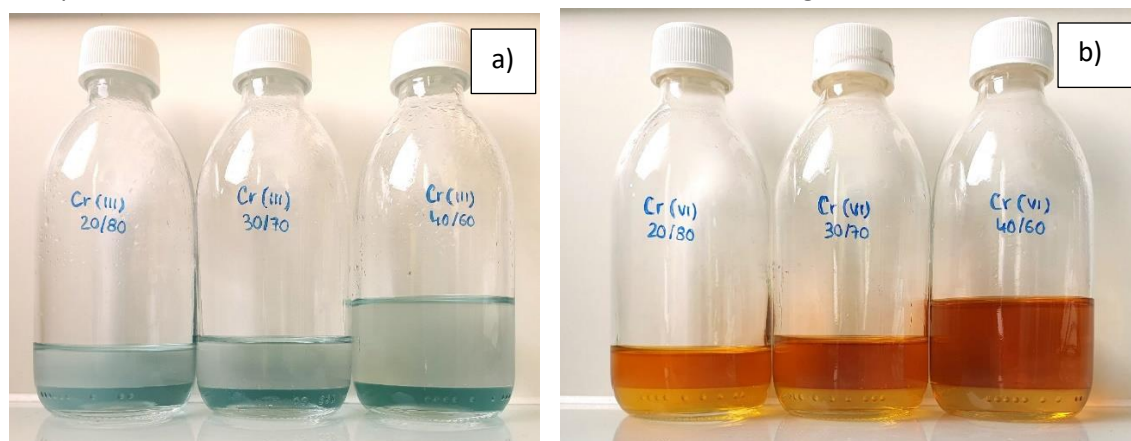


Fig. 1: Samples at 20/80 (left); 30/70 (middle); 40/60 wt%(right) of PEG-400 plus [ $\text{Na}_2\text{SO}_4 + \text{Me}(x)$ ] aqueous solution for a:  $\text{Me}(x) = \text{Cr(III)}$  and b) for  $\text{Me}(x) = \text{Cr(VI)}$ .

All upper phases and all lower phases with Na(I) alone were stable for days, while a slow crystallization process was observed for the 40/60 wt% samples with added metal ions. The same crystallization phenomenon was observed for some of the lower 30/70 wt% phases with added metal ions, on a longer time scale. Therefore, in view of analytical measurements, aliquots were taken right after phase separation or right after a heating and cooling cycle to ensure all possible crystals were dissolved.

For the general characterisation of the phases, the pH was measured with the help of a pH-meter from SI Analytics, Titration Titroline® 6000/7000, while <sup>1</sup>H NMR was used to quantify PEG-400 amounts in the lower phases of all samples, except for Mn(II) samples, due to the paramagnetic character of this ion. To this aim, the phases were diluted in DMSO/D<sub>2</sub>O and comparison of the integrals of the PEG and DMSO signals allowed PEG determination, using a calibration line (R = 0.9985) between 1.20 wt% and 38.81 wt% of PEG-400.

AAS/AES instrument is a Perkin Elmer Pinaacle 900F with an accuracy of ± 0.5%. It has been used for Co(II), Cr(III), Cr(VI), Cu(II), Fe(III), Mn(II), and Ni(II) determinations in the upper and lower phases, by the use of specific lamps, while Na(I) has been measured in the emission mode. Mo(VI) amounts in the upper and lower phases were obtained by use of ICP-MS (Perkin Elmer NexION 2000c). Standard solutions of Mo(VI) at 0, 5, 10 and 20 ppb containing a fixed concentration of an internal standard (2.5 ppb of Rh) were used for calibration. Samples were diluted (dilution factor is ca. 1000) in ultra-pure nitric acid solution (2%) to reach the calibration range and the same internal standard was added. Recorded masses are selected according to their natural occurrence and polyatomic and isobaric interferences. Analysis was performed on <sup>98</sup>Mo amu (atomic mass unit). Data were analyzed with the Syngistix for ICP-MS Software. SAA and ICP-MS results are expressed in concentrations (mg/L). Measuring the volumes of the upper and lower phases allows to access to the masses of ions in each phase. The mass balances were checked for Na(I) and all metal ions individually. These were in the ranges 91-101% for Na(I) and 92-101% for individual metal ions.

Quantification of ion presence in the upper phase was done through the percentage determination, P%(M), of a given species M, as follows:

$$P\%(M) = 100 \frac{M_u}{M_t} \quad (1)$$

where M<sub>t</sub> is the total mass of the species introduced in the system, expressed in grams, and M<sub>u</sub> is the mass of the species in the upper phase of the ABS at equilibrium, expressed in grams. Experimental uncertainties on P% values are in the range of 5% and are mainly connected to volume estimates for the upper phase and to the AAS/ICP-MS experimental uncertainties.

In a traditional extraction process for species M, P%(M) is increasing as the (organic) extracting phase amount (in our case, PEG-400) is increased. In the following, we will thus use the term “extraction” in this case, while we will use “partition” if increasing the PEG-400 amount induces a decrease in P% values.

A photometric kit by Spectroquant was used to measure sulphate ions through colorimetric analysis. The instrument used is a spectrophotometer from Xylem (WTW series, Photolab S12). The measurement principle is based on the reaction of barium ions with sulphate ions to give the poorly soluble barium sulphate salt at pH between 2 and 10. The resulting turbidity is measured by the spectrophotometer. Samples containing sulphates are pre-diluted in a concentration range of 100 to 1000 mg/L. The standard deviation of the method is 10.3 mg/L SO<sub>4</sub><sup>2-</sup>. All sulphate forms (SO<sub>4</sub><sup>2-</sup> and HSO<sub>4</sub><sup>-</sup>) of the sample are taken

into account, owing to the pH of the buffer provided in the method. Interferences in sulphate determination for the foreign substances Cu(II), Fe(III), Mn(II) and Ni(II) above 1 g/L are indicated by the manufacturer, and interferences already appearing above 0.1 g/L for Cr(III) and 0.25 g/L for Cr(VI) are mentioned. For our experiments, it has been checked that metal ion concentrations of Cu(II), Fe(III), Mn(II) and Ni(II) in the upper phases are always largely below the limit of 1 g/L, which makes the determination of P%(sulphate) through equation 1 reliable. By contrast, this is not the case for the upper phases of samples containing Cr(III) and Cr(VI) so P%(sulphate) has not been determined for these samples. The mass balance of sulphate ions in any of the sample under study has not been checked because it is subject to experimental bias in the lower phase as explained above.

Experiments with TEG-DE and PPG have also been carried out but they concerned solely Cr(VI) stock solutions, at  $T = 25\text{ }^{\circ}\text{C}$ , with the same protocol as described above. Amounts of TEG-DE or PPG were equal to 20, 30 and 40 wt%. The Cr(VI) percentage, P%(Cr(VI)) was investigated, together as the volume of upper and lower phases, densities and pH.

### **3 Results and discussion**

#### *3.1 Binodal curves: effects of metal ion type, metal ion concentration and temperature*

In a first step, Figure 2 compares the binodal curve obtained in this work for the system PEG-400/ $\text{Na}_2\text{SO}_4$ / $\text{H}_2\text{O}$ , at  $T = 25\text{ }^{\circ}\text{C}$   $\text{pH} \approx 2.2$  (no metal ions added) with the published data for PEG-400/ $\text{Na}_2\text{SO}_4$ / $\text{H}_2\text{O}$  (no pH value indicated), acquired at  $T = 30\text{ }^{\circ}\text{C}$  [33] and data from [34] for PEG-400/ $\text{Na}_2\text{SO}_4$ / $\text{H}_2\text{O}$  at  $T = 25\text{ }^{\circ}\text{C}$  (no pH value indicated). Fig. 2 evidences a very good agreement between the three data sets. In fact, temperature effects have been proved to be negligible for PEG-400/ $\text{Na}_2\text{SO}_4$ / $\text{H}_2\text{O}$  in the range  $25 - 45\text{ }^{\circ}\text{C}$  [34].

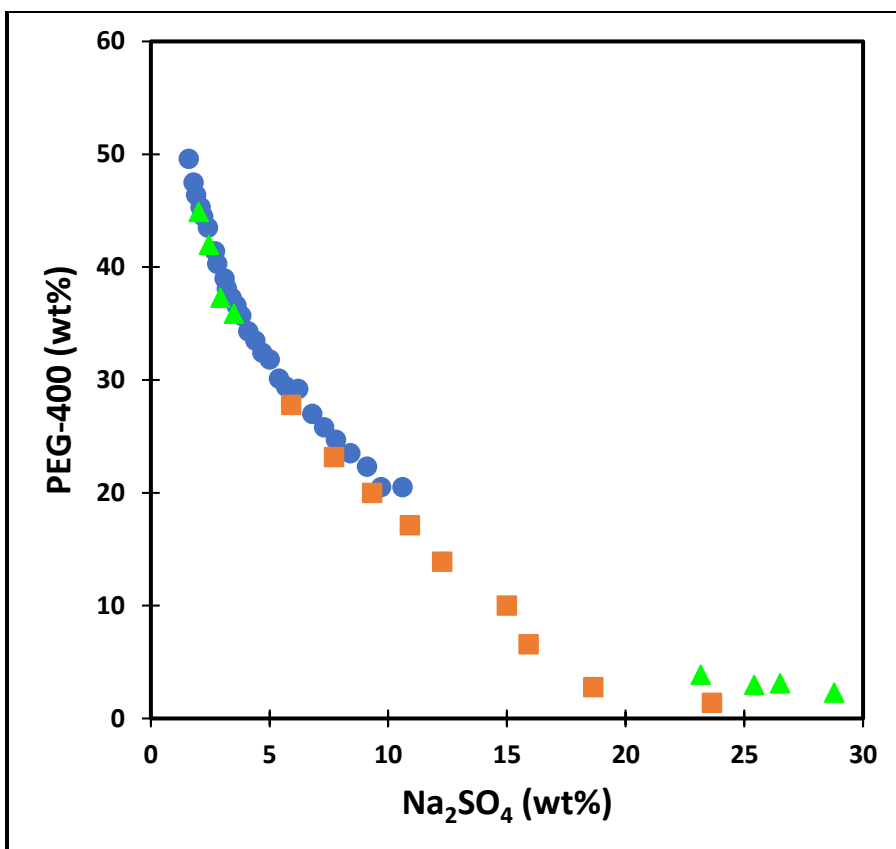


Fig. 2: Binodal curves for the system PEG-400/Na<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O. Blue circles: T = 25 °C, pH = 1.9, this work; Orange squares: T = 30 °C data from [33]; green triangles T = 25 °C, data from [34].

To the best of our knowledge, these are the two closest comparisons we can make with available literature data as the previously published papers have dealt with PEG of much larger average molar masses, and/or different temperatures or pH values. For example, Taboada et al. have used PEG-4000 [35] at T = 25 °C (no pH value indicated) while Snyder and co-workers used PEG-3350 or PEG-1000 at T = 25 °C (no pH value indicated) [36]. Furthermore, these latter data [36] have been acquired by determination of the tie-lines, which is a method more subject to experimental uncertainties than the turbidity method we used for the binodal determination. Another publication with which comparison is not straightforward displays data for PEG-600/Na<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O at T = 27 °C and pH 7, adjusted by NaOH addition [4].

In a second step, Fig. 3 gathers the binodal curves collected at T = 25 °C for Cr(III), Cr(VI), Fe(III), Mo(VI) and Ni(II) containing systems together with the data in the absence of metal ions. Then, Fig. 4 focuses on the change of concentration for Cr(VI), from 5 g/L to 20 g/L at T = 25 °C, while Fig. 5 shows the effect of increasing temperature, for Cr(VI) = 5 g/L, from T = 25 °C to 40 °C.



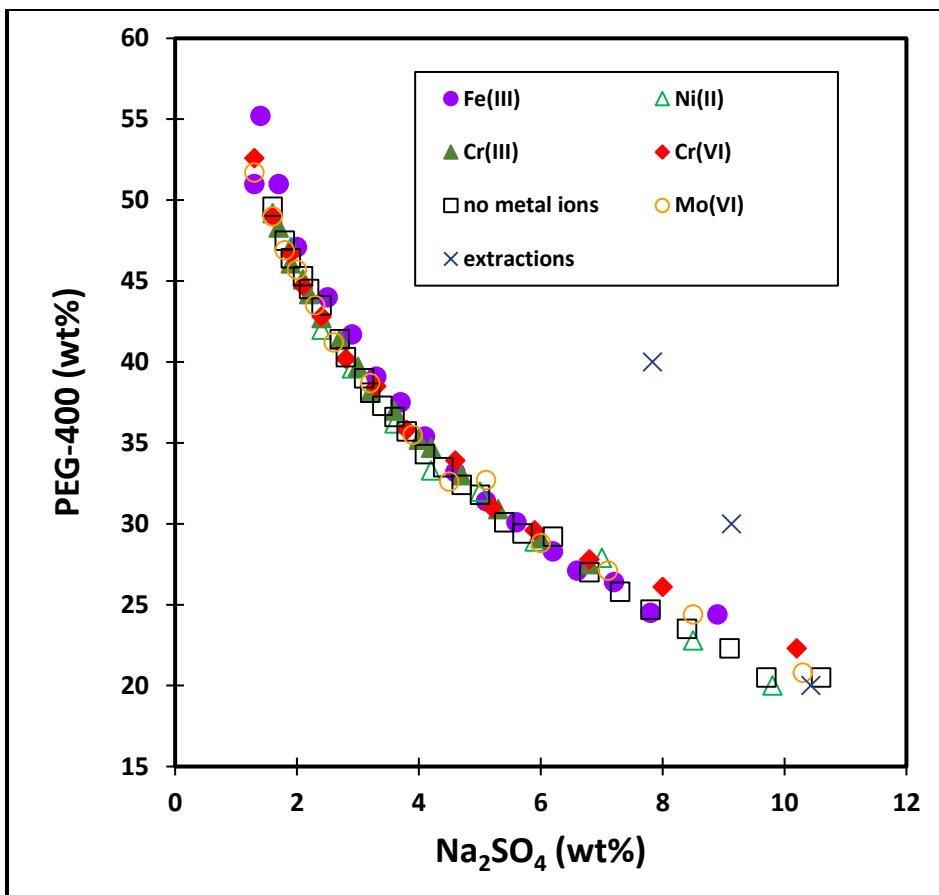


Fig. 3: Binodal curves obtained for several systems of the type PEG-400/[Na<sub>2</sub>SO<sub>4</sub>+ Me(x)]/H<sub>2</sub>O at T = 25 °C. Empty black squares: no metal added; green solid triangles: Cr(III); solid red diamond: Cr(VI); purple circles: Fe(III); orange empty circles: Mo(VI); empty green triangles : Ni(II). All data are from this work. Crosses (x) correspond to the three pristine samples studied for extraction (no metal added, see text, section 2.4).

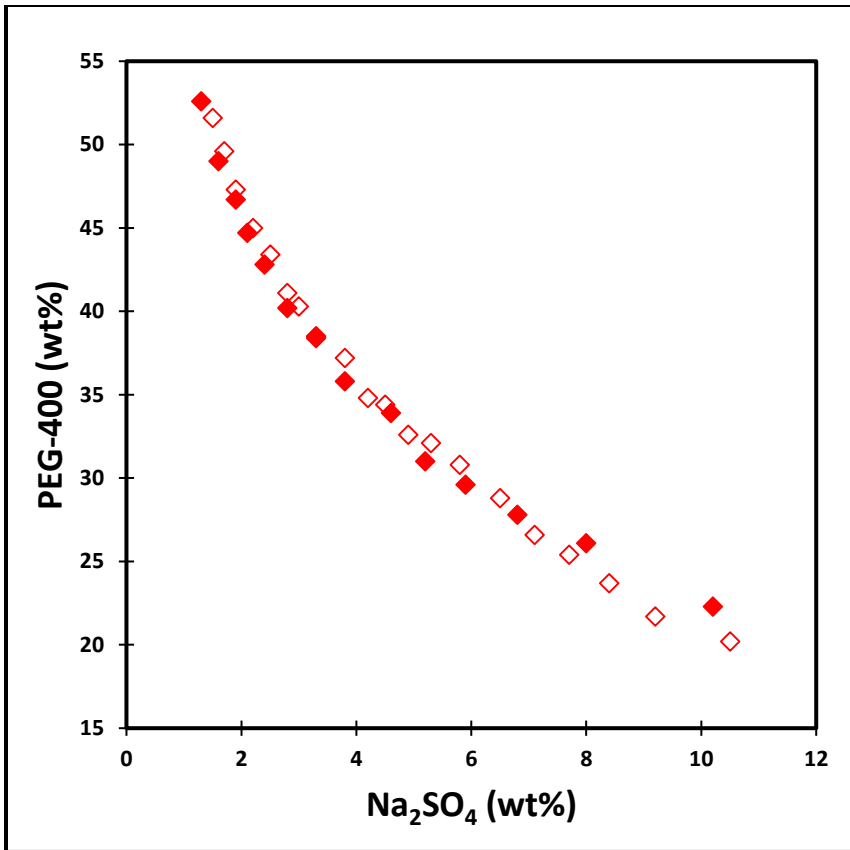


Figure 4: Binodal curves for the systems PEG-400/[Na<sub>2</sub>SO<sub>4</sub> + Cr(VI)]/H<sub>2</sub>O. Solid red diamonds: [Cr(VI)] = 5 g/L and T = 25 °C; empty red diamonds: [Cr(VI)] = 20 g/L and T = 25 °C.

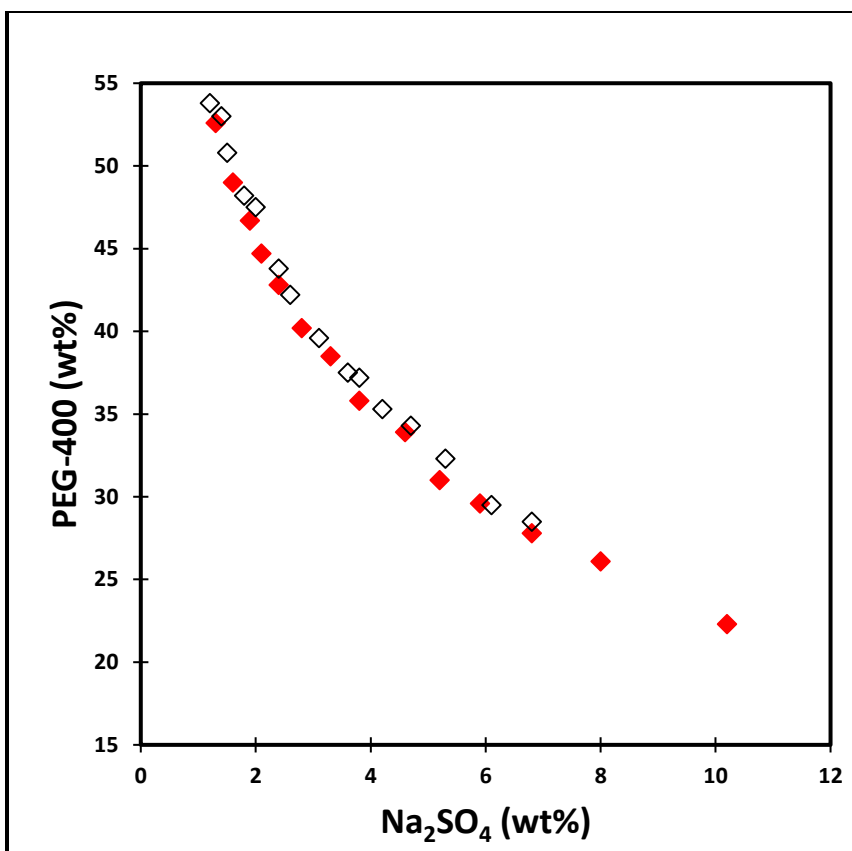


Figure 5. Binodal curves for the systems PEG-400/[Na<sub>2</sub>SO<sub>4</sub>+Cr(VI)]/H<sub>2</sub>O. Solid red diamonds: [Cr(VI)] = 5 g/L and T = 25 °C; empty black diamonds: [Cr(VI)] = 5 g/L and T = 40 °C

As can be seen from Figs. 3, 4 and 5, all curves are superimposed on the curve obtained in the absence of metal ions. The ABS PEG-400/Na<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O is not sensitive to temperature effects [34] in the range 25 – 45 °C, and this is confirmed even in the presence of Cr(VI) (see Fig. 5). As already pinpointed in the experimental section 2.3, the contribution of the metal ions to the total weight of the mixture is less than 5 wt%. Therefore, it is not surprising that all curves superimpose in Figures 3 to 5. In brief, in these experiments, the Cr(III), Cr(VI), Fe(III), Mo(VI) and Ni(II) metal ions, present either as cations or anions, are to be considered as minor additives to the ABS PEG-400/Na<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O, not disturbing the phase separation phenomenon. Several literature data show that the mixture PEG-4000/CuSO<sub>4</sub>/H<sub>2</sub>O is an ABS [37–40]. This means that even in large amounts, Cu(II) is excluded from the PEG-rich phase as Na(I) is. This phenomenon would thus not be dependent on the concentration of (at least) the Cu(II) ion and of Cr(VI) (up to 20 g/L).

As a consequence, attempts to fit the unique binodal curve we obtain will not give useful information, because none of the parameters of the empirical expressions found in the literature (for a brief review, see [14]) could be correlated to the physico-chemical parameters we investigated (addition of metal ions, change in temperature or change in metal ion concentration). This argument also holds for any other search for correlation, for example with the hydration capacity of ions or with the Hofmeister series.

The determination of binodal curves in the presence of ions as additives is rather scarce in literature. The closest possible comparison with the present work concerns the system PEG-8000/Na<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O, at T = 23 °C and pH = 7.4 (by the use of a phosphate buffer), to which NaCl or KCl were added [41]. In this case,

the protocol is slightly different from ours, because the NaCl or KCl salts were added as solutes in an aqueous solution of the phosphate buffer while in our protocol, metal salts have been added in an aqueous solution of Na<sub>2</sub>SO<sub>4</sub>. Therefore, adopting our way of notation, the system of Ferreira et al. would be written as: PEG-8000/Na<sub>2</sub>SO<sub>4</sub>/[H<sub>2</sub>O+ NaCl (or KCl)]. Another obvious difference between our data and the work of Ferreira and co-workers relies in the different chemical nature of the additives. As concerns the effect of NaCl and KCl, both salts lead to a shift of the binodal curve towards the left, with no significant difference between NaCl and KCl [41]. The maximum NaCl weight contribution is estimated to be 4 wt% (ca. 0.7 mol of NaCl per kg of sample) in these samples. NaCl was also shown to impact the position of the binodal curve for a very different ABS, namely P<sub>4,4,4,14</sub>Cl/HCl/H<sub>2</sub>O [20], where P<sub>4,4,4,14</sub>Cl is the ionic liquid tributyltetradecylphosphonium chloride. Already at 1 wt% NaCl (i.e. 0.17 mol of NaCl per kg of sample) added, a very significant shift of the binodal curve could be observed, as compared to the binodal in the absence of NaCl. For comparison, the maximum amounts we introduced are in the range of 0.05 mole per kg of sample for NiSO<sub>4</sub> and of 0.12 mole per kg of sample for Cr<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>. Striking differences can also be found when comparing the data of this work with those we previously published for P<sub>4,4,4,14</sub>Cl/[HCl + Me(x)]/H<sub>2</sub>O, where Me(x) stands for Cr(III) or Ni(II) [13]. In this previous study, increasing concentrations of Cr(III) or Ni(II) (chloride salts) induced a significant left shift of the binodal curve, provoking a phase separation at much lower ABS inducers concentrations, although the maximum weight contribution of these metal ions was in the range of a few wt%. Even more surprisingly, the addition of Fe(III)Cl<sub>3</sub> led to a strong distortion of the shape of the curve for P<sub>4,4,4,14</sub>Cl/[HCl+Fe(III)]/H<sub>2</sub>O [13].

### 3.2 Partition behaviour of metal ions: Co(II), Cr(III), Cu(II), Fe(III), Mn(II), Ni(II)

Densities of the upper and lower phases are listed in Table S1, while Table S2 displays the volume percentages of the upper and lower phases and Table S3 presents the pH values of all samples. Plots of the corresponding data can be found in Figs. S1 to S3, respectively. A remarkable stability of the upper phase density is observed, whatever the PEG amount and the metal ion added, at  $d = 1.09 \pm 0.01$ . This value is very close to the density of PEG-400 ( $d = 1.11$ ,  $T = 25^\circ\text{C}$ ) and is in line with the limited amount of PEG-400 to be present in the lower phase (see Table S4 and Fig. S4). By contrast, the density of the lower phase increases from  $1.18 \pm 0.01$  for all samples at 20 wt% PEG to  $1.30 \pm 0.02$  for 40 wt% PEG. These trends are in very good agreement with the average density of the upper phases equal to  $1.084 \pm 0.004$  for PEG-1000/Na<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O at  $T = 25^\circ\text{C}$  [36], and with an increase from 1.2 to 1.4 for the lower phase densities as mentioned for the system PEG-3350/Na<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O at  $T = 28^\circ\text{C}$  [42]. Density values of upper phases close to 1.08 were also observed for PEG-4000/CuSO<sub>4</sub>/H<sub>2</sub>O [38]. The relative volume of the upper phase significantly increases from  $(73 \pm 2)\%$  to  $(84 \pm 1)\%$  as PEG increases from 20 wt% to 40 wt%. This expected increase is independent of the presence or absence of added metal ions. Finally, one may conclude to a slight increase in pH values as the PEG amount is increased, for both the upper and the lower phases, which nevertheless display similar pH values for a given PEG amount. This can be ascribed, at least in part, to an increase of the total volume of the sample, due to PEG addition.

No significant change upon metal ion addition (up to 1 g/L in the [Na<sub>2</sub>SO<sub>4</sub>+Me(x)]/H<sub>2</sub>O starting solution) can be inferred from any of these data (density, volume ratio and pH). This observation is in line with our previous conclusion in section 3.1 above that the added metal ions are simply minor additives to the ABS PEG-400/Na<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O.

We now first focus on the pristine samples, i.e. PEG-400/ $\text{Na}_2\text{SO}_4/\text{H}_2\text{O}$  (no metal ions added) whose positions in the phase diagram are shown as crosses in Fig. 3. The first column of Table 1 displays the P%(Na(I)) and P%(sulphate) values for the three PEG amounts of this study for the pristine sample (no metal ions added). In these three samples, the formation of a biphasic state leads to the presence of Na(I) both in the lower and the upper phase, the latter one containing from 30 % to 12.6 % of Na(I) ions as PEG-400 varies from 20 wt% to 40 wt%. The mass transfer phenomenon towards the upper phase is thus not very efficient and is less effective as the amount of PEG is increased. This observation directly derives from the binodal curve in Figure 3 and is a well-known result in the ABS community [43]: increasing the amount of polymer leads to a better segregation of the other biphasic inducer, i.e. the inorganic salt  $\text{Na}_2\text{SO}_4$ , in the lower phase. Similarly, data can also be considered as the mass transfer of sulphate ions, from 42% down to ca. 19%.

Table 1: P% values of sodium and sulphate entities in the upper phase for the various metal ion extracted. The case without metal ions added is also included (first column, Na(I)).

PEG-400 (wt%)	Na(I)	Co(II)	Cr(III)	Cr(VI)	Cu(II)	Fe(III)	Mn(II)	Mo(VI)	Ni(II)
sodium									
20	30.2	32.5	38.2	39.6	32.8	35.6	32.1	33.7	32.4
30	19.6	20.7	29.9	31.0	22.3	25.1	22.7	21.9	20.9
40	12.6	11.9	21.5	23.0	12.9	18.5	13.0	15.4	11.2
sulphate									
20	42.0	43.0	n.d	n.d	39.5	51.1	40.7	39.9	40.0
30	21.9	25.5	n.d	n.d	24.0	27.4	22.4	24.2	23.5
40	18.8	15.1	n.d	n.d	12.6	20.2	15.9	16.2	17.6

n.d. not determined (see section 2.4).

Considering the neutral character of PEG-400, the displacement of Na(I) ions should be accompanied by that of sulphate ions and vice versa in order to compensate the charges. However, in order to exactly compensate for the positive +1 charge of one single sodium cation, the sulphate counter-anion can be either in the  $\text{HSO}_4^-$  form or, if under the  $\text{SO}_4^{2-}$  form, there will be two Na(I) cations transferred simultaneously. Note that the contribution of  $\text{H}^+$  to the charge compensation can be neglected, as  $\text{H}^+$  ions are ca. 2 orders of magnitude less present than Na(I) cations. From the data in Table 1, it is deduced that two Na(I) ions are not exactly charge-compensated by one sulphate ion for PEG-400 amount equal to 20 wt%, while the other two values P%(Na(I)) and P%(sulphate) are closer to one another. The only plausible explanation is that part of the sulphate ions are transferred as  $\text{HSO}_4^-$ . In other words, the salt  $\text{Na}_2\text{SO}_4$  initially introduced in the sample is partly turned to  $\text{NaHSO}_4$  in the upper phase. As a consequence, the compositions of the upper and lower phases cannot be plotted in Fig. 3, which x-axis is based on  $\text{Na}_2\text{SO}_4$  wt% contribution and not on that of  $\text{NaHSO}_4$ . In this respect, it should be stressed that in the previous works displaying tie-line data for closely related systems Na(I) was measured by AAS [35], conductivity [34] or ionic chromatography [36], but sulphate ions were never measured independently. Regardless of the results of the other publications, in the context of our work, the binodal curve in Figure 3 should be

used only as a help for the preparation of samples starting from PEG-400, ultra-pure water and  $\text{Na}_2\text{SO}_4$  and tie-lines cannot be drawn in a 2D plot.

We then turn to the systems with added metal ions. The positions of the samples in the phase diagram are almost identical to those presented in Fig. 3 in the absence of metal ions and are thus not plotted for the sake of clarity. Again, this is due to the very low contribution of the metal ions to the total mass of the samples. This plot shows that samples composed of 10 wt% of PEG-400 + 90 wt% of  $[\text{Na}_2\text{SO}_4 + \text{Me}(x)]$  aqueous stock solutions are all monophasic, as experimentally observed.

Fig. 6 shows the  $\text{P}\%(\text{Na(I)})$  values, as a function of the PEG-400 amount and depending on the added metal ions, while Fig. 7 gathers the corresponding  $\text{P}\%(\text{sulphate})$  values except for Cr(III) and Cr(VI) (see section 2.4). Data are collected in Table 1. Fig. 8 shows the individual  $\text{P}\%$  values, for Co(II), Cr(III), Cr(VI), Cu(II), Fe(III), Mn(II), Mo(VI) and Ni(II) for the three different mass contributions of PEG-400 investigated: 20, 30 and 40 wt%. The corresponding values are presented in Table 2.

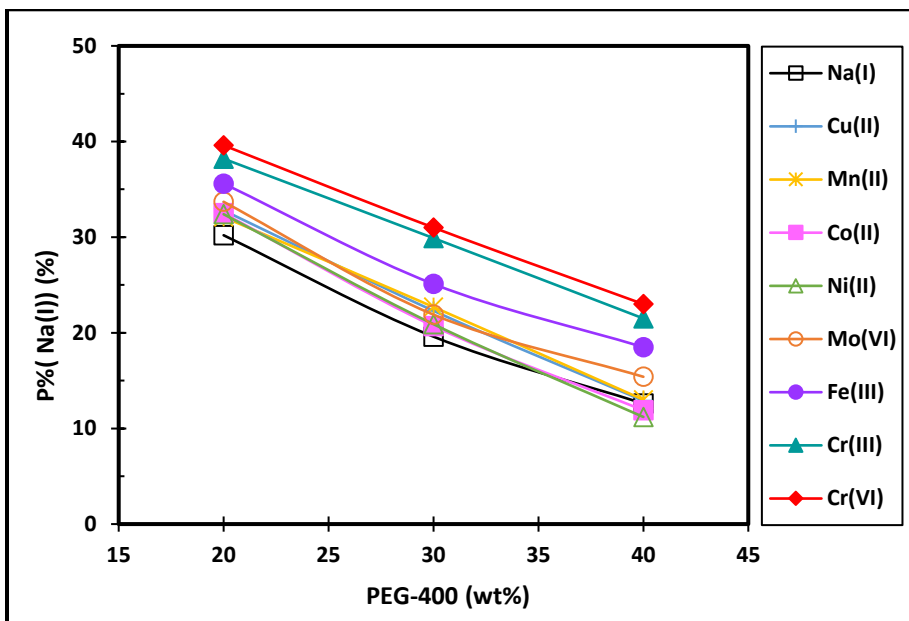


Fig. 6:  $\text{P}\%(\text{Na(I)})$  values for the three PEG compositions in samples with and without added metal ions.  $T = 25\text{ }^\circ\text{C}$ .

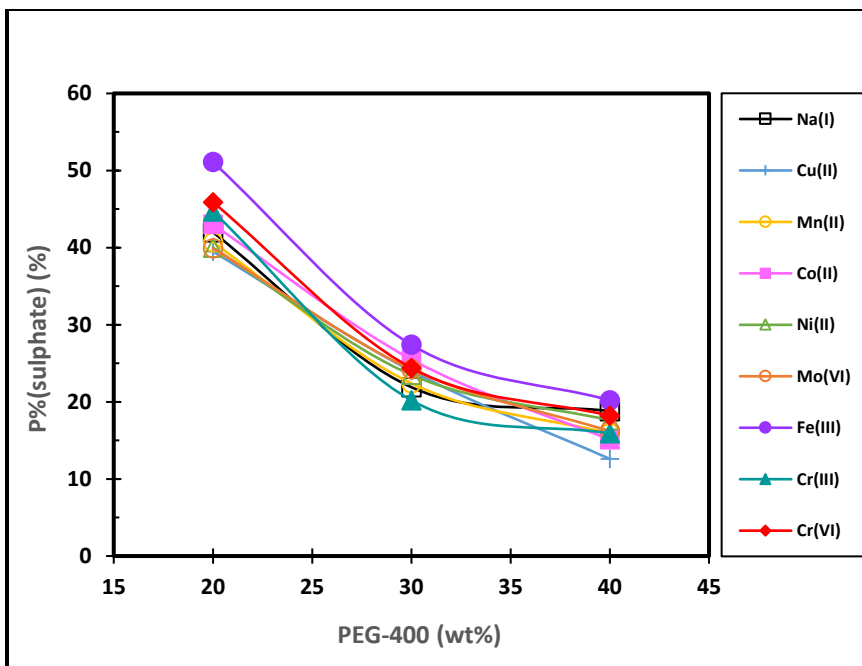


Fig. 7: P%(sulphate) values for the three PEG compositions in samples with and without added metal ions. T = 25 °C.

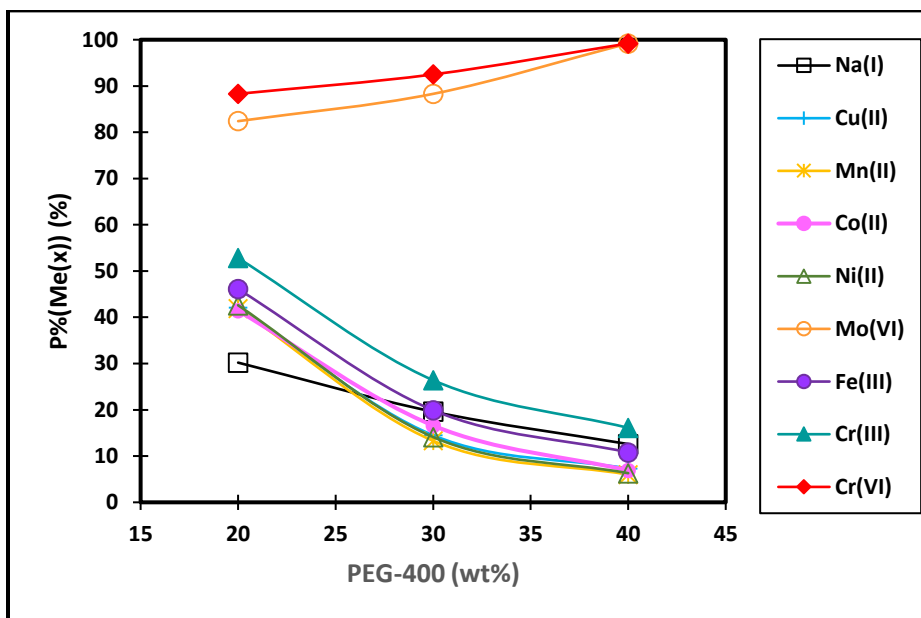


Fig. 8: P% values for metal ions as a function of PEG-400 wt%. P%(Na(I)) values for the pristine samples (no metal ions added) are also included. T = 25 °C.

Table 2. P% values of the metal ions as a function of PEG-400 amount. Data for Na(I) (no metal ions added) are also included (first column).

PEG-400 (wt%)	Na(I) (%)	Co(II) (%)	Cr(III) (%)	Cr(VI) (%)	Cu(II) (%)	Fe(III) (%)	Mn(II) (%)	Mo(VI) (%)	Ni(II) (%)
20	30.2	41.4	52.8	88.3	42.1	46.1	41.9	82.4	42.6
30	19.6	16.6	26.4	92.5	13.3	19.9	13.3	88.3	14.1
40	12.6	6.9	16.1	99.2	6.0	10.8	6.0	99.2	6.3

First, Figs. 6 and 7 evidence the difference between P%(Na(I)) and P%(sulphate), as already observed for the pristine sample. This common trend for all samples whatever the presence or absence of added metal ions is perfectly in line with the negligible impact of the latter on the biphasic state of the samples.

Second, examination of Figs. 6 to 8 evidences a common decreasing trend of P%(Na(I)), P%(sulphate) and P% values for Co(II), Cr(III), Cu(II), Fe(III), Mn(II), and Ni(II) samples as PEG amount is increased. In particular, data for Co(II), Cu(II), Fe(III), Mn(II) and Ni(II) are very close to one another, while those for Cr(III) differ slightly. Again, this is ascribed to the low amount of sulphate salts added with the metal ions. The behavior of all these metal cations means their corresponding sulphate salts are PEG-400 partners in view of ABS formation, as already discussed for Na<sub>2</sub>SO<sub>4</sub> in the pristine samples. In fact, it could be considered as a kind of additivity of two ABS formation phenomena. The major one (in terms of its component amounts) would be that of PEG-400/Na<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O ABS formation, to which the formation of PEG-400/sulphate salt of Me(x)/H<sub>2</sub>O would simply superimpose. Indeed, three of the sulphate metal salts we used, CuSO<sub>4</sub>, Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> and MnSO<sub>4</sub> are known to be ABS inducers in the systems PEG-3350/CuSO<sub>4</sub>/H<sub>2</sub>O (no temperature indicated) [44], PEG-4000/CuSO<sub>4</sub>/H<sub>2</sub>O (T = 5 °C to 45 °C) [37,38], PEG-4000/Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>/H<sub>2</sub>O at T = 50 °C [45] and PEG-2000/MnSO<sub>4</sub>/H<sub>2</sub>O (T = 25 °C) [18]. ZnSO<sub>4</sub> is also an ABS inducer together with PEG-3350 [44]. To the best of our knowledge, there are no published data for the other ions of interest to this work. Anyway, the behavior we observe for Co(II), Cr(III), Cu(II), Fe(III), Mn(II), and Ni(II) cannot be tagged as an extraction process induced by PEG-400.

### 3.3 Extraction mechanism for Cr(VI) and Mo(VI)

By contrast, the behavior of the two oxoanions Cr(VI) and Mo(VI) stands out from those of the other metal ions, as their amount in the upper phases increases as a function of PEG amount, from 88 to 99 % for Cr(VI) and from 82 % to 99 % for Mo(VI). As already pinpointed, in classical liquid-liquid extraction of metal ions, increasing the relative volume (or mass) of the organic extracting added phase promotes transfer of the targeted metal ions towards it. This is exactly what is observed in this work for Cr(VI) and Mo(VI), PEG-400 being the extracting phase in our case. The main differences between classical liquid-liquid extraction systems and so-called ABS are to be found in the absence of extractant and in the high amount of water in both phases in the ABS case [46].

Extraction/partition of Cr(VI), Cr(III), Mo(VI) and other metal ions of interest to our work, by use of systems close to ours, has already been studied in the literature. Literature data of interest to this work are gathered in Table 3. For chromium studies, P%(Cr(VI)) equal to ca. 92% and P%(Cr(III)) close to zero were measured in the system PEG-1500/Na<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O at T = 25°C [47]. Increasing the tie-line length of the



sample leads to an increase in P%(Cr(VI)), from ~ 84 % to ~100 %, which is a strong indication of an extraction mechanism according to our definition. Similarly, in view of Cr(III)/Cr(VI) separation, the system PEG-4000/Na<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O was investigated and provided (at best) P%(Cr(VI)) close to 100%, while Cr(III) was not extracted (pH = 3, no temperature indicated). Increasing the PEG-4000 amount has a positive effect on Cr(VI) extraction, but the amount of Fe(III) and Co(II), among other tested metal ions, in the upper phase was negligible [48]. The system PEG-1000/Na<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O (initial pH = 2, T from 30 °C to 60 °C) induces an increased partition of Mo(VI) from 97.7% to 99.5% as PEG is increased from 10 to 20 wt%, again a signature of an extraction process [49]. These authors also shown that the slight pH increase of the system, equal to ca 0.2 pH units, is not ascribable to the presence or absence of the Mo salt. All these data are in line with our chromium and molybdenum results.

Other very interesting published data concern the system PEG-400/Na<sub>2</sub>MoO<sub>4</sub>/H<sub>2</sub>O, which displays a binodal from 15 °C to 30 °C [50]. In this case, Mo(VI) simply follows the trend already observed for Co(II), Cr(III), Cu(II), Fe(III), Mn(II), and Ni(II), that is the sodium salt Na<sub>2</sub>MoO<sub>4</sub> is an inducer of the biphasic state and MoO<sub>4</sub><sup>2-</sup> has simply replaced SO<sub>4</sub><sup>2-</sup>. Recently, Muruchi and co-workers used the system PEG-4000/Na<sub>2</sub>MoO<sub>4</sub>/H<sub>2</sub>O to perform ReO<sub>4</sub><sup>-</sup> extraction [51]. In this case, the amount of ReO<sub>4</sub><sup>-</sup> is small as compared to that of Na<sub>2</sub>MoO<sub>4</sub> and the authors observed extraction of ReO<sub>4</sub><sup>-</sup> (P%(ReO<sub>4</sub><sup>-</sup>) = 88%) while the MoO<sub>4</sub><sup>2-</sup> role is that of an ABS inducer. Although appearing at first sight rather different from one another (see Table 3 for a list), the mixtures used in the literature are in fact chemically very close to one another.

A first comment deduced from examination of Table 3 is that the molar mass of PEG is not a determining parameter of extraction, although PEG-4000 has been widely used in the literature. More interestingly, and as already observed by other authors [49][52], the only ions to be extracted are oxoanions: As(III), As(V), Cr(VI), Mo(VI), Re(VII), Tc(VII), V(V) and W(VI) (see Table 3). However, sodium salts of some of these oxoanions can also act as ABS inducers (Na<sub>2</sub>MoO<sub>4</sub>, Na<sub>2</sub>WO<sub>4</sub>), meaning that, in this case, W(VI) and Mo(VI) are not extracted according to our definition. In the absence of other published results, the only discriminant parameter appears to be the relative amounts: The oxoanion in larger amounts is the ABS inducer while that in lower amount experiences extraction. There is a need of a sufficient amount of sodium salt (either Na<sub>2</sub>SO<sub>4</sub>, Na<sub>2</sub>MoO<sub>4</sub> or Na<sub>2</sub>WO<sub>4</sub>) to induce the ABS, as described by the binodal curve. In all the literature cited and in our own experiments, the amount of the other salt is too low to induce the ABS, so it is either extracted or not, depending on ions affinity towards the upper phase. Therefore, we postulate that extraction versus ABS inducer character is simply a matter of relative amounts of the various oxoanions in competition in the system.

On another aspect, the terms “kosmotropic” (or water-structuring) versus “chaotropic” have been used by several authors to distinguish ions that may be extracted, allegedly being chaotropic ones, while the supposedly kosmotropic ions are not [53]. Table 3 demonstrates that being kosmotropic (or chaotropic) is not an intrinsic property but is an extrinsic one, depending on the chemical composition and circumstances, which most probably reduces the interest of these terms.

Table 3: Systems of the literature of interest to this work.

system	comment	reference
PEG-4000/ $\text{Na}_2\text{MoO}_4/\text{H}_2\text{O}$	Binodal data only; $\text{Na}_2\text{MoO}_4$ as ABS inducer	[50]
PEG-2000/ $\text{Na}_2\text{WO}_4/\text{H}_2\text{O}$	Binodal data only; $\text{Na}_2\text{WO}_4$ as ABS inducer	[53]
PEG-2000/ $\text{Na}_2\text{MoO}_4/\text{H}_2\text{O}$	Binodal data only; $\text{Na}_2\text{MoO}_4$ as ABS inducer	[53]
PEG-4000/ $\text{Na}_2\text{MoO}_4/\text{H}_2\text{O}$	$\text{Na}_2\text{MoO}_4$ as ABS inducer; Re(VII) extraction	[51]
PEG-400/ $\text{CuSO}_4/\text{H}_2\text{O}$	$\text{CuSO}_4$ as ABS inducer; Re(VII) extraction	[40]
PEG-4000/ $\text{CuSO}_4/\text{H}_2\text{O}$	$\text{CuSO}_4$ as ABS inducer; Mo(VI) extraction	[38]
PEG-1000/ $\text{Na}_2\text{SO}_4/\text{H}_2\text{O}$ (and PEG 2000, PEG 4000)	$\text{Na}_2\text{SO}_4$ as ABS inducer; Mo(VI) extraction	[49]
PEG-4000/ $\text{Na}_2\text{SO}_4/\text{H}_2\text{O}$	$\text{Na}_2\text{SO}_4$ as ABS inducer; As(V) and As(III) extraction	[54]
Triblock-polymer/ $\text{Na}_2\text{SO}_4/\text{H}_2\text{O}$	$\text{Na}_2\text{SO}_4$ as ABS inducer; Mo(VI), V(V) W(VI) extraction	[55]
PEG-2000/ $\text{Na}_2\text{SO}_4/\text{H}_2\text{O}$ PEG-2000/ $\text{Rb}_2\text{SO}_4/\text{H}_2\text{O}$ PEG-2000/ $\text{Cs}_2\text{SO}_4/\text{H}_2\text{O}$	$\text{Na}_2\text{SO}_4$ , $\text{Rb}_2\text{SO}_4$ $\text{Cs}_2\text{SO}_4$ , as ABS inducers; Tc(VII) extraction	[56]
PEG-2000/ $\text{Na}_2\text{MoO}_4/\text{H}_2\text{O}$	$\text{Na}_2\text{MoO}_4$ as ABS inducer; Re(VII) and Tc(VII) extraction	[53]
PEG-2000/ $\text{Na}_2\text{WO}_4/\text{H}_2\text{O}$	$\text{Na}_2\text{WO}_4$ as ABS inducer; Re(VII) and Tc(VII) extraction	[53]
PEG-400/ $\text{Na}_2\text{SO}_4/\text{H}_2\text{O}$	$\text{Na}_2\text{SO}_4$ as ABS inducer; Mo(VI) and Cr(VI) extraction	This work

A still pending question is that of the extraction mechanism observed in this work for Cr(VI) and Mo(VI). Extraction of oxoanions by sulphate/PEG-based ABS has long been compared to the extraction properties of crown-ethers by several authors [43,44,57–60]. All these publications suggest that PEG should be considered as a flexible open-chain crown-ether. Indeed, crown-ethers (dissolved in organic solvents) are well known to extract Group(I) or Group(II) cations, depending on the size of their cavity. Obviously, the extraction of alkaline or alkaline-earth cations by crown-ethers should be accompanied by the extraction of a counter-anion, in order to insure electroneutrality of both phases. Actually, some papers discuss the extraction of Cr(VI) by use of crown-ether [61,62]. Assuming an extraction mechanism of Na(I) ions in our samples by the open ether-like chain of PEG-400, this would unavoidably lead to the concomitant extraction of the counter-anion which is not involved in the ABS formation. In our case it corresponds to oxoanions in too low amount to participate to the binodal curve, i.e. Cr(VI) or Mo(VI). There would thus be two different phenomena in our Cr(VI) and Mo(VI) samples. First, ABS formation, involving PEG-400 and the most abundant salt, which, in our experiments, is always  $\text{Na}_2\text{SO}_4$ , and, second, a “crown-ether like” extraction of Na(I), leading to the concomitant extraction of the less abundant anion of our samples, i.e. Cr(VI) or Mn(VI).

Recently, Sun et al. admitted that their previous suggestion of the formation of the  $\text{PEG.H}^+$  entity, which would have interacted with Cr(VI), was incompatible with their pH dependent studies in the system PEG-2000/ $\text{Na}_2\text{SO}_4/\text{H}_2\text{O}$  and they finally concluded that “the ether oxygen groups in the PEG could also combine with other cations such as  $\text{Na}^+$  to form positively charged  $\text{PEG.Na}^{+}$ ” [59]. In order to support the crown-ether like extraction mechanism of Cr(VI), experiments using two other organic compounds were

performed. PPG displays a sterically hindered ether function, owing to the  $-CH_3$  group inserted in the polymeric chain, while TEG-DE was chosen as a short chain, well defined, substitute of PEG-400 in which the  $-OH$  terminal groups of PEG have been replaced by  $-CH_3$  groups (see scheme 1). The partition results, expressed as  $P\%(Cr(VI))$ , are displayed in Table 4. Values for densities evidence similar trends for the three type of polymers. The upper phase density is rather constant for each compound while the density of the lower phase increases as a function of the polymer amount. Similarly, the volumes percentages of the upper and lower phase follow the same trend for PEG-400, TEG-DE and PPG, with an increase of the upper phase volume and a concomitant decrease of the lower phase percentage as the polymer amount is increased. As for the pH values of the upper and lower phases, PEG-400 and TEG-DE show rather similar trends while PPG values differ. All data can be found in the ESI (Tables S5 to S7).

Table 4.  $P\%(Cr(VI))$  values for PPG and TEG-DE for three wt% values. Data for PEG-400 are also presented for comparison purpose.

PPG/TEG-DE/PEG-400 (wt%)	PPG	TEG-DE	PEG-400
20	52.6	86.8	88.3
30	58.6	91.7	92.5
40	67.0	98.8	99.2

Examination of Table 4 shows that TEG-DE extracts  $Cr(VI)$  almost as efficiently as PEG-400 does. Slight differences in the  $P\%$  values are ascribable to the difference in mole to mole ratio between PEG/ $Cr(VI)$  and TEG-DE/ $Cr(VI)$ , for the one part, and also possibly to the slightly smaller ether chain of TEG-DE, which makes the ether chain less flexible, thus possibly less adapted to  $Na(I)$ . A preferred coordination number of  $Na(I)$  towards 6 ether oxygens has been reported [43]. The plot of the  $Na(I)$  complexation constants for several PEG-like structures, where only the terminal  $-OH$  groups have been symmetrically substituted by several motifs ( $-H$ ,  $-CH_3$ ,  $-C_2H_5$ ,  $-C_6H_5O$  or  $-C_5H_{10}N$ ), onto PEG of molecular weight ranging from 200 to 2000 shows that the most determining factor for PEG- $Na(I)$  complexation is not the nature of the terminal group but the length of the ether motif [43]. This conclusion should thus apply to the  $Na(I)$  counter-anion extraction and our results on  $Cr(VI)$  extraction are perfectly in line with this deduction. By contrast, PPG is much less efficient for  $Cr(VI)$  extraction. This is ascribable to the (partially) hindered ether function, which reduces the ability of PPG to interact with  $Na(I)$ , as compared to PEG. The comparison between PPG and TEG-DE results confirms that ether groups are necessary for extraction, thus strongly supporting the crown-ether like extraction mechanism.

#### 4 Conclusion

The main conclusions of this work, either derived from our experimental results or from a minute examination of literature data, can be summarized as follows:

- The binodal features of the ABS system PEG-400/ $Na_2SO_4$ / $H_2O$  appears to be very robust to chemical modifications, such as T variations or addition of metallic sulphate salts.

- A metallic ion introduced in small amounts in the well-known ABS system PEG-400/Na<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O as its sulphate salt, will behave as an additional ABS inducer, i.e. its P% value will decrease as the PEG amount is increased.
- In the presence of two oxoanions, the one in highest quantity will behave as the ABS inducer and the other one will be extracted, PEG and water being the other two mandatory components of the ABS.

The extraction mechanism of Cr(VI) and Mo(VI) can be related to the capacity of the PEG chain to behave as an open crown-ether chain, thus extracting the counter-cation, leading to the concomitant extraction of the oxoanion, in order to fulfill the electroneutrality principle. This extraction mechanism is rather efficient, with P% values close to 100%, while using a very cheap and non-toxic compound, PEG.

Therefore, being able to selectively extract a very toxic oxoanion, such as Cr(VI), from sulphate aqueous media by simply adding PEG-400, an affordable non-toxic chemical, has a clear and beneficial environmental impact. The change from ABS inducer to extracted ion depending on amounts has also probably a lot of applied potential. It appears as one of the first “rule of thumb” to predict the extraction or not of ions in complex industrial liquid samples. Work on this fundamental subject is currently under progress in our laboratory.

Finally, once extracted, Cr(VI) or Mo(VI) should be recovered and disposed of in a proper way, in order to fulfill environmental concerns. This recycling depends on the industrial needs for some specific chemical forms of the Cr or Mn elements (either ingot, oxide, salts or hydroxide, for example) and is currently under study in our laboratory.

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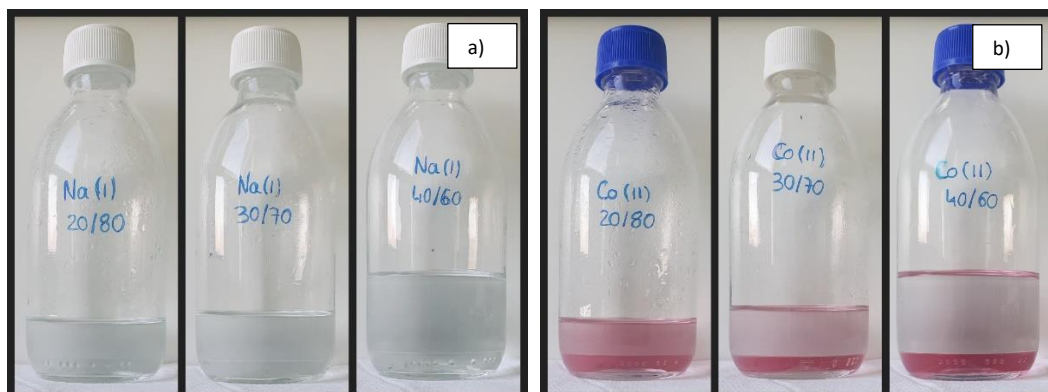
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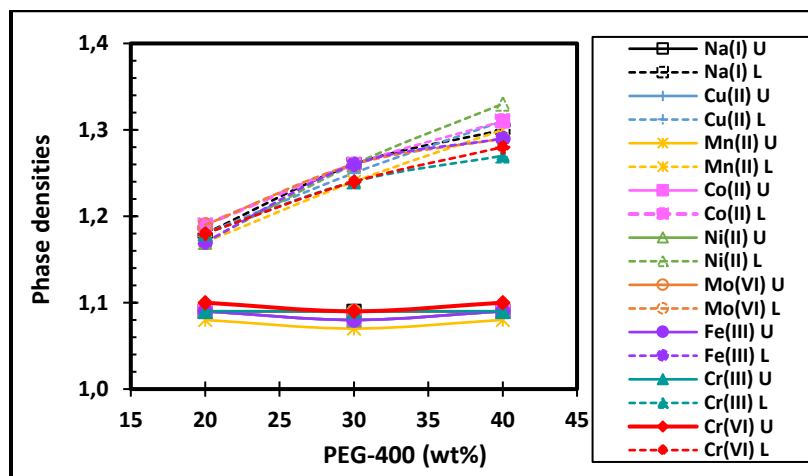
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Supplementary materials: figures S0 to S4, tables S1 to S4



**Fig. S0:** Samples at 20/80 (left); 30/70 (middle); 40/60 wt%(right) of PEG-400 plus  $[\text{Na}_2\text{SO}_4 + \text{Me}(x)]$  aqueous solution for a:  $\text{Me}(x) = \text{none}$  and b) for  $\text{Me}(x) = \text{Co(II)}$ .



**Fig. S1:** Densities of the upper(U) and lower (L) phases, as a function of PEG-400 amount, for all samples. See Table S1 for data.

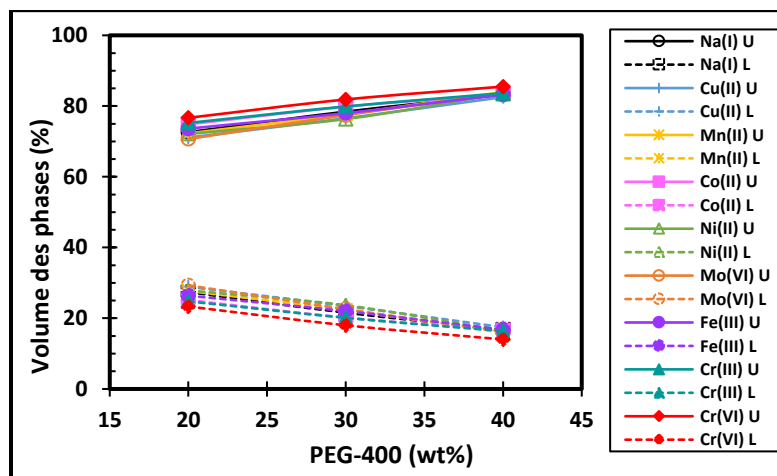


Fig. S2: Volume of the upper phase (U) and of the lower phase (L) as a function of PEG-400 amount and for all samples (calculated in percentage of the total volume). See Table S2 for data.

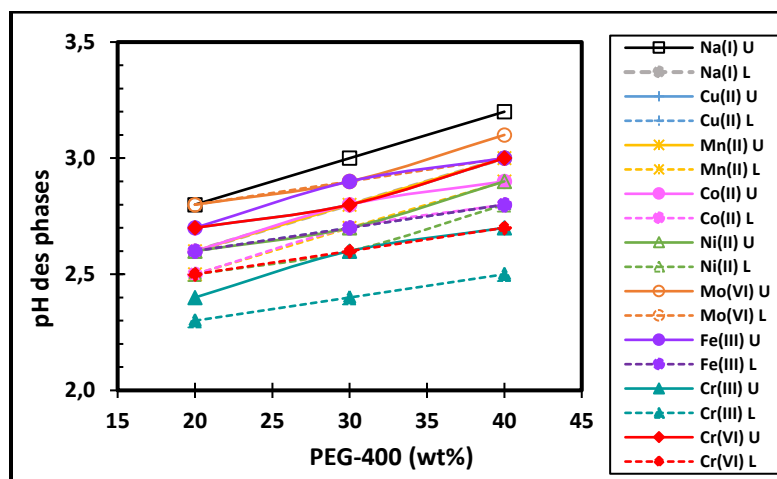


Fig. S3: pH values of the upper (U) and lower (L) phases, as a function of PEG-400 amount, for all samples. See Table S3 for data.

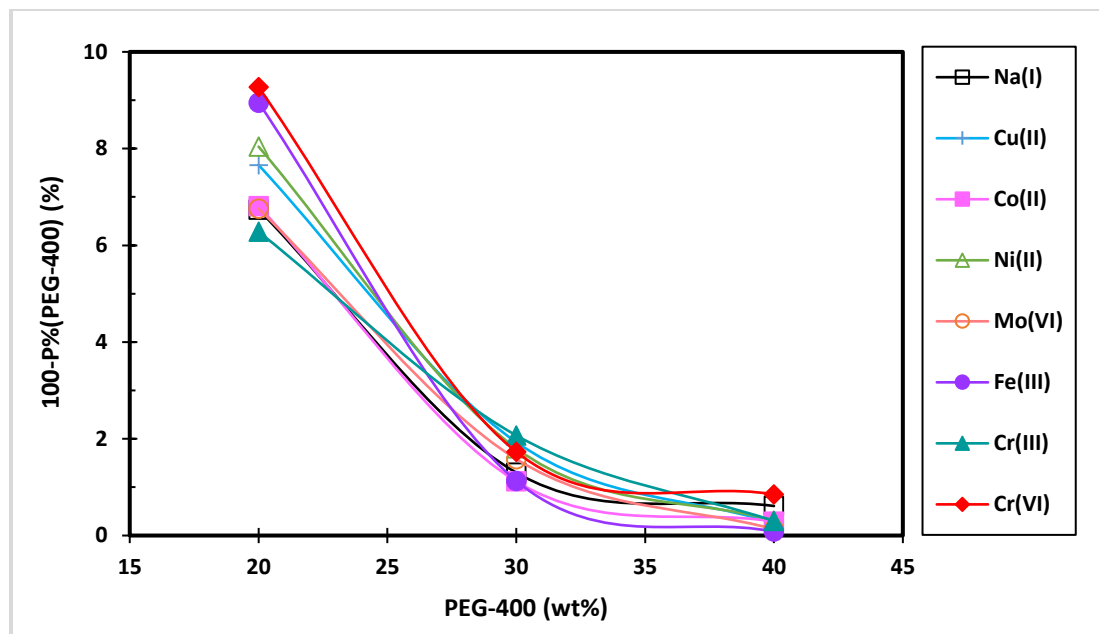


Fig. S4: PEG-400 amount in the lower phase. See Table S4 for data.

Table S1: Densities as illustrated in fig. S1.

		Phase densities									
		PEG (wt%)	Na(I)	Cu(II)	Mn(II)	Co(II)	Ni(II)	Mo(VI)	Fe(III)	Cr(III)	Cr(VI)
Upper	20	1.09	1.09	1.08	1.09	1.09	1.09	1.09	1.09	1.09	1.10
	30	1.09	1.08	1.07	1.08	1.08	1.08	1.09	1.08	1.09	1.09
	40	1.09	1.09	1.08	1.09	1.09	1.09	1.09	1.09	1.09	1.10
Lower	20	1.18	1.18	1.17	1.19	1.17	1.19	1.19	1.17	1.18	1.18
	30	1.26	1.25	1.24	1.26	1.26	1.26	1.26	1.26	1.24	1.24
	40	1.30	1.31	1.30	1.31	1.33	1.29	1.29	1.29	1.27	1.28

Table S2: Data for the upper and lower phase volume ratio (calculated in percentage of the total volume), as illustrated in fig. S2.

		Phase volumes (%)									
		PEG (wt%)	Na(I)	Cu(II)	Mn(II)	Co(II)	Ni(II)	Mo(VI)	Fe(III)	Cr(III)	Cr(VI)
Upper	20	72.6	71.1	72.3	74.8	72.1	70.7	73.6	75.2	76.7	
	30	78.4	76.5	77.7	79.8	76.3	77.4	78.0	79.9	81.9	
	40	83.2	82.5	84.0	83.4	83.6	83.7	83.3	83.7	85.5	
Lower	20	27.4	28.9	27.7	25.2	27.9	29.3	26.4	24.8	23.3	
	30	21.6	23.5	22.3	20.2	23.7	22.6	22.0	20.1	18.0	
	40	16.8	17.5	16.0	16.6	16.4	16.3	16.7	16.3	14.0	

Table S3: pH values for the upper and lower phase, as illustrated in fig. S3.

		pH of the phases									
		PEG (wt%)	Na(I)	Cu(II)	Mn(II)	Co(II)	Ni(II)	Mo(VI)	Fe(III)	Cr(III)	Cr(VI)
Upper	20	2.8	2.7	2.6	2.6	2.6	2.6	2.8	2.7	2.4	2.7
	30	3.0	2.8	2.8	2.8	2.8	2.7	2.9	2.9	2.6	2.8
	40	3.2	3.0	3.0	3.0	2.9	2.9	3.1	3.0	2.7	3.0
Lower	20	2.6	2.6	2.5	2.5	2.5	2.5	2.8	2.6	2.3	2.5
	30	2.8	2.7	2.7	2.7	2.7	2.6	2.9	2.7	2.4	2.6
	40	3.0	2.8	2.9	2.8	2.8	2.8	3.0	2.8	2.5	2.7

Table S4: PEG-400 amount in the lower phase.

		PEG-400 amount in lower phase (%)								
PEG (wt%)	Na(I)	Cu(II)	Mn(II)	Co(II)	Ni(II)	Mo(VI)	Fe(III)	Cr(III)	Cr(VI)	
20	6.74	7.66		6.81	8.04	6.76	8.95	6.28	9.27	
30	1.30	1.93		1.12	1.80	1.58	1.13	2.07	1.73	
40	0.61	0.26		0.29	0.31	0.13	0.08	0.30	0.85	

**Table S5:** Densities of upper and lower phases for the PEG-400, TEG-DE and PPG experiments on Cr(VI) repartition.

		Phase densities		
		(wt%)	PEG	TEG-DE
Upper	20	1.10	1.05	1.03
	30	1.09	1.04	1.03
	40	1.10	1.03	1.03
Lower	20	1.18	1.20	1.12
	30	1.24	1.25	1.13
	40	1.28	1.30	1.15

**Table S6:** Data for the upper and lower phase volume ratio (calculated in percentage of the total volume), for the PEG-400, TEG-DE and PPG experiments on Cr(VI) repartition.

		Phase volume (%)		
		(wt%)	PEG	TEG-DE
Upper	20	77.0	78.0	43.0
	30	82.0	79.0	52.0
	40	86.0	84.0	60.0
Lower	20	23.0	22.0	57.0
	30	18.0	21.0	48.0
	40	14.0	16.0	40.0

**Table S7:** pH values for the upper and lower phase, for the PEG-400, TEG-DE and PPG experiments on Cr(VI) repartition.

		pH of phases		
		(wt%)	PEG	TEG-DE
Upper	20	2.7	2.5	3.5
	30	2.8	2.7	3.6
	40	3.0	2.9	3.8
Lower	20	2.5	2.1	1.7
	30	2.6	2.2	1.6
	40	2.7	2.3	1.5

