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## **APPLICATION OF TBP IN SELECTIVE REMOVAL OF IRON(III) IN SOLVENT EXTRACTION AND TRANSPORT THROUGH POLYMER INCLUSION MEMBRANES PROCESSES**

*Received March 15, 2005; reviewed; accepted May 15, 2005*

The separation of iron(III) from chloride aqueous solutions containing Mn(II), Ni(II), Co(II) and Cu(II) by solvent extraction and transport through polymer inclusion membranes (PIMs) processes was studied. Tributyl phosphate (TBP) was used as the extractant/ion carrier. Extraction of Fe(III) increased with increasing of extractant concentration in the organic phase. The selective transport of Fe(III) from aqueous chloride source phase through PIM containing cellulose triacetate (CTA) as the support, *o*-nitrophenyl octyl ether (ONPOE) as the plasticizer and TBP as the ion carrier has been studied. The influence of the ion carrier and plasticizer concentration on the transport metal ions was investigated. The results show that Fe(III) can be separated very effectively from others metal ions. The atomic force microscopy (AFM) was used to obtain images of the pores in cellulose triacetate membranes containing a plasticizer.

*Key words: polymetallic sea nodules; iron(III); manganese(II); cobalt(II); nickel(II); copper(II); TBP; solvent extraction, polymer inclusion membranes*

### **INTRODUCTION**

After leaching of deep – sea nodules in hydrochloric acid, iron(III) is present in leach solutions and its elimination is a major operational problem in hydrometallurgy. The nodules, which are located at the bottom of the world's oceans, constitute a major and strategic resource and reservoir of cobalt, copper and nickel (De Schepper, 1986; DeCarlo and Zetlin, 1982).

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The recovery of iron(III) from such aqueous solutions is usually carried out by precipitation as jarosite, goethite or hematite (Ismael and Carvalho, 2003; Dutrizac, 1996). Though the iron removal is mainly achieved by precipitation techniques, the use of solvent extraction also allows the iron(III) removal from acidic aqueous solutions. Organophosphorus acid derivatives such as di(2-ethylhexyl)phosphoric acid (D2EHPA) and di(2-ethylhexyl)phosphonic acid (PC - 88A) have been used for iron(III) removal by several investigators (Lupi and Pilone, 2000; Biswas and Begum, 1998, 1999, 2001; Jayachandran and Dhake, 1997). Among neutral extractants, tributyl phosphate (TBP), methyl *iso*-butyl ketone (MIBK) (Saji and Reddy, 2001), trioctylphosphine oxide (TOPO) and Cyanex 923 (Saji et al., 1998; Gupta et al., 2003) have been used extensively for the extraction of iron(III) from chloride solutions.

A study of iron(III) transport through the supported liquid membrane using the phosphine oxide (Cyanex 921) as a ion carrier has been carried out by Alguacil and Alonso (2000). Supported liquid membrane with Alamine 336 or LIX 84, were used in the transport of Fe(III), Cu(II) and Ni(II) in a two-membrane three-compartment cell. Dilute feed contained these metal ions in 1.0 M NaCl and at pH of 2.0. Fe<sup>3+</sup> was separated from the feed by the transport through Alamine 336-loaded membrane, whereas Cu<sup>2+</sup> was transported through LIX 84 loaded membrane, while Ni<sup>2+</sup> remained in the central feed compartment of the cell. The transport fluxes of Fe<sup>3+</sup> and Cu<sup>2+</sup> through the two membranes were found to be 3.6 and 5.1  $\mu\text{mol}/\text{m}^2\text{s}$ , respectively (Gill et al., 2000). A study of iron(III) transport through an immobilised liquid membrane with phosphine oxide (Cyanex 923) as ion carrier has been carried out by Alguacil and Martinez (2000) Iron(III) can be selectively transported over chromium(VI) from 2.0 M HCl aqueous solutions.

In the present paper, the separation of iron(III) from acidic chloride solutions after leaching of polymetallic nodules by solvent extraction and transport through polymer inclusion membranes processes with TBP as the extractant/ion carrier has been studied. The source phase contained 0.10 M Fe(III), 0.30 M Mn(II), 0.020 M Ni(II), 0.010 M Cu(II), 0.0020 M Co(II), 1 M HCl and 2 M NaCl. The PIMs are formed by casting CTA as a support, ONPOE as a plasticizer and TBP as the ion carrier. The influence of the composition of the membrane and extractant concentration on the removal of iron(III) has been investigated.

## EXPERIMENTAL

### REAGENTS

Inorganic chemicals, i.e. iron(III), manganese(II), nickel(II), cobalt(II) and copper(II) chlorides, sodium chloride and hydrochloric acid were of analytical grade and were purchased from POCh (Gliwice, Poland). Organic reagents, i.e. cellulose triacetate (CTA), *o*-nitrophenyl octyl ether (ONPOE), tributyl phosphate (TBP), and dichloromethane were also of analytical reagent grade and were purchased from Fluka

and used without further purification. Distilled kerosene was used as the diluent in solvent extraction. The density of plasticizer, i.e. ONPOE, was  $1.04 \text{ g cm}^{-3}$ . Aqueous solutions were prepared with double distilled water, with a conductivity of  $0.1 \mu\text{Sm}^{-1}$ .

## PROCEDURE

### SOLVENT EXTRACTION

Solvent extraction was carried out using equal volumes of both phases ( $10 \text{ cm}^3$  each) which were mechanically shaken ( $200 \text{ min}^{-1}$ ) for 20 minutes at constant temperature ( $25 \pm 2 \text{ }^\circ\text{C}$ ). The metal ions content in the aqueous phase has been determined by means of AAS Solaar 939 (Unicam) spectrophotometer while the pH value has been measured with a CX-731 (Elmetron) pH-meter. The concentration of metals in the organic phase was calculated from the mass balance. The distribution ratio (D) and extraction percent (%E) were determined as equal to:

$$D = \frac{[Me]_{org}}{[Me]_{aq}} \quad (1)$$

$$\% E = \frac{D}{D+1} \cdot 100\% \quad (2)$$

where  $[Me]_{org}$  and  $[Me]_{aq}$  are concentrations of the metal ions in the organic and aqueous phases, respectively.

The selectivity coefficient, was calculated as:

$$S = \frac{D_{M1}}{D_{M2}} \quad (3)$$

### POLYMER INCLUSION MEMBRANE

A solutions of cellulose triacetate (CTA), ion carrier (TBP) and plasticizer (ONPOE) in dichloromethane were prepared. A portion of this solution was poured into a membrane mold comprised of a 6.0 cm glass ring attached to a glass plate with CTA-dichloromethane glue. The organic solvent was allowed to evaporate overnight and the resultant membrane was separated from the glass plate by immersion in cold water. The membrane was soaked in 0.1 M HCl aqueous solution for 12 hours and stored in distilled water.

### MEMBRANE TRANSPORT EXPERIMENTS

The transport across PIMs was carried out in a permeation cell in which the membrane film was tightly clamped between two cell compartments (Fig. 1). The effective membrane area, which was exposed to both phases was  $3.14 \text{ cm}^2$ . Both, the

source and receiving aqueous phases (50 cm<sup>3</sup> each) were stirred at 600 rpm with synchronous motors. The receiving phase was distilled water or hydrochloric acid aqueous solutions. The PIM transport experiments were conducted at room temperature (22-25 °C). The permeation of iron(III), manganese(II), copper(II), cobalt(II) and nickel(II) was monitored by periodicall sampling (0,1 cm<sup>3</sup> each) of the source phase, which were analyzed after appropriate dilution by an atomic absorption spectrophotometer. The source phase acidity was controlled by pH-meter (Cx-731 Elmetron, with a combined pH electrode, EFH-136, Hydromet, Poland), pH was kept constant by adding periodically aqueous solution of 2.0 M HCl.

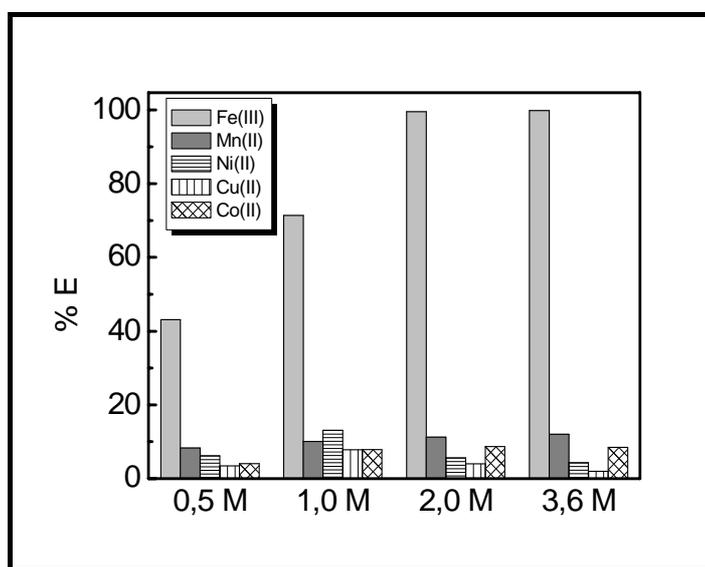


Fig. 1. Effect of TBP concentration (0,5-3,6 M) on the extraction of Fe(III), Mn(II), Ni(II), Cu(II) and Co(II) from aqueous chloride solutions

The kinetics of PIM transport was described by a first-order transport rate equation in metal ion concentration:

$$\ln\left(\frac{c}{c_i}\right) = -kt \quad (4)$$

where  $c$  is the metal ion concentration (M) in the source phase at some given time,  $c_i$  is the initial metal ion concentration in the source phase,  $k$  is the rate constant (s<sup>-1</sup>), and  $t$  is the time of transport process (s).

To calculate the  $k$  value, a plot of  $\ln(c/c_i)$  vs. time was prepared. The rate constant value for the duplicate transport experiment was then averaged and standard deviation was calculated. The permeability coefficient ( $P$ ) was calculated as follows:

$$P = - \frac{V}{A} k \quad (5)$$

where  $V$  is the volume of aqueous source phase, and  $A$  is the area of membrane. The initial flux ( $J_i$ ) was determined as equal to:

$$J_i = P c_i \quad (6)$$

## RESULTS AND DISCUSSION

### THE SOLVENT EXTRACTION OF Fe(III), Mn(II), Ni(II), Co(II) AND Cu(II) WITH TBP FROM AQUEOUS CHLORIDE SOLUTIONS

The extraction behavior of Fe(III), Mn(II), Ni(II), Co(II), and Cu(II) from 1.0 M hydrochloric acid and 2.0 M sodium chloride with TBP in kerosene as the solvent has been studied. The composition of aqueous phase is a very similar to aqueous solutions after leaching of polymetallic nodules. Nodules were leached in 2.75 M HCl solution with addition of 4.0 M NaCl (Jana, 1993). Efficiency of nodules leaching in 2.75 M HCl solution and 4.0 M NaCl was about 99 % of Cu(II), 99 % of Ni(II), 93 % of Co(II), 92 % of Fe(III) and 96 % of Mn(II) after 4 hours leaching.

The effect of TBP concentration on metal ions extraction has been studied (Fig. 1). The extractant concentration was varied between 0.5 - 3.6 M. As can be seen from Fig. 1 the extraction percent of Fe(III) was the highest for 2.0 M and 3.6 M TBP (97 % TBP) and was equal to 99,5 % and 99,8 %, respectively. The extraction of Mn(II), Ni(II), Cu(II) and Co(II) with 2.0 M TBP was 11.2 %, 5.63 %, 4.1 % and 8.7 %, respectively. The extraction of Mn(II), Ni(II), Cu(II) and Co(II) with 3.6 M TBP was 12.2 %, 4.3 %, 1.9 % and 8.5 %, respectively.

Iron(III) forms various chloride complexes. At around 4.0 M  $\text{Cl}^-$  concentrations, in the aqueous solution iron(III) exists as  $\text{FeCl}_2^{2+}$  (4 %),  $\text{FeCl}_2^+$  (19.5 %),  $\text{FeCl}_3$  (73.7 %) and  $\text{FeCl}_4^-$  (2.8 %) (Biswas and Begum, 1998). The different mechanisms take place in the extraction process and the reaction that occurs between the iron(III) complexes and TBP at aqueous - organic interface, can be defined as (Campederros and Marchese, 2000):

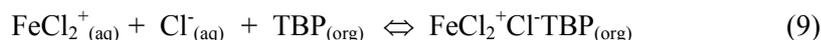
a) Adduct formation with the neutral complex



b) Ionic association with the anionic complex



c) Ionic association with the cationic complex:



The highest selectivity was obtained for Fe(III) over other metals with 3.6 M TBP. The values of selectivity coefficients for TBP are presented in Table 1. With the extractant concentration increase the selectivity coefficients increase.

Table 1. Selectivity coefficients of Fe(III) over Mn(II), Ni(II), Co(II) and Cu(II) at different TBP concentrations in solvent extraction process

Selectivity coefficient, S	TBP, M			
	0.5	1.0	2.0	3.6
$S_{\text{Fe(III)/Mn(II)}}$	9.50	17.85	350.8	480.5
$S_{\text{Fe(III)/Ni(II)}}$	11.52	16.66	535.1	715.3
$S_{\text{Fe(III)/Cu(II)}}$	21.11	29.41	751.7	1609.0
$S_{\text{Fe(III)/Co(II)}}$	1.38	3.62	137.3	346.1

#### TRANSPORT OF IRON(III) AND OTHER METAL IONS ACROSS POLYMER INCLUSION MEMBRANES FROM AQUEOUS CHLORIDE SOLUTIONS

Next, the influence of TBP concentration in PIMs, used in the transport of iron(III) was studied. PIMs contained constant amounts of the plasticizer (2.0 cm<sup>3</sup> ONPOE /1 g CTA) and the support (0.050 g CTA). The concentration of TBP was changed from 0.5 to 2.5 M. The obtained results are presented in Fig. 2. The permeability coefficient of iron(III) from source aqueous phase increases with TBP concentration increase. Transport rate of Fe(III) through PIM remained practically constant at the concentration of TBP higher than 1.5 M. For 2.5 M TBP the maximum initial flux was equal to 32.5  $\mu\text{molm}^{-2}\text{s}^{-1}$ . In all experiments of polymer inclusion membranes transport no manganese(II), nickel(II), copper(II) and cobalt(II) ions were detected in the receiving phase.

Next, the influence of ONPOE concentration as the plasticizer on the iron(III) transport with TBP was studied. The polymer inclusion membranes contained constant amounts of the support and the ion carrier: 0.050 g CTA, 0,053 g TBP and the variable amount of ONPOE used as the plasticizer. The plasticizer concentration was varied between 0.6 - 2.0 cm<sup>3</sup> /1 g CTA. The iron(III) transport into 0.1 M HCl as the receiving phase is presented in Fig. 3 and Table 2.

As can be seen from Table 2, the initial flux and the permeability coefficient of Fe(III) depends on the ONPOE concentration in the membrane. Removal of Fe(III) from the source aqueous increases with the plasticizer concentration increase. The highest flux value was obtained for the membrane which contained 2 cm<sup>3</sup> ONPOE/1 g CTA (32.90  $\mu\text{molm}^{-2}\text{s}^{-1}$ ).

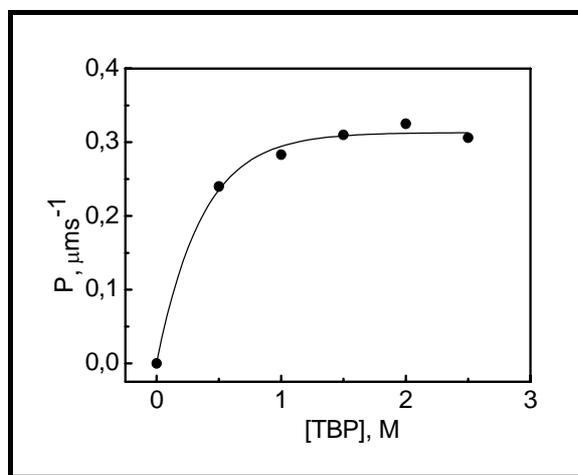


Fig. 2. Effect of TBP concentration upon initial flux for Fe(III) transport through polymer inclusion membranes. Membrane phase: 0.050 g CTA, 2.0 cm<sup>3</sup> ONPOE/1 g CTA.; receiving phase: 0.1 M HCl

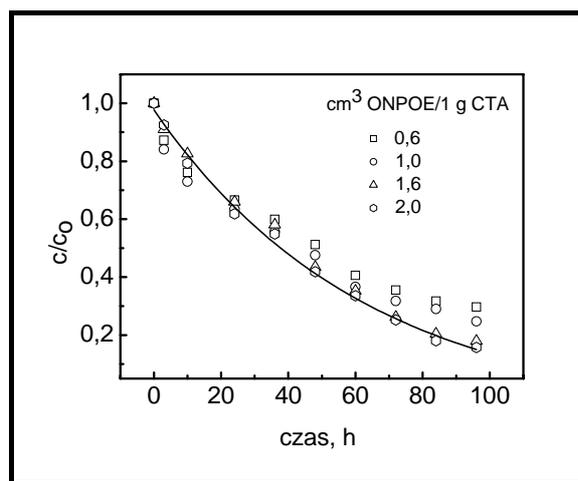


Fig. 3. Kinetics of iron(III) transport through PIMs containing different amounts of ONPOE as the plasticizer. Membrane phase: 0.050 g CTA, and 0.53 g TBP; receiving phase: 0.1 M HCl

The resulting membrane contained 19.30 wt% CTA, 60.23 wt% ONPOE and 20.47 wt% TBP. Content of plasticizer is much higher as compared to PIMs used by other authors. For example, PIMs used by Kozłowski and Walkowiak (2002) contained 41 wt% CTA, 36 wt% *orto*-nitrophenyl pentyl ether (ONPPE) and 23 wt% tri-*n*-octylamine (TOA). The unusually low content of plasticizer in PIM used in this study is due to good plasticizing properties of tertiary amines, serving as ion carriers. On the other hand, PIMs used by Nazarenko and Lamb (1997) contained 76 wt % ONPOE.

Table 2. Kinetic parameters for iron(III) transport through PIM with TBP (parameters as in Fig. 3)

Concentration of ONPOE, (cm <sup>3</sup> / 1 g CTA)	Rate constant, <i>k</i> (h <sup>-1</sup> )	Permeability coefficient, <i>P</i> (μm s <sup>-1</sup> )	Initial flux, <i>J<sub>i</sub></i> (μmol m <sup>-2</sup> s <sup>-1</sup> )
0.6	0.0138	0.241	24.09
1.0	0.0154	0.269	26.89
1.6	0.0180	0.315	31.48
2.0	0.0189	0.329	32.90

### PIM VISUALIZATION

The surface properties of polymer inclusion membranes has been studied using the atomic force microscopy (AFM). Fig. 4 shows the image of the PIM containing 2.0 M TBP, 0,05 g CTA and 2.0 cm<sup>3</sup> ONPOE/1 g CTA. This membrane possess a porous structure which facilities metal ions transport. Figure 5 shows the image of the PIM containing only the polymer support (CTA); this membrane is nonporous.

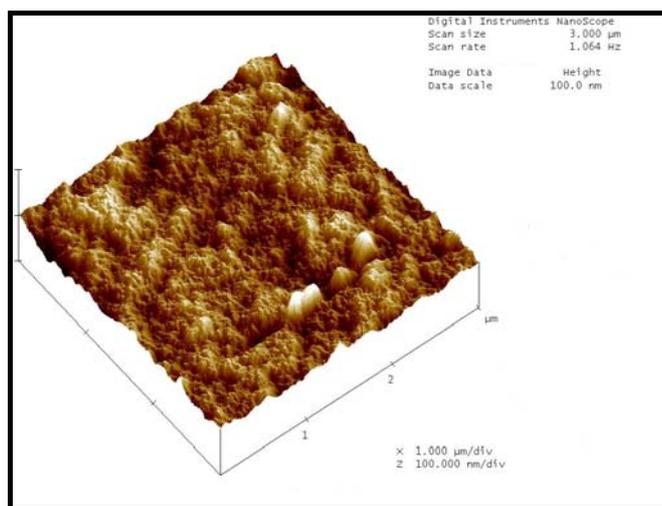


Fig. 4. The view of AFM images of PIM containing 0.050 g CTA, 2.0 cm<sup>3</sup> ONPOE/1 g CTA and 2.0 M TBP

### CONCLUSIONS

TBP used as extractant in solvent extraction process allow for selective removal of iron(III) from acidic aqueous solutions containing Mn(II), Ni(II), Co(II), and Cu(II). At concentration of TBP equal to 3.6 M 99.8 % of Fe(III) was extracted with only small amounts of other metals be coextracted – as the consequence selectivity coefficients for Fe(III) over Mn(II), Ni(II), Cu(II), and Co(II) were very high and equal to 480.5, 715.3, 1609.0, and 346.1, respectively.

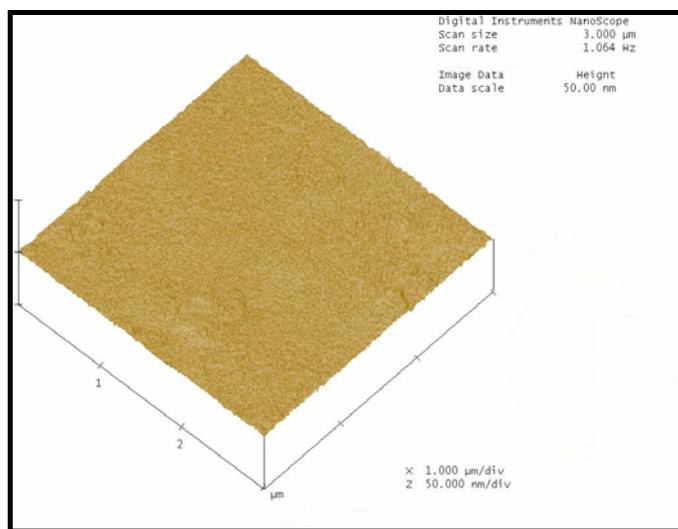


Fig. 5. The view of AFM images of PIM containing only 0.050 g CTA

Also, transport across polymer inclusion membranes with TBP as the ion carrier, ONPOE as the plasticizer, and cellulose triacetate as the support into hydrochloric acid aqueous solution as the receiving phase was found to be very selective for iron(III) removal from acidic aqueous chloride solutions containing Mn(II), Ni(II), Co(II), and Cu(II). No other metals excluding Fe(III) were detected in the receiving aqueous phase. To find the optimal conditions of polymer inclusion membrane transport, the influence of plasticizer (ONPOE) and ion carrier (TBP) concentration into membrane, as well as hydrochloric acid concentration in the aqueous receiving phase were also studied.

#### ACKNOWLEDGMENT

Financial support of this work was provided by Polish Science Foundation Grants – grant no. 3 T09C 019 26.

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**Pośpiech B., Walkowiak W., Woźniak M.J.,** *Zastosowanie TBP do selektywnego usuwania żelaza(III) w procesie ekstrakcji cieczowej i transportu przez polimerowe membrany inkluzyjne*, Physicochemical Problems of Mineral Processing, 39 (2005), 89-98 (jęz. ang.).

W pracy przedstawiono wyniki badań selektywnego wydzielania jonów Fe(III) z wodnego roztworu chlorkowego zawierającego jony Mn(II), Ni(II), Cu(II) i Co(II) w procesie ekstrakcji cieczowej i transportu przez polimerowe membrany inkluzyjne. W roli ekstrahenta/przenośnika jonów użyto fosforanu tributylu (TBP). Zbadano zależność wydajności ekstrakcji od stężenia ekstrahenta. Wydajność ekstrakcji żelaza(III) wzrastała ze wzrostem stężenia TBP w nafcie. Najwyższy procent ekstrakcji jonów Fe(III) uzyskano przy 2,0 i 3,6 M TBP i wynosił on odpowiednio 99,5 i 99,8 %.

Określono także wpływ zawartości plastyfikatora oraz przenośnika jonów w membranie na transport jonów żelaza(III) z kwaśnego roztworu chlorków Mn(II), Ni(II), Cu(II) i Co(II). W tych warunkach procesu transportu nie stwierdzono obecności jonów tych metali w fazie odbierającej. Ze wzrostem zawartości ONPOE od 0,6 do 2,0 cm<sup>3</sup>/1 g CTA wartość strumieni początkowych wzrastała. Przy stężeniu plastyfikatora wynoszącym 2,0 cm<sup>3</sup>/1 g CTA strumień początkowy wynosił 32,90 μmol/m<sup>2</sup>s. Z kolei wzrost stężenia przenośnika w membranie w zakresie od 0,5 do 1,5 M TBP (w przeliczeniu na objętość plastyfikatora) powodował wzrost wartości współczynnika przepuszczalności. Dalsze zwiększanie zawartości TBP nie wpływało na szybkość procesu. Wykorzystując mikroskopię sił atomowych (AFM) wykonano także analizę struktury powierzchni membrany zawierającej TBP, ONPOE i CTA oraz membrany z samego CTA.