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Romuald Wodzki[a]; Alicja Wyszynska[a]; Anna Narebska[a]
[a] Institute of Chemistry Nicolaus Copernicus University, Torun, Poland

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Two-Component Emulsion Liquid Membranes with Macromolecular Carriers of Divalent Ions*

ROMUALD WÓDZKI, ALICJA WYSZYŃSKA, and
ANNA NARĘBSKA
INSTITUTE OF CHEMISTRY
NICOLAUS COPERNICUS UNIVERSITY
87-100 TORUN, POLAND

Abstract

Experimental investigations are presented on the application of poly-[poly(ethylene glycol) phosphate] (PEGP) as a macromolecular, multisite, carrier of ions in an emulsion liquid membrane system. This polymer acts as a mobile carrier and surfactant-stabilizing W/O/W emulsion. The transport properties of PEGP have been checked for systems composed of (a) a feed phase containing Ni(II), Co(II) or Cu(II) ions; (b) an organic phase, i.e., PEGP dissolved in 1,2-dichloroethane; and (c) 1 *M* sulfuric acid as a receiving solution. Fast and effective membrane extraction of Ni(II) has been found for membranes with PEGP of molecular weight 22,000. It has been proved that the affinity of PEGP toward the studied ions is reversed in comparison with that for poly(ethylene glycol). The affinity order of PEGP toward the tested ions is Ni(II) > Co(II) > Cu(II).

INTRODUCTION

Liquid surfactant and emulsion liquid membranes (ELM) are considered to be effective tools for concentrating and separating a number of substances, mainly of ionic character (*1–3*). The ELM system consists of W/O/W-multiphase emulsion where the membrane is the organic (oil) continuous phase of an emulsion W/O dispersed as droplets in a relatively large volume of diluted aqueous solution of a species to be concentrated or separated. In conventional ELM a membrane phase is usually composed of an organic solvent, a carrier, and a surface-active agent. For such a

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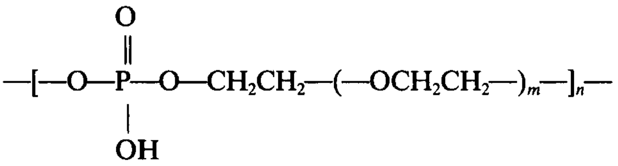
system the key to overall W/O/W emulsion stability is the use of a surfactant. Also, it is of prime importance to select the most favorable combination of membrane components and conditions of operation.

In order to simplify the ELM and to avoid the problems introduced by the presence of a surfactant (*4*), Cui et al. (*5*) developed new membranes called two-component ELM (TC-ELM). In these membranes a macromolecular acyclic carrier, i.e., poly(ethylene glycol), serves the double function of a transporting carrier and an ELM stabilizing agent. On the other hand, the use of macromolecular multisite carriers offers new liquid membrane systems with properties different from those observed for low-molecular-weight carriers or extractants (*6*, *7*). Starting with this idea, we have recently described (*8*) bulk liquid membranes with some organic polyphosphates applied as ionic carriers of Ni(II), Co(II), and Cu(II) ions. The most promising results have been found with poly[poly(ethylene glycol) phosphate] of general chemical composition (*9*):



$$-[-O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle OH}{|}}{P}}-O-CH_2CH_2-(-OCH_2CH_2-)_m-]_n- \qquad (1)$$

This polymer dissolved in 1,2-dichloroethane (DCE) has been shown to be an effective carrier of Ni(II) ions in bulk liquid membranes with a pH gradient as the driving force. However, transport across bulk liquid membranes with PEGP required several hours for completion. To be attractive in practical applications, the time of effective operation of LM should be reduced to few minutes. One of the methods is generating a large membrane area per unit volume, which is possible in ELM systems. The ability of PEGP to stabilize W/O emulsions, observed during preliminary experiments, and as a consequence, its ability to form two-component ELM, opens new ways for the concentration and separation of ions with phosphorus-containing carriers (*10*).

We herewith report on experimental studies of TC-ELM with PEGP as a mobile carrier of Ni(II), Co(II), and Cu(II) ions. The study involves the transport properties of PEGP of various molecular weights and structures (i), the effect exerted by SCN^- and some organic anions present in a feed solution (ii), as well as a comparison of TC-ELM with PEGP and PEG only (iii). The experimental measurements are limited to membrane extraction of ions from aqueous feed solution, i.e., to the first stage of the pertraction process (*11*) comprising extraction, diffusion and reextraction processes. Hence, the results presented describe the removal of ions from solution rather than the concentrating or separating processes.

EXPERIMENTAL

Reagents

PEGPs of different average molecular weight (M_n) and the mass of PEG units (M_m) were used for membrane preparations. The detailed composition of PEGPs characterized by their M_n and M_m was

PEGP-22000: $M_n = 22{,}000$, $M_m = 2{,}000$

PEGP-13000: $M_n = 13{,}000$, $M_m = 1{,}000$

PEGP-7700: $M_n = 7{,}700$, $M_m = 2{,}000$

The polymers used here were synthesized in the Centre of Molecular and Macromolecular Studies of the Polish Academy of Sciences, Łódź, Poland. The synthesis of PEGP has been described elsewhere by Penczek et al. (*9*).

PEG with molecular weights ranging from 400 to 10,000 was supplied by Fluka AG. Both PEGP and PEG were used without further purification. Twice distilled 1,2-dichloroethane (POCh, Gliwice) was applied as an organic solvent for the carriers. Other chemicals for preparing aqueous feed and strip solutions were reagent grade (from POCh, Gliwice) and were used as received.

Procedures

Organic Phase

The organic phase for the preparation of TC-ELM with PEGP or PEG has been achieved by directly dissolving the respective carrier in DCE. The concentrations of PEGP in organic solutions were 5, 4, and 12% for PEGP-22000, -13000, and -7700, respectively. The concentration of the carrier in membranes with PEG was always 8%. This organic phase composition led to the most stable W/O emulsions.

Preparation of W/O Emulsions

Water-in-oil emulsions with PEGP were produced by ultrasonification of 10 mL DCE solution with 2 mL of 1 *M* H_2SO_4 as the receiving aqueous internal solution. For this operation the ultrasonic bath UM4 (Unitra-Unima, Poland) working at 25 kHz was employed. During ultrasonification, the components in a glass tube were thermostated (298 K). Depending on the polymer used, emulsions of 2–24 h stability were obtained after 20 min of such treatment.

Emulsions with PEG as the mobile carrier and surfactant were prepared by the same method. By using this polymer, stable emulsions were obtained after ultrasonificating 15 mL PEG in DCE solution with 7.5 mL of 1 *M* KOH solution as an internal phase. Attempts of producing emulsions with an acidic internal phase as well as with 1,1-dichloroethane instead of DCE were unsuccessful.

Membrane Extraction Experiments

The TC-ELM systems were made by mechanical mixing of the respective W/O emulsions with a bulk solution containing the ions to be extracted. In order to obtain the required W/O/W system, 15 mL of an emulsion was dispersed in 50 mL of aqueous feed solution by using a spiral stirrer (200–400 rpm, 298 K). The time of extraction was measured from immediately after the W/O emulsion contacted the feed solution.

The analyses of the aqueous phase being treated were done spectrophotometrically. Samples of a feed solution (1 mL) were taken periodically, i.e., after 3, 6, 10, 15, and 25 min, by a pipet. After separating the emulsion by filtering the sample through a filter paper, the concentrations of Ni(II), Co(II), or Cu(II) were determined with a Spekol-21 spectrophotometer (Zeiss, Jena).

RESULTS AND DISCUSSION

General Remarks

Preliminary experiments on the formation of TC-ELM systems with PEGP allowed us to establish the conditions required for the stability of such systems. It has been observed that this stability depends on the concentration of PEGP in an organic phase (i), the concentration and composition of the receiving internal solution (ii), and the volume ratio of W/O emulsion to a feed solution (iii).

(i) The most favorable concentration of PEGP in a liquid membrane depends on its molecular weight. The optimum numbers are presented in the Experimental section.

(ii) Contrary to DCE solutions of PEG, stable emulsions of PEGP/DCE can be obtained with a relatively concentrated internal solution of sulfuric acid. This makes it possible to achieve processes with a countertransport mechanism. Note that transports in TC-ELM with PEG are based on the cotransport phenomenon.

(iii) As indicated in the Experimental section, the best performance of TC-ELM systems with PEGP needs a volume ratio of an organic phase to the receiving solution equal to 5:1 and a volume ratio of W/O emulsion to a feed solution equal to 1:5.

Under the listed conditions, W/O emulsions were stable for 24, 5, and 2 h when using PEGP-22000, -13000, and -7700, respectively.

Slightly different conditions were found for membranes containing PEG. The best results with this compound were found when its molecular weight was in the range 6,000–10,000 and the concentration in DCE was equal to 8%. The W/O emulsions with an alkaline internal phase prepared with a 2:1 ratio were stable for not less than 24 h. The most favorable volume ratio of W/O emulsion to a feed solution was 1:3.3.

Membrane Extraction of Ni(II), Co(II), and Cu(II) in TC-ELM with PEGP

The pertraction processes of divalent ions from monocomponent solutions were carried out for the following systems:

System	Feed solution	Membrane	Strip solution
A	0.005 *M* $MeSO_4$	PEGP-22000/DCE	1 *M* H_2SO_4
B	0.005 *M* $MeSO_4$ + 0.25 *M* NH_4SCN	PEGP-22000/DCE	1 *M* H_2SO_4

where Me denotes Ni(II), Co(II), or Cu(II).

The results of pertraction in System A are shown in Fig. 1 as plots of the percentage of metal ions extracted from an aqueous feed solution vs time of TC-ELM operation. The curves indicate that the fraction of nickel extracted with PEGP significantly exceeds that of Co(II) and Cu(II) ions. For Ni(II) the maximum reaches 98% while for the other ions it does not exceed 10%. The order of extraction selectivity of PEGP toward studied ions is then

$$\text{Ni(II)} > \text{Co(II)} > \text{Cu(II)} \tag{2}$$

Papers dealing with the properties of PEG as an extractant of cations suggest their dependence on the type of anions present in the feed solution (*12*). It has been pointed out that the best results can be reached by supplying a feed solution with an excess of SCN^- anions. In liquid membranes with neutral carriers this anion accompanies the cation-carrier complex, maintaining its electroneutrality. Some authors (*5*, *13*) provided

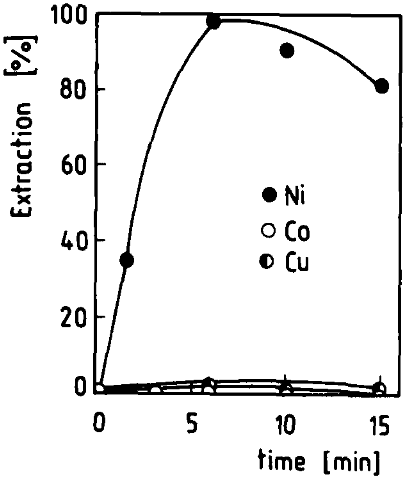


FIG. 1. Fraction of ions extracted from a feed solution vs time of operation of TC-ELM with PEGP-22000 as a carrier. System A.

evidence for the enhancement of transports mediated by PEG and macrocycle carriers when SCN^- is present in the feed solution. By taking into account the structure of PEGP, which contains repeat blocks of PEG, it was also reasonable to check the influence of SCN^- on PEGP properties. The results illustrating this effect for membrane extraction in System B are presented in Fig. 2. The experimental curves show the increase of the

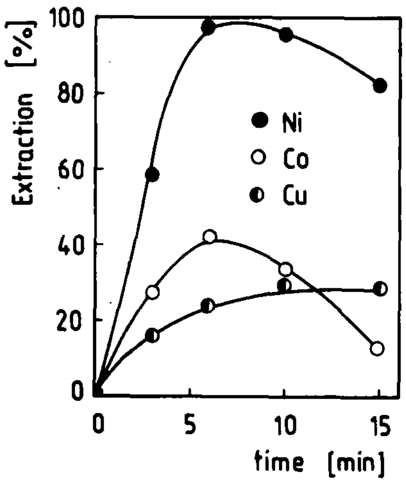


FIG. 2. Fraction of ions extracted from a feed solution containing SCN^- anions vs time of operation of TC-ELM with PEGP-22000 as a carrier. System B.

extraction of Co(II) and Cu(II) in comparison with System A. For System B the percentage of extraction reaches a maximum at 40 and 30% for Co(II) and Cu(II), respectively; for System A it ranges below 10%. It is worth noticing that the curve for Ni(II) ions remains quite the same as that observed for the system without SCN^- ions. These results prove that the addition of SCN^- puts in operation the additional transport mechanism characteristic for poly(ethylene glycol) carrier itself. However, the affinity order remains unchanged.

Membrane Extraction of Ni(II), Co(II), and Cu(II) in TC-ELM with PEG

In order to examine the role of poly(ethylene glycol) in the transport of ions, we carried out experiments with TC-ELM having in its organic phase PEG with a molecular weight of 6000:

System	Feed solution	Membrane	Strip solution
C	0.005 *M* $MeSO_4$ + 0.05 *M* H_2SO_4	PEG-6000/DCE	1 *M* KOH

The results of the experiments presented in Fig. 3 prove that the ability of PEG to extract ions is reversed in comparison to that observed for PEGP. It decreases in the order

$$\mathrm{Cu(II)} > \mathrm{Co(II)} > \mathrm{Ni(II)} \tag{3}$$

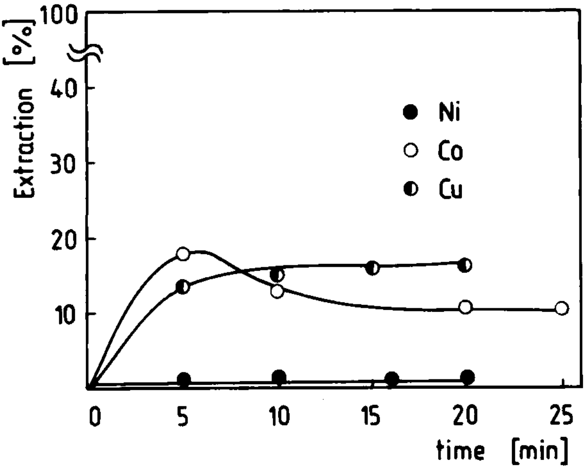


FIG. 3. Fraction of ions extracted from a feed solution vs time of operation of TC-ELM with PEG-6000 as a carrier. System C.

However, for all pertraction runs with PEG the extraction of ions does not exceed 20%, i.e., Systems C do not fulfill the requirements for highly effective emulsion liquid membranes.

To improve the performance of TC-ELM with PEG carrier, some amount of SCN^- anions was added to the feed solutions. The initial conditions for transports in System D were as follows

System	Feed solution	Membrane	Strip solution
D	$MeSO_4$, H_2SO_4, NH_4SCN	PEG-6000/DCE	1 *M* KOH

The detailed composition of a feed solution was dependent on the ion to be extracted, i.e.,

1: 0.005 *M* $NiSO_4$; 1.0 *M* NH_4SCN

2: 0.001 *M* $CoSO_4$; 0.2 *M* NH_4SCN

3: 0.0025 *M* $CuSO_4$; 0.5 *M* NH_4SCN

For all runs the ratio of SCN^- to Me(II) concentration was kept constant, i.e., 200, whereas the concentration of sulfuric acid was always 0.05 *M*. The results presented in Fig. 4 indicate that extraction with PEG from solutions containing SCN^- increases significantly as compared with the

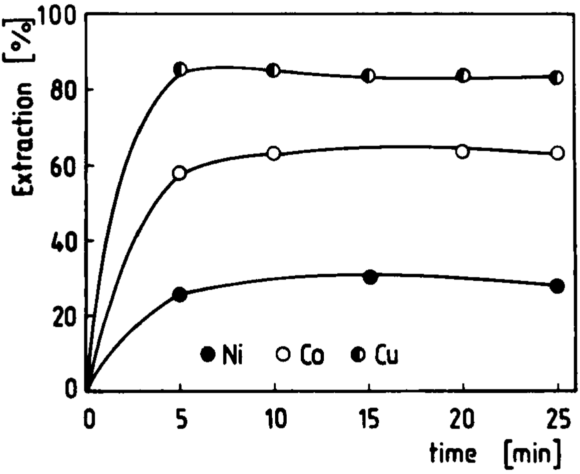


FIG. 4. Fraction of ions extracted from a feed solution containing SCN^- anions vs time of operation of TC-ELM with PEG-6000 as a carrier. System D.

results for System C (Fig. 3). The best effect corresponds to Cu(II) ions for which the extraction reaches a practical level of 80%. The affinity order for System D is the same as for the system with PEG free of SCN^-. This means that these anions facilitate only the reaction of complexes formation at the aqueous feed solution/organic solution interface.

It can be concluded from experiments with PEG-6000 that the effect of SCN^- anions on the extraction of Co(II) and Cu(II) with PEGP, viz., System B, can be related to the presence of poly(ethylene glycol) chains in the PEGP ionomer. Indeed, a high affinity of PEGP toward nickel ions seems to reflect a property of phosphodiester groups. These general conclusions point out the potent dual character of PEGP as a carrier in liquid membranes. Perhaps in dependence on the composition of a feed and/or a strip solution, PEGP could transport ions involving both counter- and cotransport mechanisms. The first is a consequence of the ionomeric character of PEGP and the second results from the properties of its component, i.e., poly(ethylene glycol) chains.

Effect of Organic Ligands on Membrane Extraction with PEGP

It is well known that hexaaquo–metal complexes are stable and inert kinetically. Thus the exchange rate of ligands in their combination sphere may appear to be critical for the overall pertraction process. The data published by Li et al. (*14*, *15*), corresponding to the pertraction of Co(II), Cu(II), and Ni(II) in liquid surfactant membranes with di(2-ethylhexyl) phosphoric acid (D2EHPA) as a carrier, prove that the presence of some organic anions (acetate, succinate, formate, tartrate) accelerate transport and enhance its effectiveness. The proposed mechanism was rationalized mainly in terms of the character of the organic ligand–metal complexes which makes possible the location of a metal at the solution/membrane interface and thereby a faster reaction step in the overall process.

To check this hypothesis with our system, we carried out experiments (System E) with the following components:

System	Feed solution	Membrane	Strip solution
E	0.005 M $MeSO_4$ + 0.05 M H_2SO_4 + 0.015–0.5 M NaOrg	PEGP-22000/DCE	1 M H_2SO_4

where NaOrg denotes sodium acetate (AC), tartrate (TAR), or formate (FOR). The concentrations of AC, TAR, or FOR in Ni(II) solutions were 0.02, 0.03, and 0.03 M whereas for Co(II) solutions they were 0.015, 0.50, and 0.37 M, respectively.

The results can be seen in Figs. 5 and 6 for Ni(II) and Co(II), respectively.

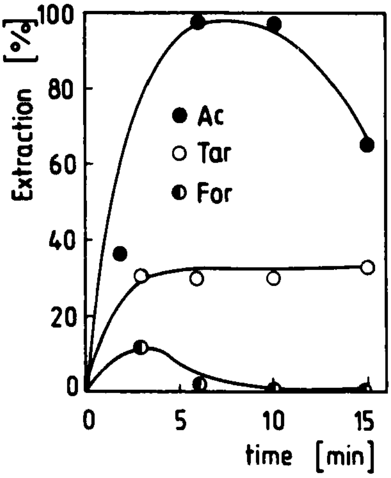


FIG. 5. The effect of organic anions on the extraction of Ni(II) from a feed solution: Ac = acetate, Tar = tartrate, For = formate. TC-ELM with PEGP-22000. System E.

From these experiments it is observed that acetate anions practically do not change the properties of the system toward Ni(II) ions whereas tartrates and formates make all extractions worse. These results can be interpreted as the effect of forming other types of complexes between an organophosphorous ionomer and metals than complexes between D2EHPA and a metal. Unfortunately, we have no suitable data to draw more detailed conclusions with respect to this problem.

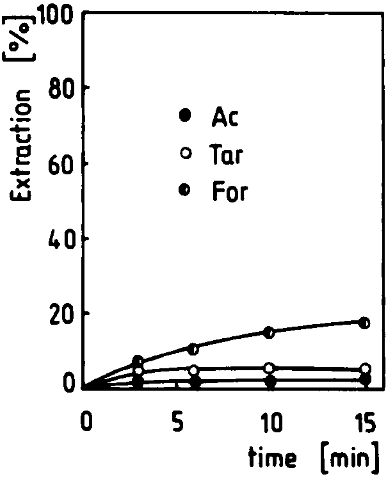


FIG. 6. The effect of organic anions on the extraction of Co(II) from a feed solution: Ac = acetate, Tar = tartrate, For = formate. TC-ELM with PEGP-22000. System E.

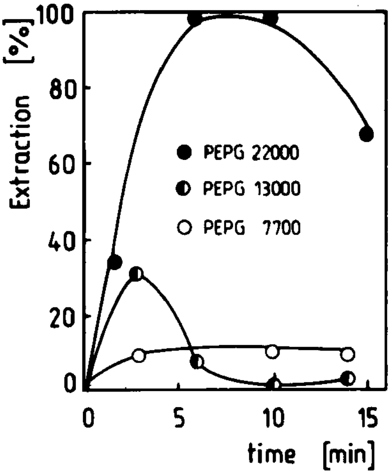


FIG. 7. The effect of PEGP molecular mass on the extraction of Ni(II). System F.

Effect of PEGP Molecular Mass on Properties of TC-ELM

Since the extraction of ions from a feed solution can be affected by the molecular weight of PEGP, we carried out experiments with PEGP of molecular weights 22,000, 13,000, and 7,700. The transports were realized in System F:

System	Feed solution	Membrane	Strip solution
F	0.005 *M* $MeSO_4$	PEGP-22000/DCE	1 *M* H_2SO_4
	0.005 *M* $MeSO_4$	PEGP-13000/DCE	1 *M* H_2SO_4
	0.005 *M* $MeSO_4$	PEGP-7700/DCE	1 *M* H_2SO_4

where Me = Ni(II) or Co(II). The results presented in Fig. 7 show that the extraction ability of PEGP toward Ni(II) ions increases with increasing PEGP molecular weight. Quite a different effect was observed for Co(II) ions, see Fig. 8, where diminishing M_n results in a slight increase of the amount of extracted ions.

CONCLUSIONS

The experimental results presented in this paper make it possible to formulate the following conclusions:

1. Poly[poly(ethylene glycol) phosphate] exhibits properties appropriate to develop stable two-component liquid membranes.

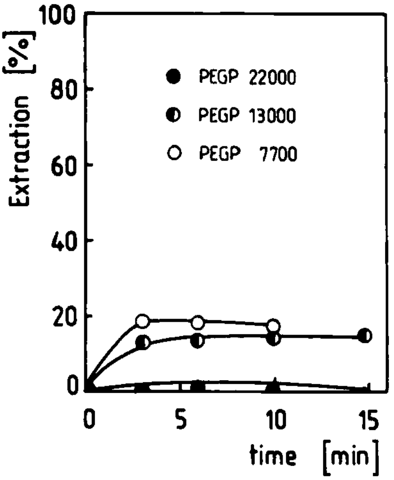


FIG. 8. The effect of PEGP molecular mass on the extraction of Co(II). System F.

2. PEGP with molecular weight 22,000 containing blocks of PEG of molecular weight 2,000 can be used as an effective carrier of nickel ions in an emulsion–liquid membrane system.
3. The difference in the extraction ability of PEGP toward Ni(II), Co(II), and Cu(II) indicates this polymer is a potent carrier for the competitive separation process.
4. The affinity order of PEGP toward the tested ions is

   Ni(II) > Co(II) > CU(II)

   i.e., it is reversed in comparison with that found for poly(ethylene glycol) as a carrier and extractant.

The properties of PEGP can be compared with the organophosphorous extractants and carriers frequently used in the hydrometallurgy of cobalt and nickel (*16*), i.e., di(2-ethylhexyl) phosphoric acid (D2EHPA) and di(2,4,4′-trimethylpentyl) phosphinic acid (Cyanex 272), which have been commonly employed as selective extractants for cobalt over nickel. Because of the selectivity of PEGP toward Ni(II), the TC-ELM with this carrier could be used alternatively in the separation of nickel over cobalt.

Acknowledgments

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