

Precipitation of Some Slightly Soluble Salts Using Emulsion Liquid Membranes

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Received February 12, 1998; accepted June 1, 1998

Emulsion liquid membranes were used for precipitation of different sparingly soluble salts: calcium oxalate, copper oxalate, nickel oxalate, cobalt oxalate, lanthanum oxalate, calcium phosphate, cobalt phosphate, copper phosphate, lanthanum phosphate, barium sulphate, strontium sulphate and calcium sulphate. For the transport of a desired cation or anion from the feed into the stripping solution, where the precipitation occurred, one of the commercial ligands (bis(2-ethylhexyl)phosphoric acid, D2EHPA; 2-hydroxy-5-nonyl-acetophenone oxime, LIX 84; trioctylamine, ALAMIN 336) dissolved in kerosene, was used as a carrier. The precipitates obtained were characterized by means of transmission electron microscopy, X-ray diffractometry, FT-IR spectroscopy and thermogravimetry. The effect of the transport mechanism on the properties of salt precipitated was studied on calcium and copper oxalate model systems. It was found that copper oxalate hemihydrate and calcium oxalate monohydrate precipitated regardless of whether oxalic acid or a cation (calcium or copper) was transported into the stripping solution. It was also found that the particles of the precipitate were smaller when oxalic acid was transported.

INTRODUCTION

The established idea of a membrane is a thin, semi-permeable and solid barrier. A liquid membrane (LM) is nothing like this. It is a liquid phase,

This article is dedicated to Professor Egon Matijević on the occasion of his 75th birthday.

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usually organic, interposed between two miscible aqueous solutions. At one side of the membrane (feed solution) the material to be transported is extracted, while at the other side (stripping solution) re-extraction occurs. Since in each of the aqueous solutions some specific, and different for each of them, thermodynamic conditions exist, the extraction and re-extraction occur simultaneously.

The liquid membrane extraction was introduced as an alternative separation technique to the liquid-liquid extraction and to the separation by means of solid polymeric membranes.¹ Several types of liquid membrane configurations were reported,² differing mainly in performance of the membrane. Figure 1 shows the most common configurations: (a) the bulk liquid membrane (BLM), (b) the supported liquid membrane (SLM) and (c) the emulsion liquid membrane (ELM). All other types of LM can be related to these ones. The BLM technique requires a simple design of the cell for the transport process to be realized (Figure 1a). The membrane liquid is placed above the feed and stripping solutions, separated with a solid barrier, thus being in contact with both of these solutions. In the SLM (Figure 1b), a porous, solid and inert, support is impregnated with the membrane phase and fixed between the two aqueous, feed and stripping, solutions. ELM are usually multiple emulsions of the water/oil/water type. To obtain this, a fine emulsion of the stripping phase in the membrane phase is produced and stabilized by a surfactant. The resulting water-in-oil emulsion is then dispersed by gentle stirring in the feed solution to create a double emulsion (Figure 1c). Thus, a large interface area between the feed solution and the emulsion globules, and even a larger surface area of the encapsulated strip-

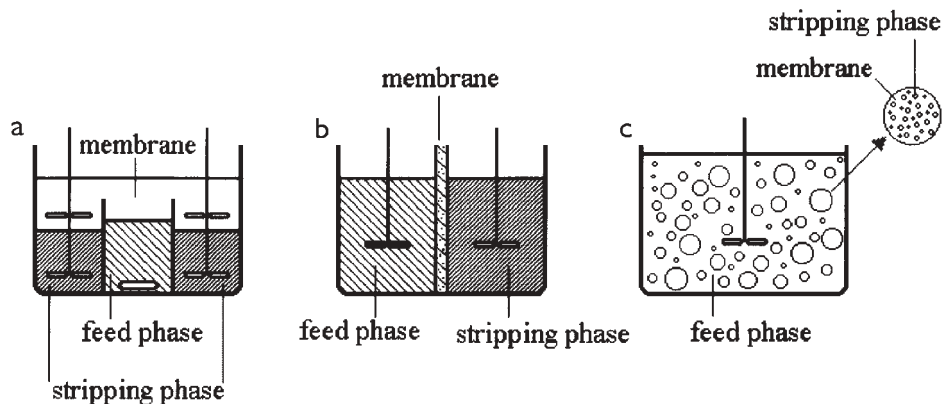


Figure 1. Liquid membrane types: (a) bulk liquid membrane, (b) supported liquid membrane, (c) emulsion liquid membrane.

ping solution, accelerating the mass transfer process in the system, are achieved.

There are two basic principles how the LMs operate (Figure 2). In the first, simple case, the permeate is transferred from the feed phase into the membrane, because of its larger solubility in the organic phase, and then from the membrane into the stripping phase, where conditions prevent back-extraction of the permeate (Figure 2a). This is the so-called »unfacilitated transport«. For the second case, »facilitated« transport (Figure 2b, c), the appropriate solubility of the permeate in the membrane phase is not required since the permeate interacts with the carrier molecule, C, dissolved in the membrane phase. This carrier should be totally insoluble in both the feed and the stripping phases and should react specifically and reversibly

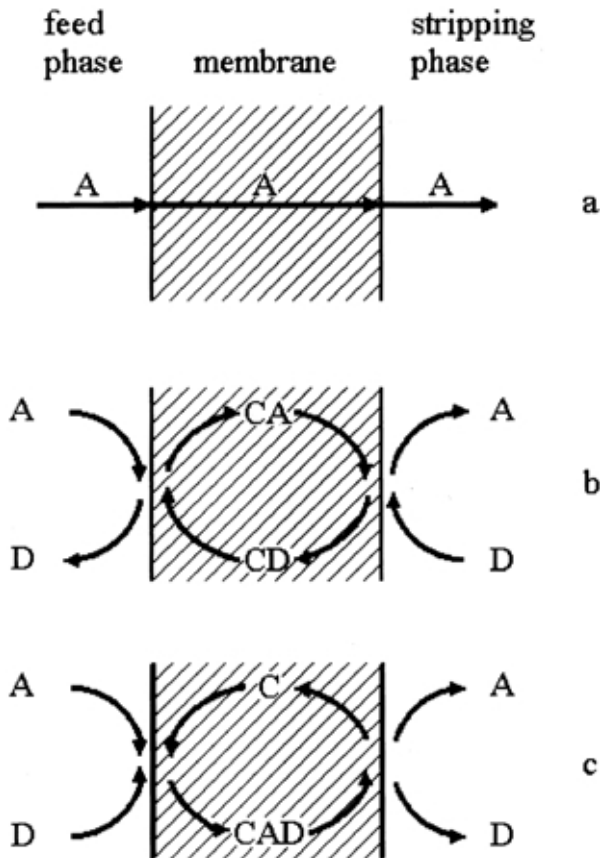


Figure 2. Schematic representation of transport mechanisms of solute through liquid membranes: (a) »unfacilitated« transport, (b) counter-transport, (c) co-transport.

with the permeate. Depending on the nature of the carrier, various feasibilities of the transport are possible. In the case of counter-transport mechanism (Figure 2b), based on ion-exchange processes that occur at the membrane interfaces, the transport of the permeate, A, is coupled with the transport of the counter ion, D, in the opposite direction. By providing a much higher concentration of counter ions against the concentration of the permeate, the permeate could be transported even in the direction opposite to its concentration gradient. The driving force for the transport of the permeate in the so-called »co-transport« mechanism (Figure 2c) is provided by the difference in concentration of the co-ion, D, between the feed and stripping solutions. If the concentration of the co-ion is much higher than the concentration of the permeate, A, the permeate could be transferred in the direction opposite to its concentration gradient (»uphill« transport).

Since their appearance in the literature, the LMs have been recognized as a perspective separation method that has attracted the attention of a number of researchers.³⁻⁷ Most of the studies of LM systems referred to the separation of a substance from homogeneous solutions, and only recently has the LM technique been applied to heterogeneous systems. In these investigations, LMs were used either to dissolve selectively one of the sparingly soluble salts from a mixture of salts of similar, low, solubilities,⁸ or to precipitate such a salt in the internal aqueous phase of an ELM system.⁹⁻¹² These recent investigations were performed with a view of making possible the control of the particle size distribution and the morphology of the precipitate, which are the most important factors in the production of fine particles. The influence of different parameters was studied, such as reactant concentrations in the feed and stripping solutions, concentrations of surfactants and carriers, and even the mode of demulsification.

According to our knowledge, only copper oxalate^{9,10} and calcium carbonate^{11,12} were precipitated by using ELMs. An attempt to trap the phosphate anion in the stripping phase by its conversion to the insoluble calcium phosphate was also mentioned.¹³ Taking this into consideration, the main objective of this study was to precipitate more sparingly soluble salts using the ELMs and also to find out the effect of different transport mechanisms on the properties of a particular precipitate.

EXPERIMENTAL

The feed and stripping aqueous phases were prepared by dissolving an appropriate salt or an acid in deionized water. The organic, membrane, phase containing a suitable carrier and an emulsifying agent, was prepared on the mass/mass basis by dissolving both these reagents in kerosene (b.p. 195 °C, density $\rho = 750 \text{ kg/m}^3$). In all

membrane preparations, Span 80, a commercial non-ionic surfactant sorbitan monooleate, mass fraction, $w = 6.5\%$, was used as an emulsifier and either bis(2-ethylhexyl)phosphoric acid (D2EHPA), 2-hydroxy-5-nonyl-acetophenone oxime (LIX 84) or trioctylamine (ALAMIN 336) was used as a carrier.

Equal volumes (30 cm^3) of the stripping phase and the organic membrane phase were mixed and emulsified by using an ultrasonic homogenizer (Sonifier Cell Disruptor, Mo 250, Branson Ultrasonic Co., USA). The emulsion thus prepared was then poured into 250 cm^3 of the feed solution and stirred mechanically at such a rate as to obtain a double, W/O/W, emulsion with droplets of about 1 mm in diameter, and long enough (usually 30 minutes) to allow precipitation to occur. The exact formulation of the feed, stripping and membrane phases is given in Table I. On stopping the agitation, the system was transferred to a separating funnel in order to separate the feed phase from the W/O emulsion containing the precipitate. The separated W/O emulsion was washed with water several times and demulsified by adding *n*-butanol.¹⁴ The organic phase, containing *n*-butanol, was taken away and the precipitated particles were filtered from the stripping phase, washed thoroughly with water and dried at 105°C .

The transport of the metal ions removed from the feed phase was followed by taking small samples of the feed phase during its contact with the W/O emulsion. The concentration of the transporting ions was determined using atomic absorption spectroscopy, AAS. The size and morphology of the particles formed were observed with a transmission electron microscope, TEM (Zeiss EM 10). The precipitates were characterized using X-ray diffractometry, XRD (Philips counter diffractometer with graphite monochromatized Cu-K α radiation), thermogravimetry, TGA (Mettler TG 50 thermobalance with TC 11 TA processor) and Fourier transform infrared, FT-IR, spectroscopy (Mattson FT-IR spectrophotometer, Genesis Ser.)

RESULTS AND DISCUSSION

Although the kinetics of transport processes is not the subject of this study, the time changes of concentration of metal ion species, extracted and transported from the feed phase, have been determined. Figure 3 shows typical curves of the removal of Cu^{2+} from the feed solution (System 1, Table I). It can be noted that the removal of copper ions from the feed solution proceeds more rapidly when stripping is accompanied by precipitation. In this case, the precipitate is copper oxalate hemihydrate, $\text{CuC}_2\text{O}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$, frequently used as a model system suitable to demonstrate the application of ELMs in controlling the size and morphology of particles. Thus, the systems in which copper was transported by means of an acid (D2EHPA) or an acid chelating extractant (LIX 84), and then precipitated in oxalic acid, were reported.^{9,10} The reason why this particular salt has so often been used in these studies is that a number of commercial extractants for copper are available and, what is more important, that copper oxalate can readily pre-

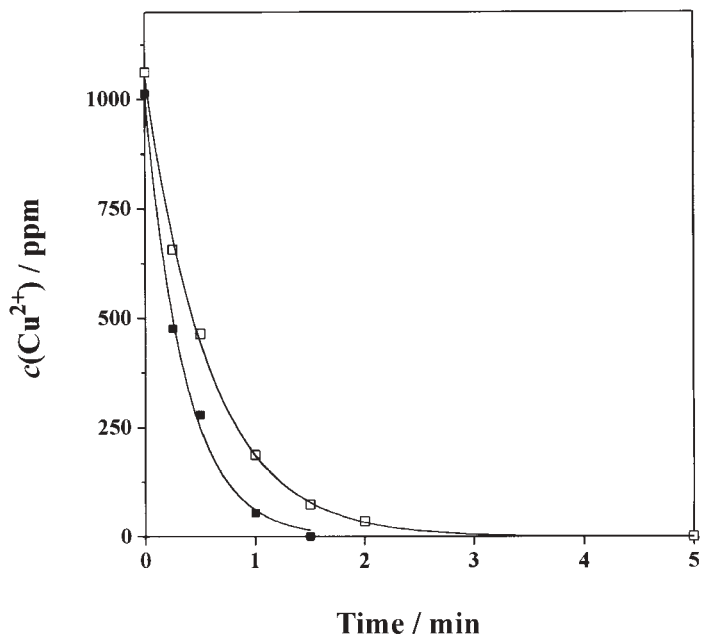


Figure 3. Concentration of copper ions in the feed phase as a function of time in the course of copper transport with precipitation of copper oxalate hemihydrate in the stripping phase (solid squares) and with no precipitation (open squares).

precipitate in solutions of relatively low pH, which is the case of employing oxalic acid as a stripping solution additionally acidified by HCl.*

Besides performing the precipitation of copper oxalate by using acidic extractants (Systems 1 and 2, Table I), we succeeded in precipitating it by transporting oxalic acid into the stripping solution, containing copper ions (System 3, Table I), using ALAMIN 336 as a carrier. This extractant belongs to the group of anion exchangers, and the charge balance in the system was maintained by transporting of chloride ions in the opposite direction.

In order to make possible the study of the role of the transport mechanism (carrier) on the composition, morphology and the crystal size distribution, the total concentrations of oxalic acid and copper ions added were identical in all experiments. It was assumed that the total amount of either copper or oxalic acid added to the feed solution would be transported into the stripping phase. It was found that, regardless of the extractant used,

* Using either of the mentioned extractants, the re-extraction of copper complexes can take place only at very low pH.

TABLE I

Experimental conditions and results of the precipitate analyses

Sys-tem No.	Feed phase	Stripping phase	Carrier	Transported species	Precipitate species
1	0.01 M $\text{Cu}(\text{NO}_3)_2$ * pH = 4.6	0.16 M $\text{H}_2\text{C}_2\text{O}_4$ 0.5 M HCl	LIX 84	Cu^{2+}	$\text{CuC}_2\text{O}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$
2	0.01 M $\text{Cu}(\text{NO}_3)_2$ * pH = 4.6	0.16 M $\text{H}_2\text{C}_2\text{O}_4$ 0.5 M HCl	D2EHPA	Cu^{2+}	$\text{CuC}_2\text{O}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$
3	0.02 M $\text{H}_2\text{C}_2\text{O}_4$ pH = 2.5	0.08 M $\text{Cu}(\text{NO}_3)_2$ 2 M NaCl	ALAMINE 336	$\text{C}_2\text{O}_4^{2-}$	$\text{CuC}_2\text{O}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$
4	0.01 M CaCl_2 * pH = 4.6	0.16 M $\text{H}_2\text{C}_2\text{O}_4$ 0.5 M HCl	D2EHPA	Ca^{2+}	$\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$
5	0.02 M $\text{H}_2\text{C}_2\text{O}_4$ pH = 2.5	0.08 M CuCl_2 2 M NaCl	ALAMINE 336	$\text{C}_2\text{O}_4^{2-}$	$\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$
6	0.01 M NiSO_4 * pH = 4.6	0.16 M $\text{H}_2\text{C}_2\text{O}_4$ 0.5 M HCl	D2EHPA	Ni^{2+}	$\alpha\text{-NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$
7	0.01 M $\text{Co}(\text{NO}_3)_2$ * pH = 4.6	0.16 M $\text{H}_2\text{C}_2\text{O}_4$ 0.5 M HCl	D2EHPA	Co^{2+}	$\beta\text{-CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$
8	0.02 M $\text{H}_2\text{C}_2\text{O}_4$ pH = 2.5	0.08 M LaCl_3 2 M NaCl	ALAMINE 336	$\text{C}_2\text{O}_4^{2-}$	$\text{La}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$
9	0.01 M CaCl_2 * pH = 4.6	1.0 M H_2SO_4	D2EHPA	Ca^{2+}	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
10	0.01 M $\text{Ba}(\text{NO}_3)_2$ * pH = 4.6	1.0 M H_2SO_4	D2EHPA	Ba^{2+}	BaSO_4
11	0.01 M SrCl_2 * pH = 4.6	1.0 M H_2SO_4	D2EHPA	Sr^{2+}	SrSO_4
12	0.02 M H_3PO_4 pH = 2.5	0.05 M LaCl_3 2 M NaCl	ALAMINE 336	PO_4^{3-}	** LaPO_4
13	0.02 M H_3PO_4 pH = 2.5	0.05 M $\text{Cu}(\text{NO}_3)_2$ 2 M NaCl	ALAMINE 336	PO_4^{3-}	** $\text{Cu}_3(\text{PO}_4)_2$
14	0.02 M H_3PO_4 pH = 2.5	0.05 M $\text{Co}(\text{NO}_3)_2$ 2 M NaCl	ALAMINE 336	PO_4^{3-}	** $\text{Co}_3(\text{PO}_4)_2$
15	0.02 M H_3PO_4 pH = 2.5	0.05 M CaCl_2 2 M NaCl	ALAMINE 336	PO_4^{3-}	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$

* pH was adjusted by acetic acid/sodium acetate buffer.

** Precipitates were amorphous according to XRD.

copper oxalate precipitated as $\text{CuC}_2\text{O}_4 \cdot n\text{H}_2\text{O}$, $0 < n < 1$.¹⁵ The particles formed within microdroplets were small and irregular in shape, and their size depended on the type of carrier used; when ALAMINE 336 was used (Figure 4a), particles (probably aggregates of even smaller particles) were smaller (up to 0.5 μm) than in the case of using D2EHPA (Figure 4b). Similar results were obtained for the precipitation of calcium oxalate (Systems 4 and 5, Ta-

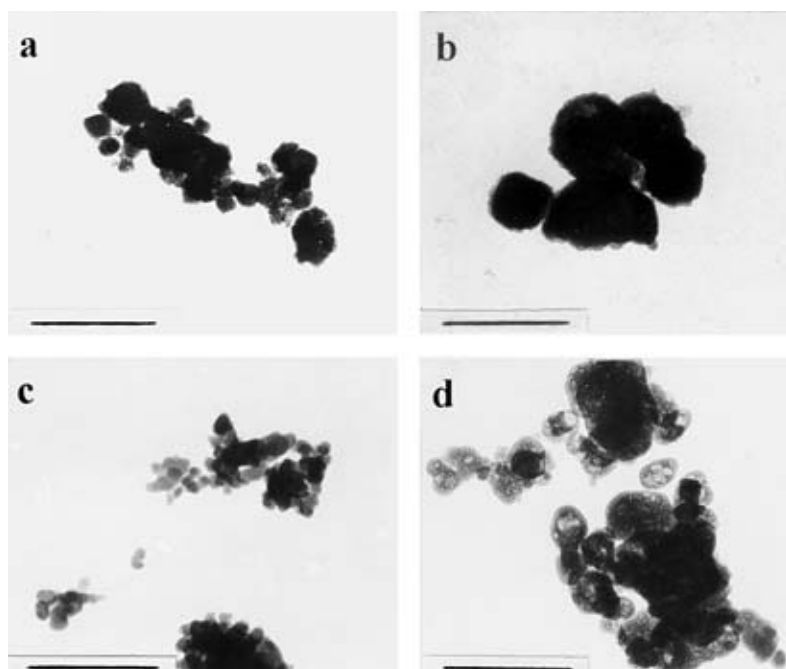


Figure 4. Transmission electron micrographs of copper oxalate (a, b) and calcium oxalate (c, d) precipitated by using anionic (a, c) and cationic (b, d) transport. Scale bar = 2 μm .

ble I); the particles were smaller when oxalic acid was transported to the stripping solution containing Ca^{2+} (Figure 4c), than when calcium ions were transported (Figure 4d). Regardless of the type of carrier, the precipitate consisted of calcium oxalate monohydrate, $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$, as confirmed by XRD (Figure 5a, b), FT-IR and TGA.

The observed effect of the transport mechanism on the size of particles could probably be attributed to the permeation rate of copper or oxalic acid. This is not surprising if one knows that the properties of the precipitate, such as the size distribution or morphology, are mainly determined during the first stage of a precipitation process, *i.e.* nucleation, which is, again, strongly influenced by the initial concentration of the reacting species. Therefore, additional work is forthcoming on the kinetics and mechanism of precipitation, the kinetics of permeation through the ELM, hydrodynamics within microdroplets and specific interactions between precipitate, tenside, aqueous and organic phases, so that this effect can be completely elucidated and an appropriate mathematical model made.

In addition to copper and calcium oxalates we succeeded in precipitating $\alpha\text{-NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (System 6, Table I), $\beta\text{-CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (System 7, Table I)

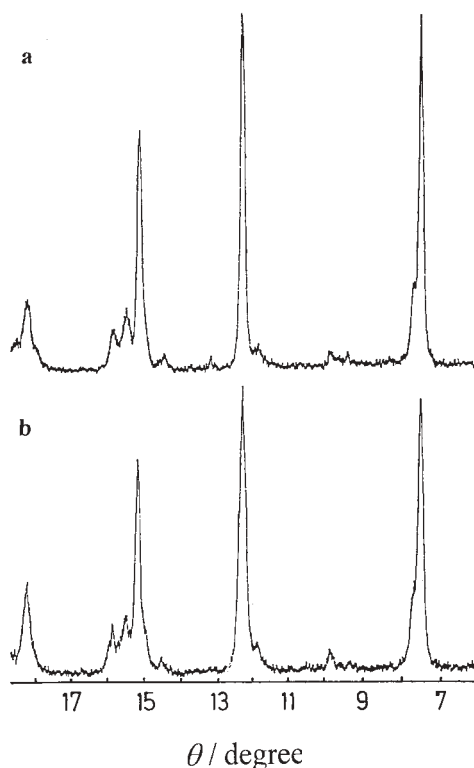


Figure 5. Characteristic parts of XRD patterns of calcium oxalate monohydrate obtained using (a) cationic and (b) anionic transport.

and $\text{La}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$ (System 8, Table I), using either D2EHPA or ALAMIN 336 as carriers.

The transport of calcium, barium and strontium into the stripping solution containing sulphuric acid and using D2EHPA as a carrier, gave rise to the precipitation of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (System 9, Table I), BaSO_4 (System 10, Table I) and SrSO_4 (System 11, Table I). These precipitates showed characteristic X-ray diffractograms and FT-IR spectra. Although D2EHPA is known as a good extractant for transition metals, the alkali-earth metals used in this work were transported at a satisfying rate and extent, because the interface area available for the transport is extremely large in ELM systems. Besides, the distribution of metal ions between the organic phase and the stripping solution is shifted toward the stripping solution, as a consequence of precipitation.

Using ALAMINE 336 as a phosphoric acid carrier, the phosphate salts of lanthanum (System 12, Table I), copper (System 13, Table I) and cobalt

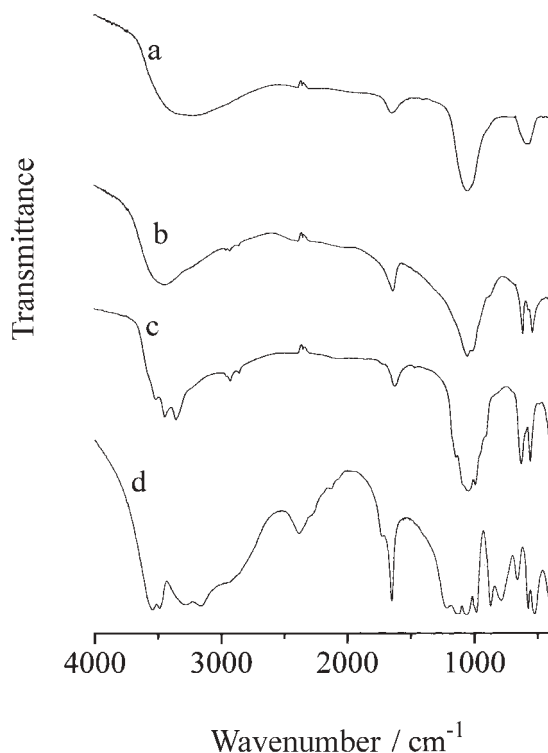


Figure 6. FT-IR spectra of (a) cobalt phosphate, (b) lanthanum phosphate, (c) copper phosphate and (d) calcium hydrogenphosphate dihydrate, in KBr pellets.

(System 14, Table I) were also precipitated. All of them were amorphous or poorly crystalline, as confirmed by XRD. Therefore, these salts were identified on the basis of FT-IR and TG analysis. Their FT-IR spectra exhibited bands at $1000\text{--}1100\text{ cm}^{-1}$ and at $550\text{--}600\text{ cm}^{-1}$, assigned to the P=O stretching and the O-P-O bending mode, respectively (Figure 6a, b, c), characteristic also of amorphous calcium phosphates.¹⁶ The H-O-H bending mode ($\approx 1600\text{ cm}^{-1}$), indicating bound water, was observed in all these spectra. In contrast to the phosphates mentioned above, calcium phosphate precipitated as a well crystalline calcium hydrogenphosphate dihydrate $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ (Figure 6d), was also identified by XRD.¹⁵ Precipitation of this phosphate phase had to be expected, in spite of a variety of calcium phosphate phases. Under the conditions used in our experiments, such as high supersaturation, room temperature and $\text{pH} = 5\text{--}6$, calcium hydrogenphosphate dihydrate precipitates initially and is a stable modification.¹⁷

Besides the above mentioned salts, we also tried to precipitate sulphides of cobalt and cadmium by transporting the appropriate cation into the strip-

ping solution containing Na_2S using ALAMINE 336. The colour of the resulting double emulsion turned respectively to either black or yellow soon after the process started, thus indicating the precipitation of the respective salts.** Unfortunately, because of the impossibility of breaking the sponge-like emulsion, which was additionally stabilized by colloidal particles, we did not succeed in identifying these precipitates.

CONCLUSIONS

Using the emulsion liquid membranes we have succeeded in precipitating a number of slightly soluble salts of phosphoric (lanthanum phosphate, copper phosphate, cobalt phosphate and calcium hydrogenphosphate dihydrate), oxalic (copper oxalate hemihydrate, calcium oxalate monohydrate, nickel oxalate dihydrate, cobalt oxalate dihydrate and lanthanum oxalate decahydrate) and sulphuric acid (barium sulphate, strontium sulphate and calcium sulphate dihydrate). The precipitates of calcium and copper oxalates were obtained by transporting either the cationic (Ca^{2+} , Cu^{2+}) or the anionic ($\text{C}_2\text{O}_4^{2-}$) component from the feed into the stripping solution. For these purposes, bis(2-ethylhexyl)phosphoric acid, 2-hydroxy-5-nonyl-acetophenone oxime or trioctylamine were used as carriers. By studying these models, we have concluded that under given conditions their morphology is not influenced by the type of carrier used, but the particles are smaller when the anionic component is transported.

Acknowledgement. – The authors wish to thank Dr. Nikola Ljubešić for his TEM work.

REFERENCES

1. N. N. Li, *AIChE J.* **17** (1971) 459–463.
2. L. Boyadzhiev and Z. Lazarova, *Liquid membranes (liquid pertraction)*, in: R. D. Noble and S. A. Stern (Eds.), *Membrane Separations Technology. Principles and Applications*, Elsevier Sci. B.V., Amsterdam, 1994, pp. 283–352.
3. W. Halwachs and K. Schügerl, *Int. Chem. Eng.* **20** (1980) 519–528.
4. R. Marr and A. Kopp, *Int. Chem. Eng.* **22** (1982) 44–60.
5. P. R. Danesi, *Sep. Sci. Technol.* **19** (1984/85) 857–894.
6. B. J. Raghuraman, N. P. Tirmizi, B.-S. Kim, and J. M. Wiencek, *Environ. Sci. Technol.* **29** (1995) 979–984.
7. A. Zouhri, M. Burgard, and D. Lakkis, *Hydrometallurgy* **38** (1995) 299–313.

** Three of four sulfide salts of cobalt are black or dark gray, while cadmium sulfide is yellow/orange.

8. D. Kralj, G. M. Breembroek, G. J. Witkamp, G. van Rosmalen, and Lj. Brečević, *Solvent Extr. Ion Exch.* **14** (1996) 705–720.
9. M. Yang, G. A. Davies, and J. Garside, *Powder Technology* **65** (1991) 235–242.
10. T. Hirai, K. Nagaoka, N. Okamoto, and I. Komasaawa, *J. Chem. Eng.* **29** (1996) 842–850.
11. R. J. Davey and T. Hirai, *J. Cryst. Growth* **171** (1997) 318–320.
12. T. Hirai, S. Hariguchi, I. Komasaawa, and R. Davey, *Langmuir* **13** (1997) 6650–6653.
13. N. N. Li, U.S. Patent 3,410,794, 1968.
14. K. Larson, B. Raghuraman, and J. Wiencek, *J. Membrane Sci.* **91** (1994) 231–248.
15. Powder Diffraction File, Inorganic Card No. 9–77, 20–231, 21–297, 25–250 and 25–581, International Centre for Diffraction Data, Newtown Square, PA, USA.
16. Lj. Brečević and H. Füredi-Milhofer, *Calc. Tiss. Res.* **10** (1972) 82–90.
17. H. Füredi-Milhofer, B. Purgarić, Lj. Brečević, and N. Pavković, *Calc. Tiss. Res.* **8** (1971) 142–153.

SAŽETAK

Taloženje nekih teško topljivih soli korištenjem emulzijskih tekućih membrana

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Primjenom emulzijskih tekućih membrana (ELM) istaložen je niz teško topljivih soli: kalcijev oksalat, bakrov oksalat, niklov oksalat, kobaltov oksalat, lantanov oksalat, kalcijev fosfat, kobaltov fosfat, bakrov fosfat, lantanov fosfat, barijev sulfat, stroncijev sulfat i kalcijev sulfat. Pri transportu željenog kationa ili aniona, iz otopine u kojoj se zbiva ekstrakcija u otopinu gdje dolazi do reekstrakcije i taloženja soli, korišteni su ligandi dostupni na tržištu (bis(2-etilheksil)fosforna kiselina, D2EHPA; 2-hidroksi-5-nonil-acetofenonoksim, LIX 84; trioktilamin, ALAMIN 336). Ligand otopljen u kerozinu poslužio je kao nosač transportiranog iona kroz membranu. Dobiveni su talozi analizirani primjenom transmisijske elektronske mikroskopije, rentgenske difraktometrije, FT-IR spektroskopije i termogravimetrije. Učinak mehanizma transporta na svojstva istaložene soli proučavan je na modelnim sustavima kalcijeva i bakrova oksalata. Pri tome je nađeno da se bez obzira na to je li kroz membranu transportirana oksalna kiselina ili jedan od kationa (kalcijev ili bakrov ion), uvijek taloži kalcijev oksalat monohidrat ili bakrov oksalat hemihidrat. Također je nađeno da su čestice taloga dobivene transportom oksalne kiseline znatno sitnije.