

The influence of the type of polymer matrix on the transport of oxalic, tartaric and lactic acids using polymer inclusion membranes

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Abstract

In this work was started research on the problem of transport of organic acids such as oxalic, tartaric and lactic acids using polymer inclusion membranes. The aim of the study was to determine the effect of kind of polymer matrix on the transport of organic acids through polymer inclusion membranes (PIMs). In this study cellulose triacetate (CTA), cellulose acetate propionate (CAP) and cellulose acetate butyrate (CAB) were used as a polymer matrix. 1-alkylimidazole with alkyl chain length of 10, 11, 12, 14 and 16 carbon atoms were used as a carrier. Results of this study show that the type of polymer matrix used has a significant effect on the rate of transport of organic acid. At the same time, on the basis of the study showed that there are differences in the rate of transport oxalic, tartaric and lactic acids.

1. Introduction

Oxalic, tartaric and lactic acids are widely used in many industries. Lactic and tartaric acids are used primarily in the food industry as acidifiers. In addition, thanks to probiotic, exfoliating and cleansing properties they are also used in the pharmaceutical and cosmetic industries. What is more, the latest application of lactic acid is the production of biodegradable plastics. Yearly global production of lactic acid is 100 000 tons while tartaric acid is about 80 000 tons. However, oxalic acid is mainly used in the textile industry and in the hydrometallurgy of heavy metals. Global production of oxalic acid is 65 000 ton/year [1][2][3][4].

Tartaric and oxalic acids may be obtained by chemical methods, but the main method of production of oxalic, tartaric and lactic acids is fermentation. Safe and environmentally friendly fermentation processes are in recent years of broad interest among methods of organic compounds production. This method reduces chemical production and reduces costs and resulting by-products and impurities [5]. During industrial processes, mainly food and agricultural large quantities of waste products are produced. Inter alia sugars or glycerol fraction. By using suitable microorganisms the fermentation process can be carried out to obtain the fermentation broth containing high quality products, for example, oxalic, tartaric and lactic acids [6][7]. The final qualitative and quantitative composition of the fermentation broth depends on the type of microorganism and the conditions of the fermentation process [8]. After the fermentation process, a problem concerning the separation of the desired products occurs. The most commonly used methods are precipitation and extraction. However, these methods are usually associated with the separation of by-products and the necessity of using large amounts of often expensive and harmful solvents. It is therefore important to develop a fully-effective separation method, which allows for the selective separation of high-quality products of fermentation solutions [9][10]. One

of the possibilities are the use of separation techniques using polymer inclusion membranes [11].

Previous work has been devoted to the issue of the use of polymer inclusion membranes for the separation of metal ions such as copper, cobalt or nickel [12][13]. However, recently were created literature reports on the transport of organic compounds by PIM [14]. These studies, are still very limited, so PIM in the future may become the technique of separation of wide research opportunities. PIM as liquid membranes have many advantages such as high diffusion coefficients, high selectivity, low cost, low energy consumption. Polymer inclusion membranes are more chemical stability and mechanical strength compared with the most commonly used liquid membrane, the emulsion liquid membrane (ELM) and supported liquid membranes (SLM) [15][16].

As shown by previous studies on the ability of the separation polymer inclusion membranes affects among other things, the type of used carrier, membrane thickness and the temperature of the process [17]. Very important factor that contributes significantly to transport the compound through the polymer inclusion membrane is type used of the polymer matrix. The most commonly used polymer matrix is cellulose triacetate (CTA) and polyvinyl chloride (PVC) [18][19]. Base polymers used for the preparation of polymer inclusion membranes are primarily responsible for the strength of the membrane as well as have a significant impact on the transport of compounds by PIM. The membrane based on cellulose triacetate (CTA) has a high polarity[20][21]. This compound has in its structure, hydroxy groups and acetyl groups, which are capable of forming oriented hydrogen bonds which means that the membranes are characterized by a high degree of crystallinity. Polyvinyl chloride (PVC) but contains in its structure-functional C-Cl. The dominant interactions are impact intermolecular thus PVC is a polymer amorphous with a low degree of crystallinity. The possibility of the occurrence of hydrolysis of the CTA in particular strongly acidic creates a barrier the application of the polymer as a base in contact with concentrated acids. It should be noted that the CTA-based membranes are characterized by high mechanical strength which is directly related to the structure of crystalline CTA and strong interactions between the polymer chains [16]. Properties of base polymers play an important part in the selection of a suitable carrier which is related to the compatibility of the polymer matrix with the active compounds.

There are many of references, including any Walkowiak [22] and Gardner [23] on the effect of the polymer matrix used for the transport of metal ions through PIM. These studies compared the matrix made with cellulose derivatives as well as the matrix in the form of polyvinyl chloride. Obtained significant differences in the rate of transport of the test compounds. These differences were caused by the hydrophilic-hydrophobic properties of the matrix as well as the quantitative and qualitative composition.

2. Experimental part

2.1. Process conditions

In this study cellulose triacetate (CTA), cellulose acetate propionate (CAP) and cellulose acetate butyrate (CAB) were used as a polymer matrix. Table 1 shows quantitative and qualitative composition polymer matrix.

Table 1

Characteristics of polymer matrix

Polymer matrix	CTA	CAB	CAP
M _n	72000-74000	65000	25000
wt.% acetyl	43.7	29.3	2.5
wt. % propionyl	0	0	45
wt.% butyryl	0	18	0

1-alkylimidazole was applied as a carrier. The alkyl chain in the imidazole contained 10, 11, 12, 14 or 16 carbon atoms (IMI-n). The 0.1 M solutions of organic acids, oxalic, tartaric or lactic acid, were used as a feeding phase. The deionized water was applied as a receiving phase. Each investigation ran for 24 hours. The temperature of process was 25°C. The thickness of membrane was in the range 10-16 micrometers.

2.2. Membrane preparation

A solution of polymer matrix and carrier were placed in a 3.6 cm diameter flat bottom glass petri-dish. The solvent, dichloromethane, evaporated for 12 hours at room temperature. Then, the obtained membrane was slightly and carefully removed from the glass ring. Finally, all membranes were weighed and the thickness of each was measured using thickness gauge. Before the process of organic acid transport, polymer membrane was placed in glass beaker for 24 hours in order to achieve homogeneity of its structure. Also, after the research, membrane was soaked in water for 24 h and after drying was weighed again.

2.3. Experimental apparatus

The transport of organic acids across polymer inclusion membranes using two glass chambers was performed. One chamber contained feeding phase while second chamber contained receiving phase. The chambers were separated by PIM. Both feeding and receiving phases were constantly and intensively stirred. The volume of both phases was the same and equal to 60 cm³. The surface of membrane was equal to 4.15 cm². A diagram of the experimental apparatus is shown in Figure 1.

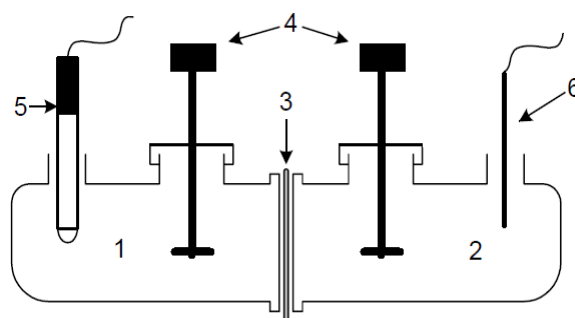


Fig.1. Experimental apparatus diagram 1–chamber with receiving phase, 2–chamber with feeding phase, 3–polymer inclusion membrane, 4–stirrers, 5–electrode, 6–temperature sensor

To determine the concentration of organic acids, conductivity of receiving phase was measured every 7 minutes for the duration of the process. Based the previously determined calibration curve, the conductivity was converted to the molar concentration of organic acid in the receiving phase.

2.4. Mathematical model

Based on the fundamental dependencies a simplified mathematical model that describes the transport of ions using polymer inclusion membrane has been proposed (equation 2.1.). The fundamental dependencies are as follows:

- the concentration of transferred compound in the membrane is very small in comparison to the concentration of the carrier, so it can be assumed that the concentration of free carrier in the membrane is constant,
- the compound transport through the membrane occurs according to Ficks law, and the concentration gradient across the membrane is linear,
- Rate of reaction on the surface of the membrane is high enough that to assume the equilibrium of the system,
- diffusion of compound in the liquid film on the surface of the membrane is much faster than the diffusion of the complex through the membrane,
- feeding and receiving phase are perfectly stirred.

$$-\frac{1}{2} \ln \left(1 - \frac{2 \cdot C}{C_0} \right) = k \cdot t \quad (2.1)$$

This relationship shows high linear correlation, therefore using linear regression analysis can be determined the coefficients k . Knowing the k , the volume of feed phase and the surface of membrane permeability coefficient can be determined permeability coefficient (P [m/s]):

$$P = \frac{V}{A} \cdot k \quad (2.2)$$

The characteristic value of ions transport across polymer inclusion membrane is flux of organic acid. It is the amount of organic acid passing through the border surface of membrane per unit time. The initial flux (J_0 [mol/(m²*s)]) can be described as:

$$J_0 = \frac{V}{A} \cdot k \cdot C_0 \quad (2.3)$$

where:

C_0 - the initial concentration of the organic acid [mol/dm³],

C - concentration of organic acid in the receiving phase at time t [mol/dm³],

V - volume of feeding/receiving phase [m³],

A - surface of membrane [m²],

t - time [s].

For each of the processes the permeability coefficient and flux of organic acid have been determined.

3. Results

While research has been examined transport of oxalic, tartaric and lactic acid using polymer inclusion membranes. For the preparation of polymer inclusion membranes used CTA, CAB and CAP. In the membranes were used 1-alkylimidazoles as a carrier. The alkyl chain of the imidazole contained 10,11,12,14 or 16 carbon atoms. The transport was carried out at 25°C for 24 hours. Figure 2 shows an example of the initial transport of organic acid by PIM line with agreed objectives, and proposed a mathematical model (2.1.). In Figure 2. were presented results obtained for oxalic acid during the process of separation by a PIM for the three different matrixes of the carrier in the form of IMI-14. As you can see the initial process transport of organic acid by PIM is highly linear so demonstrated high value, close to unity, the coefficient of determination R^2 . Therefore the use of a linear regression analysis can determine the slope of the line and then according to equation (2.2) and (2.3), and the permeability coefficient and initial flux of organic acid. Value of flux of organic acid is the value characterizing transport of compound used the membrane techniques.

As can be seen in Figure 2 for a process using a CTA is the highest slope in relation to the initial flux value is the highest. Using CAB is a lower slope while in the case of CAP no significant changes indicative of oxalic acid transport by PIM For each of the other processes carried out, the initial flux was determined in the same way.

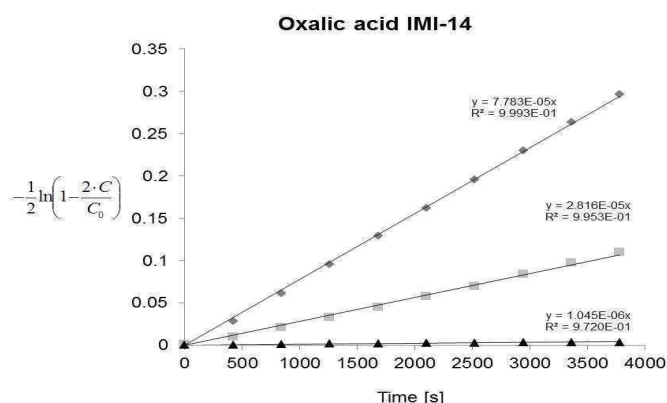


Fig.2. Initial transport of oxalic acid. Feeding phase: 0.1 M solution of oxalic acid. Receiving phase: deionized water. Polymer matrix: CTA,CAB,CAP. Carrier: IMI-14. Temperature: 25°C.

Figure 3 shows a comparison of the values of initial flux obtained of oxalic acid for each of the used polymer matrix and each of the carrier used. As can be seen the highest values obtained for cellulose triacetate then the cellulose acetate butyrate, to the end for cellulose acetate propionate. When using the CAP obtained values are almost equal to zero so it can be assumed that in this case the transport of the organic acid does not occur. As can be seen, the rate of transport of the organic acid increases with increasing number of carbon atoms in the substituent from 10 to 14. The study achieved a maximum equal to $7.82 \cdot 10^{-4} \text{ mol/m}^2 \cdot \text{s}$ for IMI-14. However, further increase in chain length to 16 carbon atoms causes a decrease in the rate of transport. This relationship is observed when it using cellulose triacetate as a polymer matrix. In case of CAB maximum equal to $4.1 \cdot 10^{-4} \text{ mol/m}^2 \cdot \text{s}$ also achieved the IMI-14, but there was no similar as in the case according to the CTA.

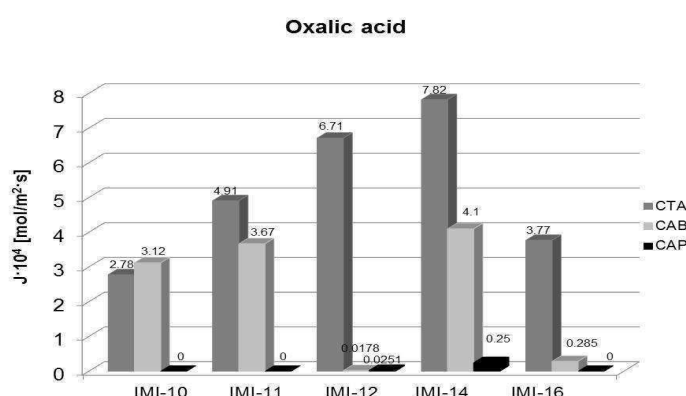


Fig.3. Comparison of the rate of transport of oxalic acid through the PIM for three polymer matrix.
Feeding phase: 0.1 M solution of oxalic acid. Receiving phase: deionized water. Polymer matrix: CTA,CAB,CAP. Carrier: IMI-n. Temperature: 25°C.

Analyzing the data presented in Figure 4, a similar relationship can be observed as in the case of oxalic acid obtained the highest values for the matrix of the CTA. The maximum value of initial flux of tartaric acid is $3.34 \cdot 10^{-4} \text{ mol/m}^2 \cdot \text{s}$, while it is 2 times lower than in the case of oxalic acid. Using the IMI-11, the values obtained for the CAB are slightly higher than for the CTA. During the process, using CAP transport of tartaric acid is observed only using IMI-12 a carrier. However, this value is six times lower than for a process using a CTA.

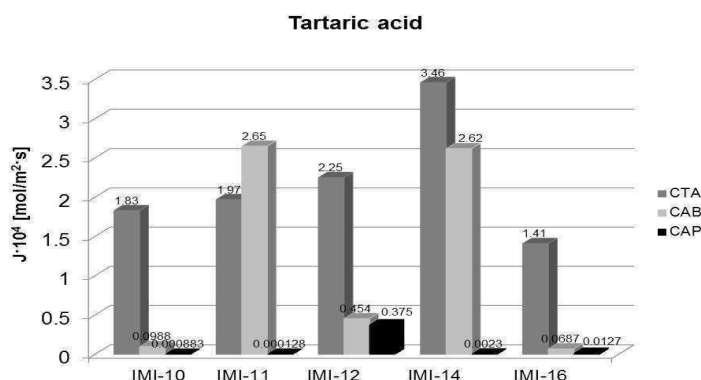


Fig.4. Comparison of the rate of transport of tartaric acid through the PIM for three polymer matrix. Feeding phase: 0.1 M solution of tartaric acid. Receiving phase: deionized water. Polymer matrix: CTA,CAB,CAP. Carrier: IMI-n. Temperature: 25°C.

For the process of transport of lactic acid also shows the differences for each of the cellulose matrix used. This comparison is shown in Figure 5. In this case the highest value obtained for the CTA. Maximum was reached for CTA and IMI-14, this value was $3.73 \cdot 10^{-4}$ mol/m²·s. During the tests with lactic acid and CAB is observed a minimum transport of the organic acid. The values are, however, almost 10 times lower than for the CTA. Using CAP transport of lactic acid was not achieved.

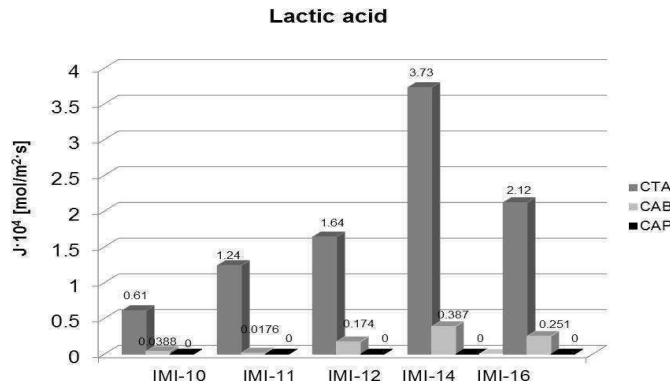


Fig.5. Comparison of the rate of transport of lactic acid through the PIM for three polymer matrix. Feeding phase: 0.1 M solution of lactic acid. Receiving phase: deionized water. Polymer matrix: CTA,CAB,CAP. Carrier: IMI-n. Temperature: 25°C.

Each process was carried out for 24 hours. Such a long time for some process was not necessary, because the time to reach equilibrium was significantly shorter. The Figure 6 shows the process of oxalic acid for three different matrix with using the IMI-14. The diagram shows the ratio concentration of acid at a time to the value of the initial concentration as a function of time. As can be seen, using CTA and CAB, steady state was reached after about 7 hours after the start of the process, compared to the same time in the using CAP achieved only about 10% of the steady state.

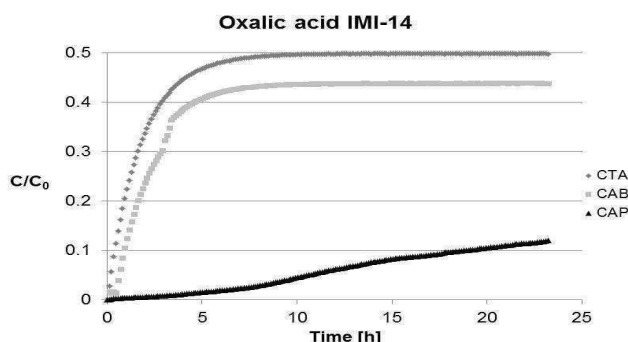


Fig.6. Change of the concentration of oxalic acid in the receiving phase during the separation process by PIM. Feeding phase: 0.1 M solution of oxalic acid. Receiving phase: deionized water. Polymer matrix: CTA,CAB,CAP. Carrier: IMI-14. Temperature: 25°C.

Using the CTA and CAB with IMI-14 during transport of tartaric acid, the time to reach steady state is longer than that of oxalic acid and is approximately 15 hours. Exemplary process transport of tartaric acid is shown in Figure 7. While, Figure 8 shows a process for lactic acid, in this case, steady state is reached only for CTA, and the time to achieve it was about 20 hours. Using CAB after 24 hours of only less than 60% of the equilibrium was achieved.

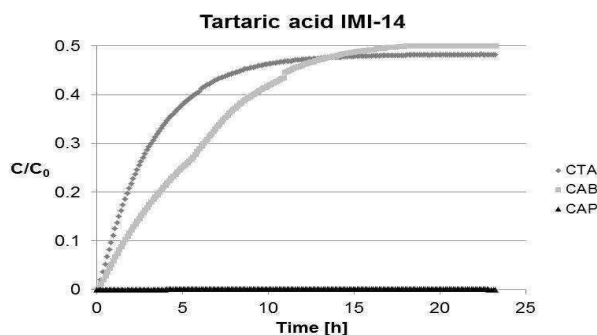


Fig.7. Change of the concentration of tartaric acid in the receiving phase during the separation process by PIM. Feeding phase: 0.1 M solution of tartaric acid. Receiving phase: deionized water. Polymer matrix: CTA,CAB,CAP. Carrier: IMI-14. Temperature: 25°C.

Based on these results it can be seen that there are differences in both applied for each of the cellulose matrix as well as for each of the acids. Figure 8 shows a comparison of oxalic, tartaric and lactic acids for cellulose triacetate and 1-alkylimidazoles as carrier. Comparing the data presented in Figure , the differences in the rate of transport of analyzed acids using cellulose triacetate as the polymer matrix can be observed. For other polymer matrix similar dependences are also observed. The highest flux values were obtained for the transfer of oxalic acid then tartaric acid the lowest for lactic acid. Obtained result suggests that selective separation of oxalic,

tartaric and lactic acids by polymer inclusion membranes is possible with an appropriate composition of the membrane. Research shows that polymer inclusion membranes are the separation method with of wide research capabilities.

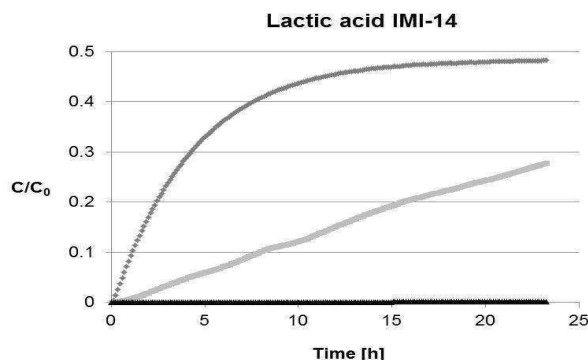


Fig.8. Change of the concentration of lactic acid in the receiving phase during the separation process by PIM. Feeding phase: 0.1 M solution of lactic acid. Receiving phase: deionized water. Polymer matrix: CTA,CAB,CAP. Carrier: IMI-14. Temperature: 25°C.

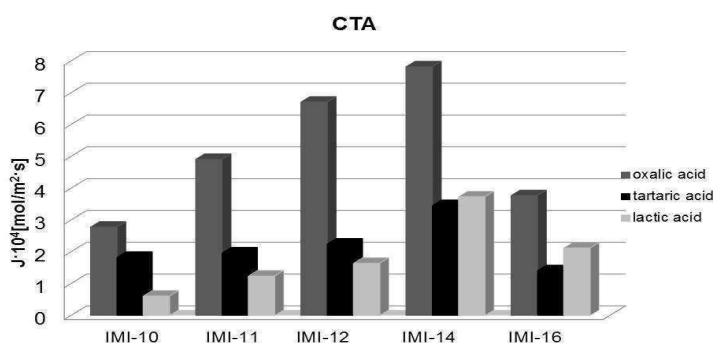


Fig.9. Comparison of the rate of transport of oxalic, tartaric and lactic acid through the PIM. Feeding phase: 0.1 M solution of oxalic, tartaric or lactic acid. Receiving phase: deionized water. Polymer matrix: CTA. Carrier: IMI-n. Temperature: 25°C.

4. Summary

Research has shown that the type of polymer matrix used has a significant influence on the rate of transport of organic acid. Research suggests that with increasing the percentage of the acetyl groups in the composition of the polymer matrix increases the rate of transport of the organic acid. The highest values were obtained for the CTA, respectively CAB and CAP. At the same time on the basis of the study demonstrated that there are differences in the rate of transport of oxalic acid, tartaric acid and lactic acid which is the basis to carry out further studies on the separation of a mixture of organic acids. When using CTA and CAB highest values were obtained for oxalic acid then tartaric acid and successively lactic acid. The membrane of CAP has a significant preference for only tartaric acid. These differences

are caused by the structure of the active compound and the compatibility of carrier with the polymer matrix used. It is believed that with appropriate selection of the matrix it is possible to selectively separate the components of the mixture of organic acids by using the polymer inclusion membrane.

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