

UDC 542.61:541.123

## Extraction Capabilities Inherent in the Delaminating System Water – Oxyphos B – Sodium Sulphate

S. A. DENISOVA<sup>1</sup>, N. N. OSTANINA<sup>2</sup>, A. E. LESNOV<sup>2</sup> and O. S. KUDRYASHOVA<sup>1</sup>

<sup>1</sup>Perm' State University,  
Ul. Bukireva 15, Perm' 664990 (Russia)

E-mail: lesnov\_ae@mail.ru

<sup>2</sup>Institute of Technical Chemistry, Ural Branch of the Russian Academy of Sciences,  
Ul. Akademika Koroleva 3, Perm' 614013 (Russia)

(Received December 12, 2012; revised July 17, 2013)

### Abstract

In the paper we proposed to use the delaminating system water – oxyphos B – sodium sulphate for the purposes of extraction. Solubility isotherms have been obtained for the system at 25 °C. Concentration ranges have been established for the region of two-phase liquid equilibrium. An interphase distribution of certain metal ions has been studied at a concentration thereof equal to  $1 \cdot 10^{-4}$  mol/L in the presence of HCl or H<sub>2</sub>SO<sub>4</sub>.

**Key words:** delaminating system, solubility isotherm, oxyphos B, extraction

### INTRODUCTION

Liquid-liquid extraction is one of the most widely used methods for separation and concentration. This method is universal, rapid, and it is characterized by a simple technique of performing. As far as the efficiency of the separation of complex mixtures is concerned, the extraction method often is better than other methods. In most cases, there are extraction systems with water and an organic phase used, wherein the delamination is performed owing to a limited mutual solubility of water and an organic solvent. Using the organic solvents is one of the major drawbacks of extraction, since organic solvents generally represent toxic, highly volatile and explosive compounds. In order to reduce the toxicity and enhance the safety of extraction processes it is worthwhile to use extraction systems those contain no organic solvent [1]. These comprise, for example, a system such as water – surfactant (SA) – inorganic salt, wherein the delamination

into two liquid phases occurs due to a salting-out process [2–4].

Oxyphos B ( $[\text{C}_n\text{H}_{2n+1}\text{O}(\text{C}_2\text{H}_4\text{O})_m]_2\text{POOK}$ , where  $n = 8-10$ ,  $m = 6$  (potassium bis(alkylpolyoxyethylene) phosphate)) is a low toxic, biodegradable, comparatively cheap large-tonnage product of chemical industry, belonging to anionic SA [5]. Aqueous solutions thereof can delaminate into two liquid phases under introducing a number of inorganic salts therein. The presence different functional groups in the molecule of oxyphos B determines its ability of complex formation. The potassium cation in the –ROOK group can be substituted by another metal cation. The oxygen of the ether group can be protonated in acidic media, wherein a cation reacts with acido complexes of the metal to form an ion associate [6].

### EXPERIMENTAL

The solubility isotherm of the ternary system such as water – oxyphos B – sodium sul-

phate was obtained using an isothermal cross-section method at 25 °C [7]. As a physical property under measurement, we used refractive index of the liquid phase that was determined by means of an IRF-454B refractometer. Phase transition boundaries were determined basing on the breaks of the refractive index curve depending on the concentration. The position of the critical point was determined according to the Alekseev rule. In fact, the system could be considered a conditionally ternary one because oxyphos B represents a mixture of homologues and contains technological impurities.

In order to investigate the influence of inorganic acids and alkalis on the phase state of the system we used graduated test tubes with sealing plugs. Therein were added 2.4 mL of a 40 % oxyphos B solution, 6.5 mL of a 20 % solution of  $\text{Na}_2\text{SO}_4$ , and a corresponding amount of acid or alkali. The volume of the mixture was adjusted to a 15 mL value with distilled water being further shaken for 1 min. After establishing the equilibrium, we determined a ratio between the volumes of the phases with measuring the  $\text{pH}_{\text{eq}}$  of the aqueous phase.

The distribution of metal ions at the concentration of  $1 \cdot 10^{-4}$  mol/L was studied *via*

placing 1 mL of 0.1 mol/L salt solution, 2.4 mL of a 40 % solution of oxyphos B, 6.5 mL of a 20 % solution of  $\text{Na}_2\text{SO}_4$  and corresponding amount of an acid into a separatory funnel. The volume was adjusted to 15 mL with distilled water and shaken then for 1 min. The extraction (recovery) level for metal ions was determined by means of complexometry basing on the residual content thereof in the aqueous phase after phase separation. The absence of any effect exerted by oxyphos B on the results of complexometric titration was previously proved using a method of additives *via* determining a known amount of metal ions introduced in the environment of blank experiment raffinate. The distribution of thallium (III) ions was studied basing on their content in the aqueous phase and in the extract. To do this, we quantitatively transferred the extract into a titration flask, added 50–70 mL of distilled water, adjusted pH to the value required with further determining the amount of metal extracted *via* complexometric titration [8]. Vanadium (V) was determined by means of redox titration [9]. Rhenium (VII) was determined basing on the residual content thereof in the aqueous phase with the use of an extraction-photometric method [10].

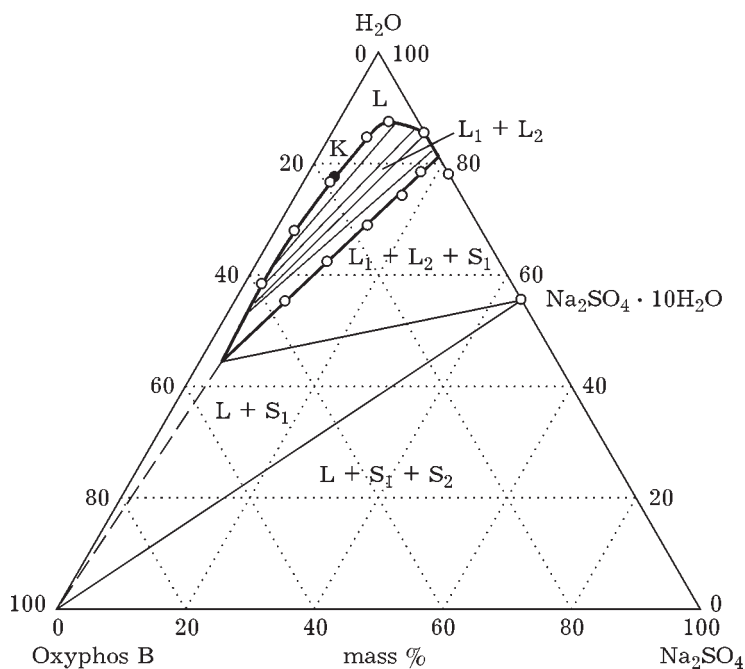


Fig. 1. Solubility diagram for water – oxyphos B – sodium sulphate system at 25 °C. For designations, see text.

## RESULTS AND DISCUSSION

Oxyphos B is infinitely soluble in water, with the formation of viscous homogeneous mixtures. Sodium sulphate can not be dissolved in oxyphos B, whereas its solubility in water amounts to 22.0 mass % [11].

The phase diagram for the ternary system water – oxyphos B – sodium sulphate at 25 °C is shown in Fig. 1. The solubility isotherm exhibits the following phase regions: L – homogeneous solutions,  $L_1 + L_2$  – delamination,  $L_1 + L_2 + S_1$  – monotectic equilibrium,  $L + S_1$  – crystallizing the crystal hydrate of sodium sulphate,  $L + S_1 + S_2$  – co-crystallizing the sodium sulphate decahydrate and anhydrous sodium sulphate. The delamination persists until the salt isoconcentrate corresponding to 5.5 %. The delamination region comes rather close to the system top corresponding to water; *i. e.* the delamination persists in sufficiently dilute solutions. The area near the surfactant was not studied in detail, since the mixtures formed are rather viscous and the equilibrium can be established for a long time.

The presence of the region of two-phase liquid-liquid equilibrium determines the prospects of using this system for extraction. The choice of a particular ratio between the components was made on the basis of the following requirements:

- 1) Minimum content of surfactant and salt;
- 2) The amount of surfactant phase sufficient for practical purposes (ratio between the aqueous phase and the surfactant phase being of about 1 : 5);
- 3) Transparency of the phases;
- 4) Possibility of varying the amount of water while conserving the delamination.

Basing on this, in order to study the extraction equilibrium we have chosen a mixture with the following composition (%): oxyphos B 7.0,  $\text{Na}_2\text{SO}_4$  10.5, water 82.5. At these relationships between the components and the total volume of the system amounting to 15 mL the volume of the surfactant phase is equal to 2.7 mL; the two phases are transparent, the acidity of the aqueous phase corresponds to  $\text{pH}_{\text{eq}}$  7.0.

Inorganic acid (HCl,  $\text{H}_2\text{SO}_4$ ), ammonia and sodium hydroxide effects on the phase equilibria in the system were studied. The region of

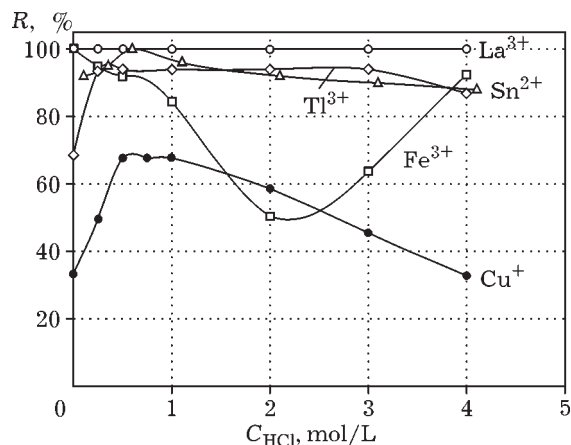


Fig. 2. Recovery level  $R$  for  $1 \cdot 10^{-4}$  mol/L concentration of metal ions in the system of water – oxyphos B –  $\text{Na}_2\text{SO}_4$ –HCl.

two-phase liquid equilibrium is conserved in a wide acidity range up to 6 mol/L HCl, and 4 mol/L  $\text{H}_2\text{SO}_4$ . Thereby, with increasing the acid concentration the surfactant phase volume exhibits a decrease down to 1.5 mL. At a higher concentration of acid a solid phase is observed to appear. The addition of ammonia solutions at the concentration up to 1.5 mol/L and sodium hydroxide (up to 4 mol/L) to the system also does not result in breaking the two-phase liquid-liquid equilibrium. Both phases are transparent within the entire range of  $\text{NH}_3$  and NaOH concentrations, but it should be noted that there is a slight decrease in the phase volume of the surfactant from 2.7 to 1.6 mL observed in the case of NaOH.

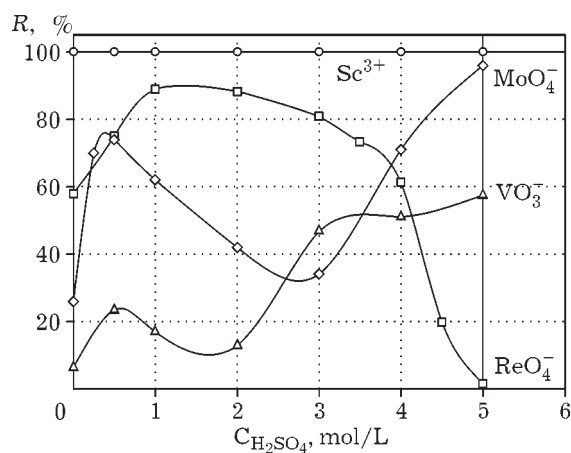


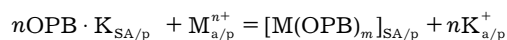
Fig. 3. Recovery level  $R$  for  $1 \cdot 10^{-4}$  mol/L concentration of metal ions the system of oxyphos B –  $\text{Na}_2\text{SO}_4$  – water –  $\text{H}_2\text{SO}_4$ .

Figure 2 demonstrates the results of studying the level of extraction from hydrochloric solutions for the metal ions under investigation. According to the character of the curve corresponding to the extraction of iron (III) one could that there occur two extraction mechanisms. At a low HCl concentration, there prevails a coordination mechanism, accompanied by the release of a white floccular precipitate. When the HCl concentration is above 0.5 mol/L, both phases become transparent. At a high acid concentration there prevail an anion-exchange extraction mechanism.

Within the entire range of HCl concentration the extraction of lanthanum was accompanied by releasing a white foam-shaped precipitate floated into the phase of surfactant. The maximum extraction level for copper (I) amounts to 68 %. For the quantitative extraction of tin (II), the required HCl concentration is equal to 0.6 mol/L, whereas further increasing the HCl concentration is accompanied by a slight decrease of the extraction level.

Figure 3 presents data concerning the level of extraction for some metal ions from sulphuric acid solutions. The greatest interest in this system is presented by a quantitative extraction of scandium (III) within the entire range of H<sub>2</sub>SO<sub>4</sub> concentrations. A fairly high level of extraction is exhibited by molybdate ions (up to 96 %) and perrhenate ions (up to 88 %). Vanadium (V) does not exhibit any quantitative extraction from the sulphate solutions.

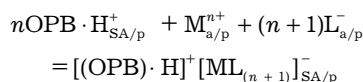
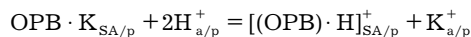
Analyzing the results obtained, it can be concluded that in the water – oxyphos B – sodium sulphate system there occur two extraction mechanisms. Rigid cations (basing on Pearson's classification) such as triply charged scandium, iron, lanthanum can be extracted according to cation exchange mechanism:



where OPB · K is oxyphos B; subscripts SA/p and a/p denote the surfactant phase and the aqueous phase, respectively.

For metals those can be extracted in the form of acido complexes (Fe<sup>3+</sup>, Tl<sup>3+</sup>, Cu<sup>+</sup>, Sn<sup>2+</sup>),

there is an anion-exchange mechanism of extraction realized:



## CONCLUSION

Thus, the presence of a region of two-phase liquid-liquid equilibrium in water – oxyphos B – sodium sulphate system allows using the system for extraction. The region of delamination exists within a sufficiently wide range of acidity level from 6 mol/L of HCl (4 mol/L of H<sub>2</sub>SO<sub>4</sub>) to 1.5 mol/L of NH<sub>3</sub> (4 mol/L of NaOH). Conditions have been found for the quantitative extraction of lanthanum, tin (II), scandium. The system proposed is favourable owing to the absence of organic solvents and other toxic substances, as well as due to the availability and low cost of the components.

## REFERENCES

- 1 Lesnov A. E., Denisova S. A., *Vestn. Perm. Nauch. Tsentra*, 1 (2010) 26.
- 2 Kudryashova O. S., Lesnov A. E., Popova M. A., *Zh. Fiz. Khim.*, 82, 4 (2008) 786.
- 3 Lesnov A. E., Kudryashova O. S., Denisova S. A., Chepkasova A. V., *Zh. Fiz. Khim.*, 82, 6 (2008) 1180.
- 4 Lesnov A. E., Denisova S. A., Kudryashova O. S., Chepkasova A. V., Kataeva E. Yu., Mokhnatakina N. N., *Zh. Prikl. Khim.*, 83, 8 (2010) 1379.
- 5 Abramzon A. A., Bocharov V. V., Gaevoy G. M., *Poverkhnostno-Aktivnye Veshchestva (Handbook)*, Khimiya, Leningrad, 1979.
- 6 Kudryashova O. S., Mokhnatakina N. N., Lesnov A. E., Denisova S. A., *Zh. Neorg. Khim.*, 55, 10 (2010) 1712.
- 7 Nikurashina N. I., Mertslin R. V., *Metod Secheniy. Prilozheniye Yego k Izucheniyu Mnogofaznogo Sostoyaniya Mnogokomponentnykh Sistem*, Saratov, 1969.
- 8 Shvarzenbach G., Flashka G., *Komplexonometricheskoye Titrovaniye*, Khimiya, Moscow, 1970.
- 9 Busev A. I., Tiptsova V. G., Ivanov V. M., *Rukovodstvo po Analiticheskoy Khimii Redkikh Elementov*, Khimiya, Moscow, 1978.
- 10 Borisova L. V., Ermakov A. N., *Analiticheskaya Khimiya Reniya*, Nauka, Moscow, 1974.
- 11 Kirgintsev A. N., Trushnikova L. N., Lavrentieva V. G., *Rastvorimost' Neorganicheskikh Veshchestv v Vode (Handbook)*, Khimiya, Leningrad, 1972.