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Polymer Inclusion Membranes as an Extraction Device for Isolation of Pharmaceuticals from Water Samples

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Abstract: PIMs (Polymer Inclusion Membranes) are popular in molecular transport in different solutions. Most often they are used in the transport and removal of ionic compounds, for example metal ions or organic ionic compounds. In this work, membranes were used as extraction devices for isolation of pharmaceuticals from water samples. PIMs were composed of CTA (Cellulose Triacetate) as polymeric matrix, 2-NPOE (2-Nitrophenylo Octyl Ether) as plasticizer, and alkyl quaternary ammonium salt (Aliquat 336) was used as the carrier. The influence of the carrier and plasticizer presence on PIM's extraction efficiency was described. This extraction deice was used for isolation of ibuprofen, ascorbic acid and paracetamol form water samples. The best retention percentage on polymer membranes was achieved between 80%-100% for three components membranes. The extraction ability of polymeric membranes was described and confirmed using HSP (Hansen Solubility Parameter) determined for each analyte and membrane components. Determination of these parameters allows describing the interaction between the analytes and membrane and concludes which membrane composition gives the best properties. All qualitative and quantitative analysis was done using HPLC (High Performance Liquid Chromatography).

Key words: PIMs, separation techniques, extraction, HSPs.

1. Introduction

The composition of PIMs (Polymeric Inclusion Membranes) is mainly responsible for their efficiency, both in the ionic transport and extraction processes. The basic component is polymeric matrix. Very often CTA (Cellulose Triacetate) or poly(vinyl)chloride are used as stable matrix for all membrane. In the polymeric material composition the plasticizers are important. In membrane materials most popular plasticizers are organic ethers: 2-NPOE (2-Nitophenyl Octyl Ether) or 2-NPPE (2-Nitrophenyl Pentyl Ether). To achieve or improve the transport properties the carriers are used as another membrane component. The most popular are trihexyltetradecylphosphonium chloride (Cyphos IL101), bis-(2,4,4-trimethylpentyl) phosphinate (Cyphos IL104), tributhyltetradecylphosphonium chloride (Cyphos IL167) and alkyl quaternary ammonium salts, for example methyltrioctylammonium chloride (Aliquat-336) [1-4].

The use of membranes in technology or laboratory research is widely described in the literature [5, 6], but most often they are used for ionic transport or isolation. In this work the extraction properties of PIM are described. The extraction process on membranes material is not based on adsorption and desorption processes, because PIMs are not sorbents, but this extraction was based on the solubility properties of polymeric materials [7]. The solubility properties of different material are widely described in the literature [8-11]. It is very important in polymeric materials, for their composition and properties. Important parameter, which allows describing the solubility and the interaction between two materials (compounds) is HSP (Hansen Solubility Parameter). This parameter is based on cohesive energy, and its components are connected with dispersive, polar and hydrogen bonding interaction. It can be determined and calculated for each compound. Based on this

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component, we can determine the solubility parameter, and the value of the square of differences between solubility parameter determined for two compounds, which gives us information about the force of interaction. When the square of differences is small, the interactions are strong. When the square of differences is high, the interactions are weak. In this work the HSP was used for description of extraction properties of PIMs in relation to pharmaceuticals: ibuprofen, ascorbic acid and paracetamol isolated from water samples. The detailed description of HSP determination is presented in previous papers [8, 12].

In this work PIMs were used in the extraction process of ibuprofen, ascorbic acid and paracetamol from water systems. Membranes consisted of the following components: CTA, 2-NPOE and methyltrioctylammonium chloride (Aliquat 336). In this way, three types of PIMs were created, two of them differed in the mass ratio of the polymeric matrix and the plasticizer, while the third one additionally had a carrier. The degree of retention and the recovery rate were used to determine the effectiveness of the process. HSP was used to describe the interaction between analytes and individual membrane components.

2. Experimental Setup

2.1 Materials

Organic compounds: pure CTA, 2-NPOE > 99%, methyltrioctylammonium chloride (Aliquat 336) > 97%, ibuprofen, ascorbic acid and acetaminophen (paracetamol) > 98% were purchased from Sigma-Aldrich (Germany). Solvents: dichloromethane, acetonitrile and methanol pure for analysis were purchased from POCh (Poland).

2.2 HPLC (High Performance Liquid Chromatography) Analysis

For HPLC qualitative and quantitative analysis liquid chromatograph HP 1100 was used, kolumn: C18 150 × 4.6 mm (Thermo Scientific), UV-DAD detector. Chromatographic condition: isocratic analysis, mobile phase: 80% water with H_3PO_4 (pH = 2), 20% acetonitrile, flow rate 1 mL/min.

2.3 PIM Preparation

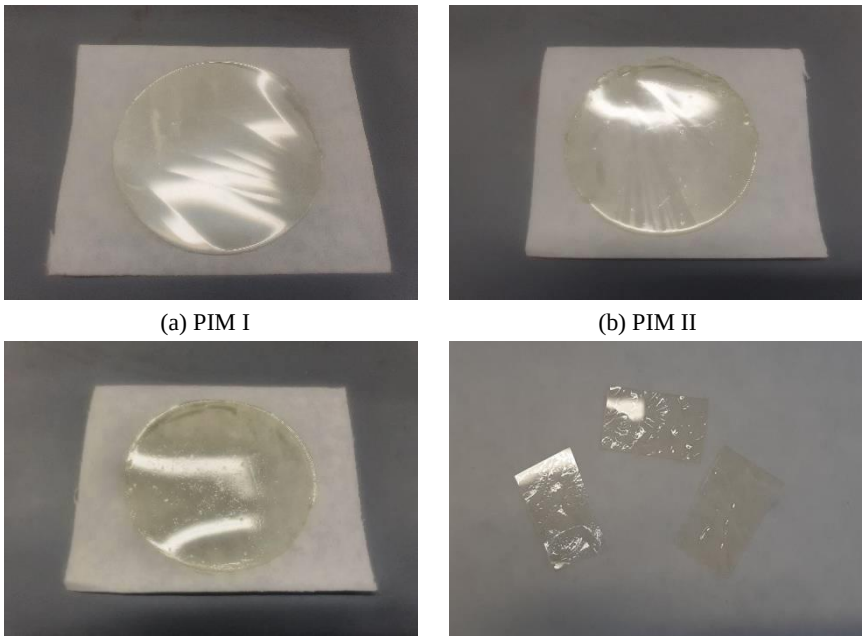
Membrane components were dissolved in the organic solvent (dichloromethane) during 2 h using ultrasonic bath. Then the solution was poured into the Petri glass. Then the solvent evaporated in air for 24 h. Then the formed membrane was dried at temperature 50 ℃ for 24 h. Three kinds of membranes were prepared, with different amount of components. The percentage of each membrane is given in Table 1. Fig. 1 presents membranes before extraction.

2.4 Extraction Procedure

The extraction of three analytes: ibuprofen, acetic acid and paracetamol were carried out in the following way: First the water solutions of analytes were prepared: 0.2 mg/mL separately for each analyte. The volume of extraction water sample was 10 mL. Then the extraction devices (pieces of membrane) were put into the solution for extraction time: 30, 60 and 90 min. After this time extraction devices were drained on the laboratory paper, and then was elution step. During this step extraction devices were put into 3 mL of methanol for 30, 60 and 90 min respectively. After this time 1 mL of each solution (water matrix and methanol) was analysed on HPLC chromatograph.

Table 1 Percentage of membrane components.

membrane	CTA (%)	2-NPOE (%)	Aliquat 336 (%)	Average membrane mass (mg)
PIM I	50	50	0	95.50
PIM II	20	80	0	90.64
PIM III	20	45	35	79.86



(a) PIM I (b) PIM II

(c) PIM III (d) a piece of membrane before extraction process

Fig. 1 Prepared membranes.

Table 2 HSPs and the square of differences determined for analytes, PIM's components and eluent.

Compound	δ ($(J/cm^3)^{1/2}$)	$(\delta - \delta_{CTA})^2$ (J/cm^3)	$(\delta - \delta_{2\text{-NPOE}})^2$ (J/cm^3)	$(\delta - \delta_{Aliquat336})^2$ (J/cm^3)	$(\delta - \delta_{methanol})^2$ (J/cm^3)
CTA	11.72	0.00	6.60	23.33	1.64
2-NPOE	14.29	6.60	0.00	5.11	14.82
Aliquat-336	16.55	23.33	5.11	0.00	37.33
Methanol	10.44	1.64	14.82	37.33	0.00
Ibuprofen	11.29	0.19	9.00	27.67	0.73
Ascorbic acid	18.34	43.82	16.40	3.20	62.41
Paracetamol	12.38	0.48	3.65	17.39	0.0025

2.5 HSP Determination

HSP was determined for each analyte, each membrane's component, for methanol as eluent and for total membrane. These parameters were determined using calculation procedure described by van Knevelen and Te Nijenhuis [11]. The total solubility parameter δ ($(J/cm^3)^{1/2}$) for each compound was calculated from Eq. (1).

$$\delta = \sqrt{\frac{E_{coh}}{V}} \quad (1)$$

where V is molecular volume.

The molecular volume (V (cm^3/mol)) was taken from literature [11] and total cohesive energy was calculated based on literature [10, 11]. The squares of differences of total solubility parameters were determined from Eq. (2).

$$(\delta_A - \delta_B)^2 \quad (2)$$

These values were determined for the following systems: analyte-each membrane's component, analyte-eluent, eluent-each membrane's component and between membrane's components. The total HSPs and the square of differences calculated for each analyte, and each membrane's component and eluent are given in Table 2.

2.6 Extraction Efficiency

The extraction efficiency was described using three parameters:

Retention factor (E (%])):

$$E = \frac{c_0 - c}{c_0} \cdot 100\% \quad (5)$$

where:

c_0: concentration of analyte in water sample before extraction;

c: concentration of analyte in water sample after extraction.

Loss of membrane mass (M (%)):

$$M = \frac{m_p - m_k}{m_p} \cdot 100\% \quad (6)$$

where:

m_p: membrane mass before solvent immersion;

m_k: membrane mass after solvent immersion.

Recovery (R (%)):

$$R = \frac{c_s}{c_0} \cdot 100\%$$

where:

c_s: concentration of analyte in eluat.

3. Results

3.1 Extraction

Results achieved in extraction process on three different membranes are presented in Tables 3-5. We can see that the tested membranes are suitable only for ibuprofen extraction. The retention of ascorbic acid

Table 3 Parameters that describe the extraction process PIM I.

compound	Extraction time (min)	Concentration of analyte in water sample before extraction (mg/mL)	Concentration of analyte in water sample after extraction (mg/mL)	Concentration of analyte in eluent (mg/mL)	Retention factor (%)	Recovery (%)
Ibuprofen	30	0.227	0.090	0.46	60.35	43.69
	60	0.177	0.071	0.08	59.89	18.33
Ascorbic acid	30	0.203	0.161	0.00	20.0	0.00
	60	0.223	0.194	0.00	13.0	0.00
Paracetamol	30	0.230	0.206	0.00	10.4	0.00
	60	0.212	0.300	0.00	0.00	0.00

Table 4 Parameters that describe the extraction process PIM II.

compound	Extraction time (min)	Concentration of analyte in water sample before extraction (mg/mL)	Concentration of analyte in water sample after extraction (mg/mL)	Concentration of analyte in eluent (mg/mL)	Retention factor (%)	Recovery (%)
Ibuprofen	30	0.190	0.076	0.12	60.00	13.15
	60	0.203	0.00	0.26	100.0	30.69
Ascorbic acid	30	0.190	0.154	0.00	18.95	0.00
	60	0.200	0.132	0.00	34.00	0.00
Paracetamol	30	0.207	0,227	0.00	9.50	0.00
	60	0.214	0.224	0.00	4.60	0.00

Table 5 Parameters that describe the extraction process PIM III.

compound	Extraction time (min)	Concentration of analyte in water sample before extraction (mg/mL)	Concentration of analyte in water sample after extraction (mg/mL)	Concentration of analyte in eluent (mg/mL)	Retention factor (%)	Recovery (%)
Ibuprofen	30	0.210	0.036	0.049	82.86	6.76
	60	0.200	0.000	0.205	100.0	24.24
Ascorbic acid	30	0.210	0.180	0.00	0.00	0.00
	60	0.240	0.233	0.00	0.00	0.00
Paracetamol	30	0.218	0.206	0.061	5.60	28.0
	60	0.220	0.216	0.027	1.90	12.5

and paracetamol is very low and strong, these analytes are not eluted from the extraction device. It can be connected with the molecular structure of these analytes. Only ibuprofen has carboxylic group and longer carbon chain in the molecule. So it is connected with the polarisation of the molecule and with resulting polarity of the compound.

In Fig. 2, the adsorption and desorption percentage is presented. It can be seen that adsorption of ibuprofen is near 100% for all membranes, but the desorption percentage is very low. It is connected with strong retention on membranes' material. Only paracetamol is eluted in high percentage from PIM III, but the retention is not high.

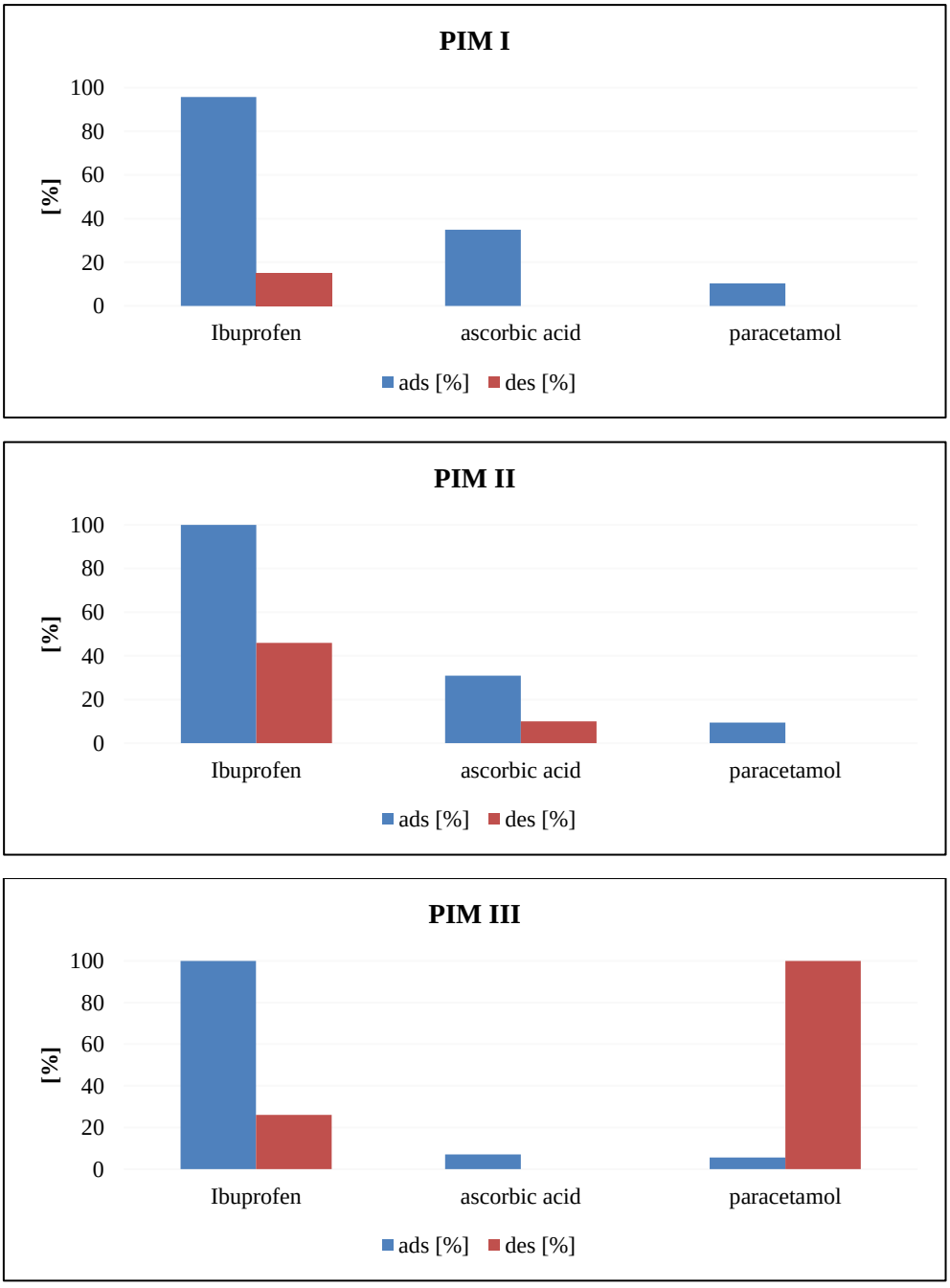


Fig. 2 Adsorption and desorption percentage achieved for ibuprofen, ascorbic acid and paracetamol on three kinds of membranes: PIM I, PIM II, PIM III.

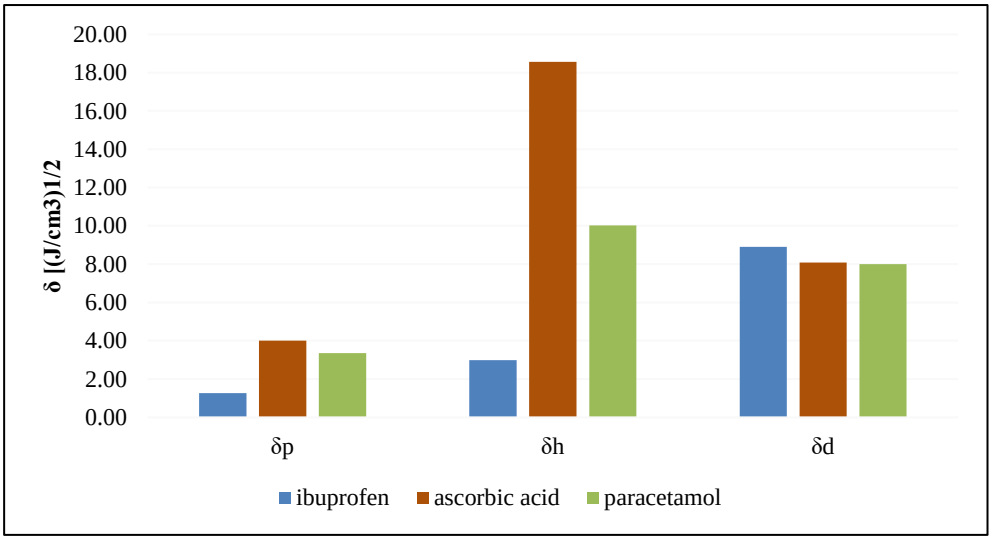


Fig. 3 The values of polar, hydrogen bonding and dispersive components of HSP determined for ibuprofen, ascorbic acid and paracetamol.

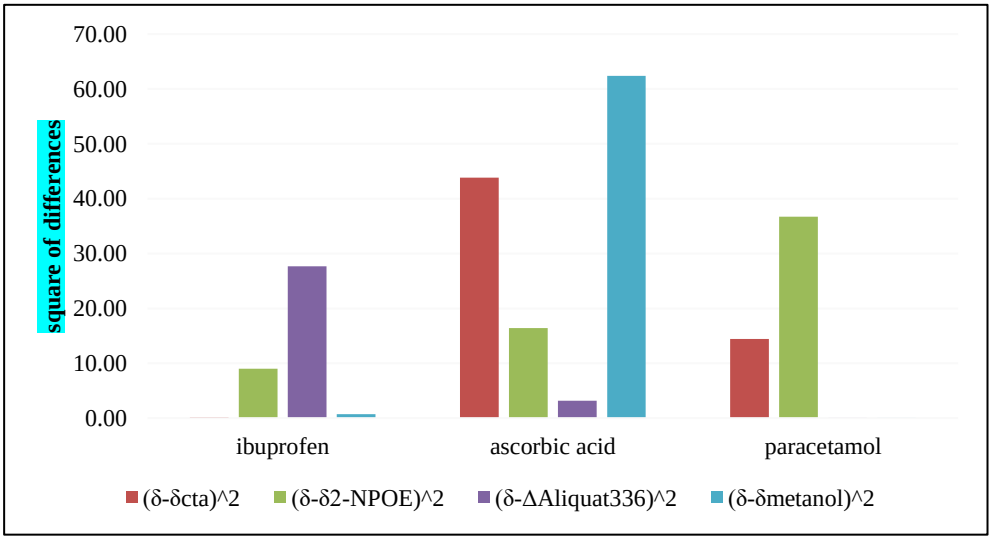


Fig. 4 Interaction between membranes' components, eluent and ibuprofen, ascorbic acid, paracetamol given by squares of differences HSPs.

Presented relationships are confirmed with HSP analysis. In Fig. 3, the value of partial solubility parameters is presented. In can be seen, that the dispersion interaction plays the important role for all analytes. Taking into account polar and hydrogen bonding interaction we can see that highest hydrogen bonding interactions are for ascorbic acid. This is due to the presence of four hydroxyl groups in the molecular structure. The values of polar components of HSP for all analyte are relatively low.

Extraction efficiency of membrane device can be described with square of differences between HSP determined for each component. These values are given in Table 2 and Fig. 4. Interaction between ibuprofen and CTA is very strong, so the retention is high. The interaction between ibuprofen and methanol as eluent is strong too, so it can be eluted from extraction device. For ascorbic acid all interactions are rather weak, so the retention and elution are unsatisfactory and this analyte is not isolated in these extraction systems. For paracetamol the interactions with membrane are strong, and with eluent too. It confirms the high elution percentage of paracetamol.

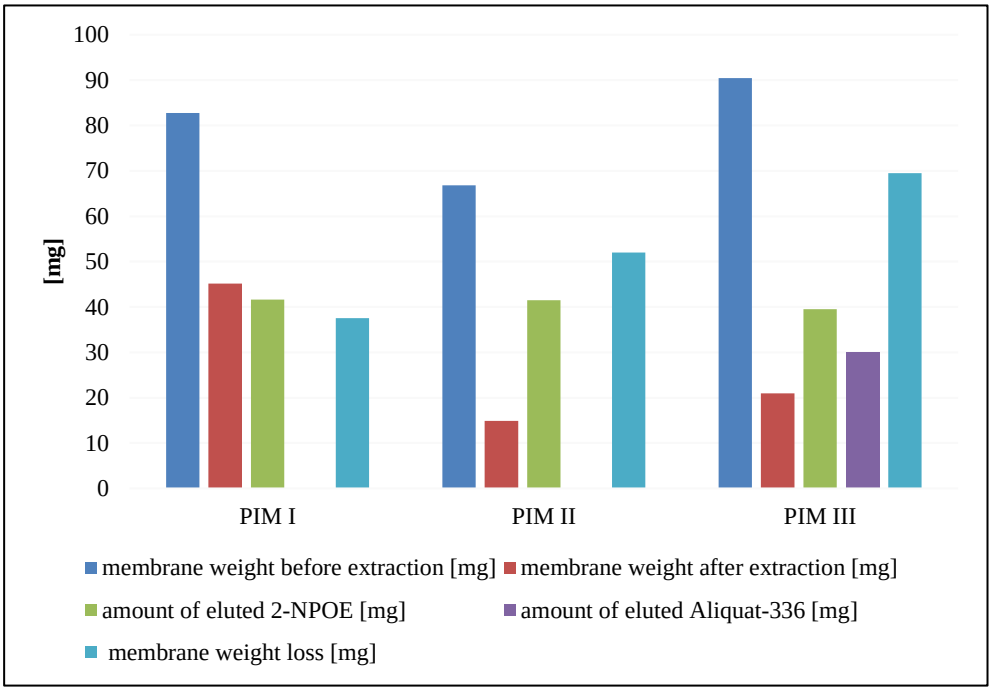


Fig. 5 The elution of membrane components.

Some problem which appears during the extraction process was the solubility of membrane components in methanol. The research has shown that during elution the plasticizer and the carrier are eluted from the membrane device, too. The results are present in Fig. 5. The membrane weight lost is between 45% and 78% for two-component membranes, and near 77% for three-component membrane. It shows that only membrane matrix (CTA) is not eluted with methanol. For PIM I and PIM II the membrane weight lost is the same as amount of 2-NPOE, and for PIM III it is the same as amount of 2-NPOE and Aliquat 336. It proves that methanol is not suitable eluent in this extraction system.

4. Conclusion

Three kinds of PIMs were used for isolation of ibuprofen, ascorbic acid and paracetamol from water samples. These membranes differed in composition, two of them have two components in different percentage of matrix and plasticizer, and one of them has three components: matrix, plasticizer and the carrier. The extraction results were achieved with experiment and additionally it was confirmed by HSPs determination. As we can see, the retention factor determined for all kinds of membranes is satisfactory mainly for ibuprofen (near 100%) but the extraction recovery is not high. It is connected with too strong interaction between analyte and membranes' material. For ibuprofen the strongest interactions are with polymeric matrix. It is given by square of differences of HSP determined for each pair of compounds. For ascorbic acid the stronger interactions are with the carrier and plasticizer. There is the retention of ascorbic acid, but there is no elution. This may be due to not very strong interaction between ascorbic acid and methanol.

For parcetamol, the stronger interactions are with polymeric matrix plasticizer and methanol, so the best desorption of these analytes is achieved.

The main conclusion of the work is that the use of HSPs for determination and detailed description of the interaction between analytes and extraction device components is very suitable. It is very important and useful tool in the planning stage of extraction process. These calculations allow for fast and accurate selection of extraction conditions.

Acknowledgement

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