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ULTRAFILTRATION MEMBRANES MADE OF: POLYANILINE, IONIC LIQUID AND CELLULOSE

MEMBRANY ULTRAFILTRACYJNE UTWORZONE Z:
POLIANILINY, CELULOZY ORAZ CIECZY JONOWEJ

Abstract

The study determined the method of obtaining UF membranes from cellulose, polyaniline and ionic liquid as the gelling agent. The impact of the applied coagulation agent and the conducting polymer (polyaniline) on the transport and separation properties of the obtained membranes was examined.

Keywords: ionic liquids, solvents, ultrafiltration, membrane

Streszczenie

W artykule określono sposób otrzymywania membran ultrafiltracyjnych z surowców: celulozy, polianiliny oraz cieczy jonowej jako substancji żelującej. Zbadano, jaki wpływ na właściwości transportowe i separacyjne otrzymanych membran mają zastosowany koagulant oraz polimer przewodzący (polianilina).

Słowa kluczowe: ciecze jonowe, rozpuszczalniki, ultrafiltracja, membrana

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1. Introduction

The development of environmentally friendly materials, products and processes has clearly been motivated by the growing environmental awareness of the society. The principles of “green chemistry” (i.e. chemistry that aims to optimize the processes in order to reduce the pollution of the environment) and the related hazards to human health clearly indicate the need to substitute the volatile organic solvents with environmentally friendly ones (in line with Principle 5 of the green chemistry) [1]. This requires chemical compounds that will not only be easy to obtain, isolate and purify, but will also provide economic benefits.

The recent years have witnessed a breakthrough in the development of chemical sensors with polyaniline as the main component [2]. These next generation sensors make it possible to assay even complex mixtures of substances in biomaterial, soil, air or sewage. The conducting (due to the addition of polyaniline), environmentally neutral (due to the use of ionic liquid as the solvent) UF membranes may have a significant impact on the separation processes. Such membranes could find application as biosensors in certain production processes, in medicine and in the treatment of specific waste.

2. Ionic liquids

Ionic liquids are liquids composed exclusively of ions, being defined as salts with melting point lower than the boiling point of water (100°C). There are also ionic liquids that melt at temperatures below the room temperature (20°C), called the room temperature ionic liquids [4–7]. The most popular molten salts are dialkylimidazolium salts, due to their attractive physical properties and ease of synthesis. Ionic liquids are usually composed of a large, organic cation and an inorganic or organic anion. Number of possible cation – anion combinations equals to 10^{18} . The liquid state of ionic liquids at room temperature arises from the low lattice energy caused by high asymmetry of the ions making up the liquids [8]. Ionic liquid can be either hydrophilic or hydrophobic. The solubility depends on the anion, the length of alkyl substituents of the cation, and the temperature. Ionic liquids also dissolve alcohols, ethyl acetate, chloroform, acetone, DMF, DMSO, inorganic salts, certain polymers and minerals [8, 9]. The boiling point of ionic liquid is also its breakdown temperature (300°C–400°C). The properties of ionic liquids, such as viscosity, density, melting point and miscibility with other substances change depending on the structure of the cation and the anion. As a result, ionic liquids have been dubbed task-specific solvents [10]. Currently, ionic liquids are widely used in organic chemistry as the environment for a number of industrial-grade chemical reactions [6, 11, 12, 14].

3. Polyaniline

Polyaniline is a conductive organic polymer with semiconductor or metallic conductivity along the chain. Polyaniline comes in several forms, differing by the oxidation state, of which

only emeraldine salt (dark green powder) is conductive. It is one of the most temporally stable conductive polymers. Unfortunately, it is a material that is difficult to process. Among the conductive polymers, polyaniline has the widest potential field of application. It is used in anti-corrosion agents for metals, as an ingredient of varnishes, membranes for gas separation and biosensors [2, 3].

4. Cellulose

Cellulose consists of glucose particles (β -D-glucose) linked by glycosidic bonds (β -1,4 bond). It is insoluble in water and common organic solvents. Select ionic liquids dissolve cellulose very well. The literature contains reports that ionic liquids containing imidazolium cation and anions, such as chloride, octane and formate, are characterized as having exceptionally good dissolving properties. Ionic liquid cation and anion structure and its tenacity has an effect on the process of dissolving cellulose in ionic liquids (compounds of lesser tenacity dissolve larger amounts of polymer). Anion of ionic liquid that dissolves cellulose well should have the capability of creating hydrogen bonds with hydroxyl groups. The role of cation is not entirely defined (e.g. aromatic cations – the highest cellulose solubility).

5. Phase inversion method

The most widely used method of membrane production is phase inversion [15]. The method is based on precipitating the polymer (the membrane) from a homogeneous solution. Phase inversion is found in processes such as solvent evaporation, precipitation through controlled evaporation, thermal precipitation, precipitation from the gaseous phase and immersion precipitation. The key process used by the phase inversion is precipitation by immersion in liquid [16–18].

6. Methodology

Membrane preparation by phase inversion (wet method) required the use of an applicator, a feeler gauge, a glass plate and a cuvette for the coagulator for the gelling process.

The first series of membranes was obtained from a membrane-forming solution containing 10% of cellulose (supplied by Merck), dissolved in ionic liquid (1-ethyl-3-methylimidazolium acetate), supplied by Fluka Riedel-de Hën. The solution was used to pour flat membranes with the following thicknesses: 0.2; 0.25; 0.3; 0.35 and 0.4 mm. Following the conditioning, the obtained membranes were tested by filtering deionized water through the membrane to determine the permeability and the relation of the volumetric water flux to the transmembrane pressure. Next, the membranes were coated with a 0.15 mm polyaniline film. For this

purpose, the secondary membrane with 10% polyaniline solution in ionic liquid (1-ethyl-3-methylimidazolium acetate) was poured on cellulose supports. Unfortunately, during the gelling in water bath, the polyaniline layer would partially separate from the cellulose support, rendering this method of obtaining membranes ineffective.

Therefore, it was decided to prepare membrane-forming solutions composed of cellulose, polyaniline and 1-ethyl-3-methylimidazolium acetate. Four types of solutions were prepared, hereafter referred to as solution 1, 2, 3 and 4, respectively. All solutions were 10% cellulose solutions in ionic liquid and differed in terms of polyaniline content, whereby solution 1 did not contain polyaniline at all. Solution 2 contained 1% polyaniline, solution 3–5%, and solution 4–10%. In order to determine the impact of the coagulator on the properties of the membranes, the membranes were gelled in: methanol, ethanol, 1-propanol, 2-propanol, butanol and deionized water. The composition of membrane-forming solutions, the type of applied coagulator and the symbols of obtained membranes that will be used hereafter, are listed in Table 1.

Table 1

Composition of a film-forming solutions and identification of tested membranes

Solution	1-propanol	metanol	H ₂ O	butanol	2-propanol	pentanol	ethanol
1.10% cellulose	1A	1B	1C	1D	1E	1F	1G
2.10% cellulose + 1% polyaniline	2A	2B	2C	2D	2E	2F	2G
3.10% cellulose + 5% polyaniline	3A	3B	3C	3D	3E	3F	3G
4.10% cellulose + 10% polyaniline	4A	4B	4C	4D	4E	4F	4G

The tests to determine the properties of membranes were conducted with the use of the system illustrated in Fig. 1.

The following parameters were used to assess the transport properties of UF membranes:

- J_v – volumetric water flux, $\frac{\text{m}^3}{\text{m}^2 \cdot \text{s}}$
- L_w – water permeability, $\frac{\text{m}^3}{\text{m}^2 \cdot \text{s} \cdot \text{MPa}}$

The membranes were conditioned with deionized water at room temperature (20°C) in 0.2 MPa and mixing speed of 50 rpm. The filtration was continued until a constant volumetric water flux was achieved. A single membrane was conditioned for 2 to 4 hours.

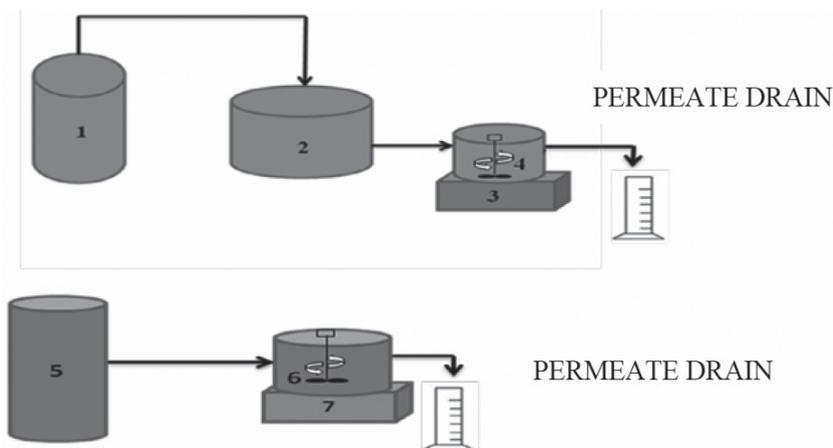


Fig. 1. Measuring position plan: 1, 5 – pressurized gas supply system; 2 – supply tank; 3, 7 – magnetic mixers; 4, 6 – ultrafiltration chambers

The transport properties of membranes were determined by filtering deionized water through the membranes and applying variable transmembrane pressure (ranging from 0.1 to 0.3 MPa) and a constant mixing speed of the filtered medium – 100 rpm. The volume of deionized water filtered over 15 minutes in 2 iterations was assessed. The volumetric water flux was calculated and the relation J_v to the transmembrane pressure was determined.

The separation properties of the membranes were determined by filtering dextran solution with the nominal molecular weight 200,000 Da, through the membranes. The solution mass concentration was 5 g/dm³. The filtration was conducted with transmembrane pressure of 0.2 MPa. 10% of the feed was received, assaying the shares of individual molecular weights of dextran in the permeate and the retentate, using gel permeation chromatography. On the basis of the recorded chromatograms, the dextran content could be quantified in specific molecular weight thresholds, into which the whole feed and permeate stream had been divided. The retention factor for dextran was calculated from the following correlation [9]:

$$R_0 = \frac{1 - c_p}{c_n} \quad (1)$$

$$R_i = \frac{1 - c_{pi}}{c_{ni}} \quad (2)$$

where:

- R_0 – general retention factor,
- c_p, c_n – general dextran concentration in permeate and feed, mol/dm³,
- R_i – retention factor determined for individual molecular weight thresholds,
- c_{pi}, c_{ni} – dextran concentrations in individual molecular weight thresholds in permeate and feed, mol/dm³.

On the basis of the values of the retention factor R_i , determined for the whole range of the tested molecular weights, the curves were drawn, showing the correlation between the retention level of dextran molecules and their molar weight, and thus the cut-off permeability of the tested membranes. The samples of permeate and feed, collected during membrane testing, were analysed in a gel permeation by Schimadzu, equipped with a NUCLEOGELaq-OH50-8 column (Machery-Nagel), RID-6A refractive index detector, (Schimadzu), and C-R4A Chromatopac computing integrator (Schimadzu) for data processing.

7. Results and discussion

The results obtained for the first series of membranes are illustrated in Fig. 2, which clearly shows that, with the increase of the membrane thickness, the volumetric water flux drops across the entire range of applied pressure values.

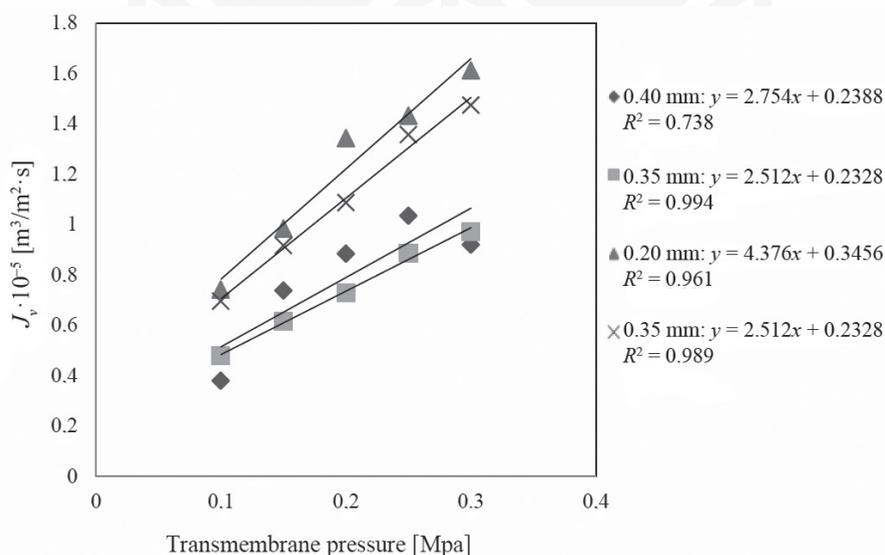


Fig. 2. The dependence of volumetric deionized water flux on pressure for cellulose membranes 0.20–0.40 mm thick

As it can be seen, during the gelling in water bath, the polyaniline layer partially separated from the cellulose support, rendering this method of obtaining membranes ineffective.

Next, the transport and separation properties of the 1A to 4B membranes were assayed. Fig. 3 illustrates the relation of the volumetric water flux to the transmembrane pressure for membranes 1A to 1G.

With the increase of the pressure, the J_v values calculated for all membranes increased as well. The best transport properties were observed in membrane 1D (gelling solution –

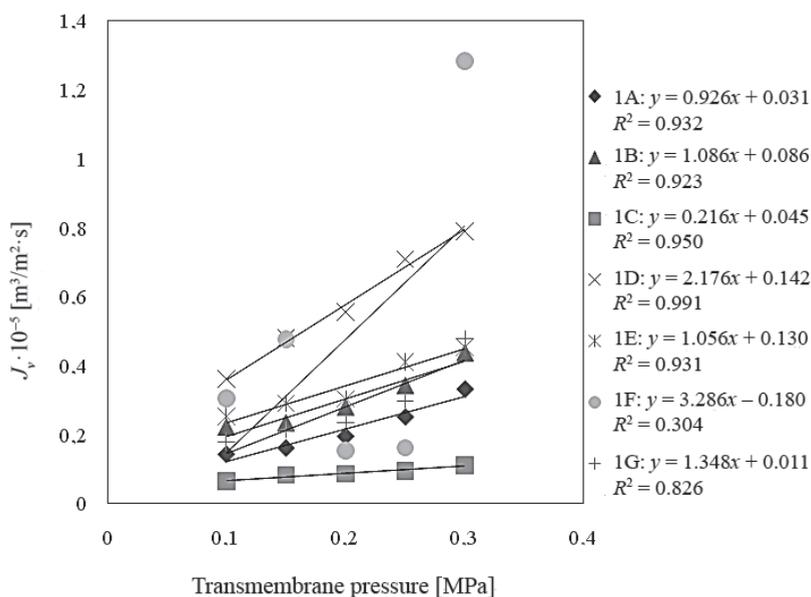


Fig. 3. The dependence of volumetric deionized water flux on pressure for membranes 1A to 1G

butanol) and the poorest in membrane 1C (gelling solution – water). The volumetric water flux ($J_v = 0.087 \cdot 10^{-5} \text{ m}^3/\text{m}^2 \cdot \text{s}$) calculated for membrane 1C was 6 times lower than the J_v value calculated for membrane 1D ($J_v = 0.56 \cdot 10^{-5} \text{ m}^3/\text{m}^2 \cdot \text{s}$ – for 0.2 MPa transmembrane pressure). Also membrane 1A turned out to be dense (gelling solution – 1-propanol) – $J_v = 0.15 \cdot 10^{-5} \text{ m}^3/\text{m}^2 \cdot \text{s}$. The volumetric water flux of other membranes were similar and fell within the range from 0.21 to $0.28 \cdot 10^{-5} \text{ m}^3/\text{m}^2 \cdot \text{s}$.

Diagrams 4a, 7a, 10a and 13a illustrate the correlation between the chromatogram peak height and the molecular weight, while diagrams 4b, 7b, 10b and 13b illustrate the cumulative share of molecules in the analysed samples. Figs. 5, 8, 11 and 14 show the cut-off curves, which illustrate the correlation between the dextran retention level and the molecular weight.

Among the membranes obtained from pure cellulose, the best separation properties were observed for membrane 1C (gelled in deionized water). The cut-off molecular weight for that membrane is 9 kDa. Slightly poorer properties were observed in membranes 1B (gelled in methanol) and 1A (gelled in 1-propanol). The cut-off molecular weights for those membranes are: 50 kDa and 80 kDa, respectively. Membrane 1E (gelled in 2-propanol) and 1F (gelled in pentanol) retained only 60% of molecules with 80 kDa molecular weight, while membrane 1D (gelled in butanol) retained only 30% of those molecules.

Fig. 6 illustrates the relation of the volumetric water flux (J_v) to the transmembrane pressure for membranes 2A to 2G. With the pressure rise, the volumetric water flux (J_v) would increase for all membranes. The best transport properties were observed in membrane 2D (gelling solution – butanol) and the poorest in membrane 2G (gelling solution – ethanol). The volumetric water flux ($J_v = 0.668 \cdot 10^{-5} \text{ m}^3/\text{m}^2 \cdot \text{s}$) calculated for membrane 2D was 3.5 times lower than the J_v

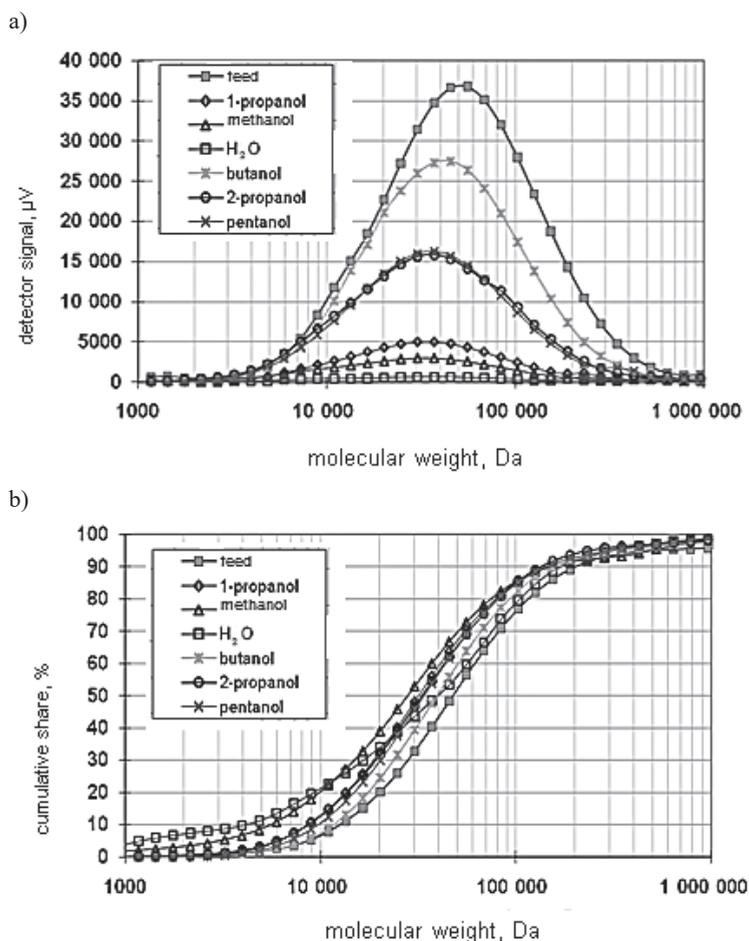


Fig. 4. Dextran molecular weight distribution curves in the feed and the permeates originating from the tests of membranes 1A to 1G (pure cellulose, gelled in various non solvents b) cumulative share of dextran molecules with the given weight

value calculated for membrane 2G (gelling solution – ethanol; $J_v = 0.187 \cdot 10^{-5} \text{ m}^3/\text{m}^2\text{s}$ – for 0.2 MPa transmembrane pressure). Transport properties similar to membrane 2G were also observed in membrane 2E (gelling solution – 2-propanol). For the transmembrane pressure $p = 0.2 \text{ MPa}$, the calculated J_v was $0.195 \cdot 10^{-5} \text{ m}^3/\text{m}^2\text{s}$. The volumetric water flux calculated for other membranes were similar and fell within the range from $0.36 \cdot 10^{-5} \text{ m}^3/\text{m}^2\text{s}$ to $0.48 \cdot 10^{-5} \text{ m}^3/\text{m}^2\text{s}$.

Analysis of Figs. 7 and 8 indicates that among the membranes obtained from the membrane-forming solution, containing 10% of cellulose and 1% of polyaniline, the best separation properties are observed for membrane 2A (gelled in 1-propanol). The cut-off molecular weight for that membrane is 11 kDa. Membranes 2D (gelled in butanol) and 2E (gelled in 2-propanol) retained 75% of molecules with 11,000 Da molecular weight;

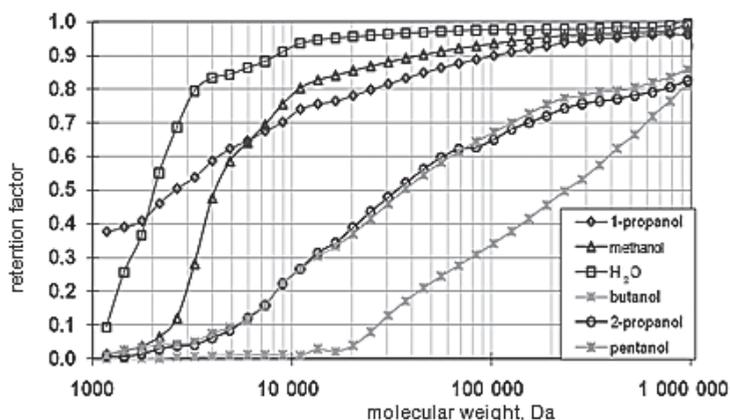


Fig. 5. Relationship between the retention factor and dextran molecular weight, as determined for membranes 1A-1G

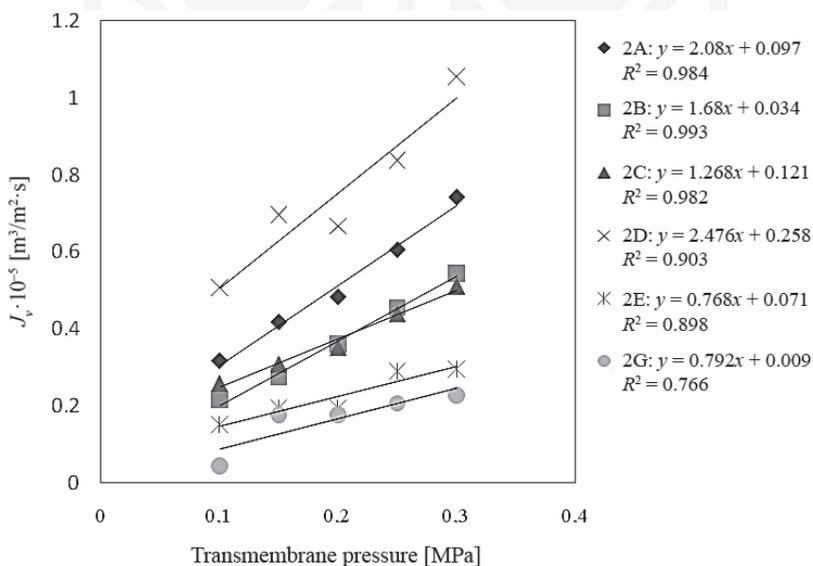


Fig. 6. The dependence of volumetric deionized water flux on pressure for membranes 2A to 2E, 2G

membrane 2G (gelled in ethanol) retained 62% of those molecules, while membrane 2C (gelled in deionized water) retained only 15% of the molecules.

Fig. 9 illustrates the relation of the volumetric water flux (J_v) to the transmembrane pressure for membranes 3B to 3G. With the transmembrane pressure increase, the volumetric water flux (J_v), calculated for all tested membranes, would increase. The best transport properties were observed in membrane 3F (gelling solution – pentanol) and the poorest in membrane 3C (gelling solution – water). The volumetric water flux ($J_v = 0.182 \cdot 10^{-5} \text{ m}^3/\text{m}^2 \cdot \text{s}$) calculated

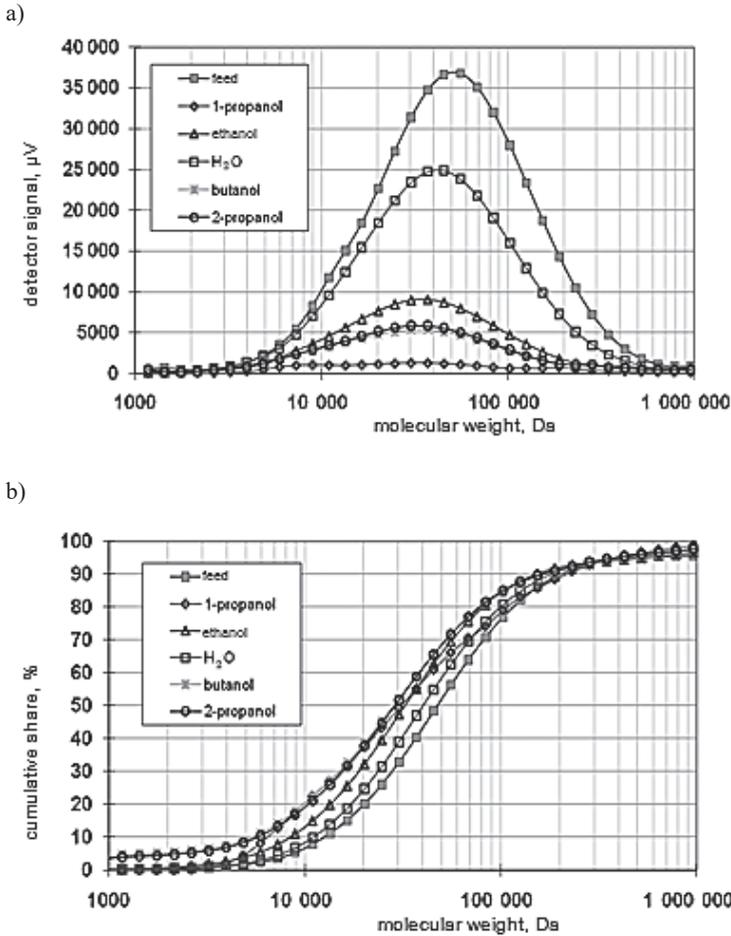


Fig. 7. Dextran molecular weight distribution curves in the feed and the permeate, obtained from the tests of membranes 2A to 2E, 2G: a) correlation of the chromatogram height and dextran molecular weight, b) correlation between the cumulative share of dextran molecules and their molecular weight

for membrane 3C was 4 times lower than the J_v value calculated for membrane 3F ($J_v = 0.795 \cdot 10^{-5} \text{ m}^3/\text{m}^2\text{s}$ (characteristic values for 0.2 MPa transmembrane pressure)). Transport properties similar to membrane 3C were also observed in membrane 3G (gelling solution – ethanol). For the transmembrane pressure $p = 0.2 \text{ MPa}$, the calculated J_v was $0.186 \cdot 10^{-5} \text{ m}^3/\text{m}^2\text{s}$. The volumetric water flux calculated for other membranes were similar and fell within the range from $0.597 \cdot 10^{-5} \text{ m}^3/\text{m}^2\text{s}$ to $0.612 \cdot 10^{-5} \text{ m}^3/\text{m}^2\text{s}$.

It has been observed that, among the membranes obtained from the membrane-forming solution, containing 10% of cellulose and 5% of polyaniline, the best separation properties are observed for membrane 3G (gelled in ethanol). The cut-off molecular weight for that membrane is 10 kDa. Membrane 3C (gelled in water) retained 85% of molecules with 10 kDa

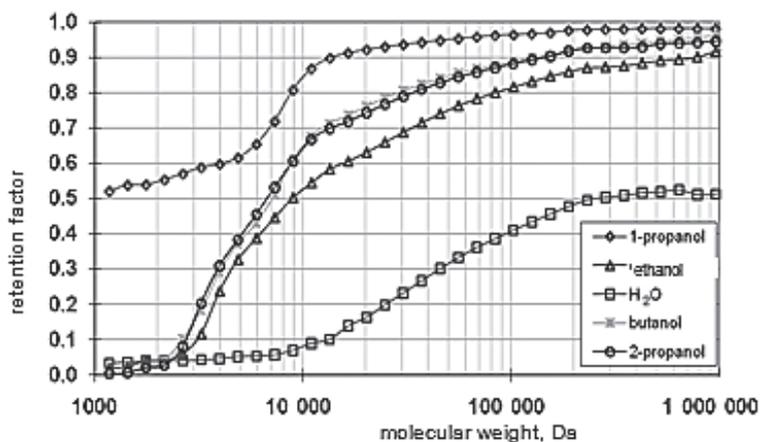


Fig. 8. Relation between the retention factor and dextran molecular weight, as determined for membranes 2A-2E, 2G

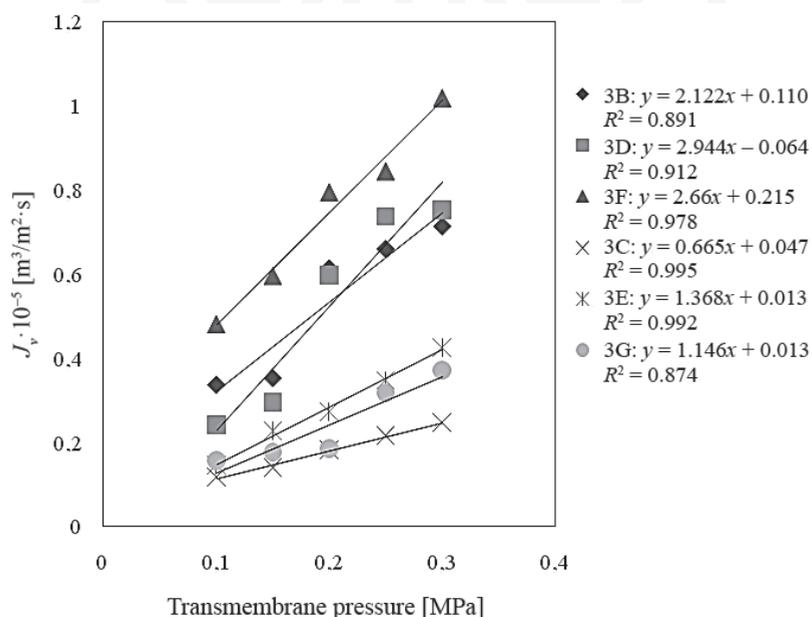


Fig. 9. The dependence of volumetric deionized water flux on pressure for membranes 3B to 3G

molecular weight; membrane 3E (gelled in 2-propanol) retained 30% of those molecules, while membrane 3F (gelled in pentanol) retained only 10% of the molecules. Thus, in this series of membranes, the best separation properties were observed in membrane 3G, while the poorest in membrane 3F.

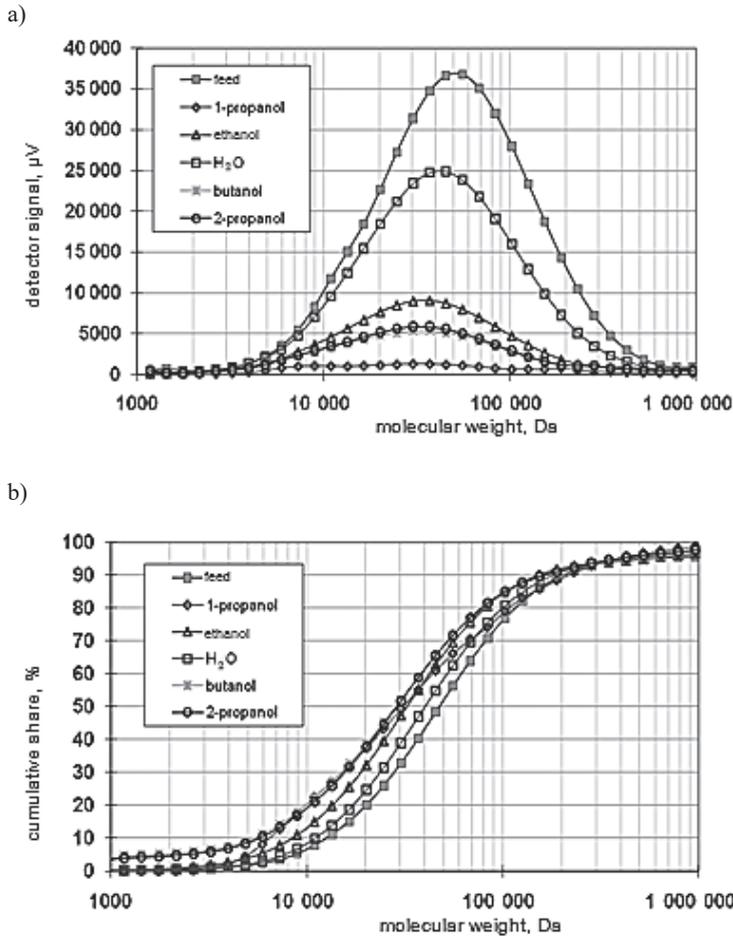


Fig. 10. Dextran molecular weight distribution curves in the feed and the permeate, obtained from the tests of membranes 3B-3G: a) correlation of the chromatogram height and dextran molecular weight, b) correlation between the cumulative share of dextran molecules and their molecular weight

Fig. 12 illustrates the relation of the volumetric water flux (J_v) to the transmembrane pressure for membranes 4A to 4G (cellulose membranes with 10% addition of polyaniline, gelled in various solvents). Similarly to previous cases, the volumetric water flux (J_v) would increase with the pressure increase. The best transport properties were observed in membrane 4D (gelling solution – butanol) and the poorest in membrane 4A (gelling solution – 1-propanol). The volumetric water flux ($J_v = 0.463 \cdot 10^{-5} \text{ m}^3/\text{m}^2 \cdot \text{s}$) calculated for membrane 4C was 3 times lower than the J_v value calculated for membrane 4A ($J_v = 0.161 \cdot 10^{-5} \text{ m}^3/\text{m}^2 \cdot \text{s}$) (characteristic values for 0.2 MPa transmembrane pressure). Transport properties similar to membrane 4A were observed for membranes 4B, 4E, 4F and 4G. The volumetric water flux

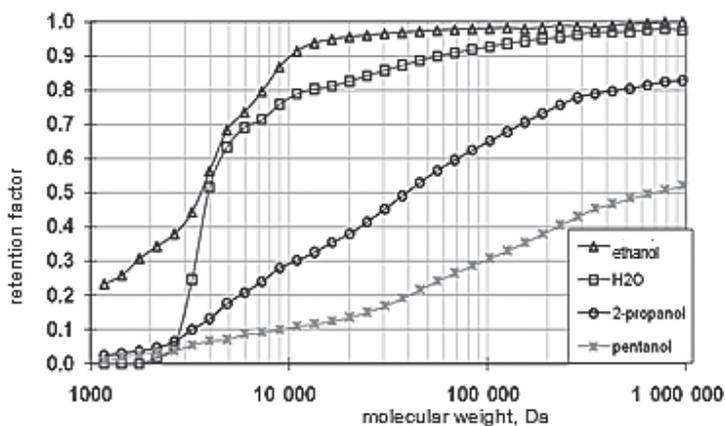


Fig. 11. Relation between the retention factor and dextran molecular weight, as determined for membranes 3B-3G

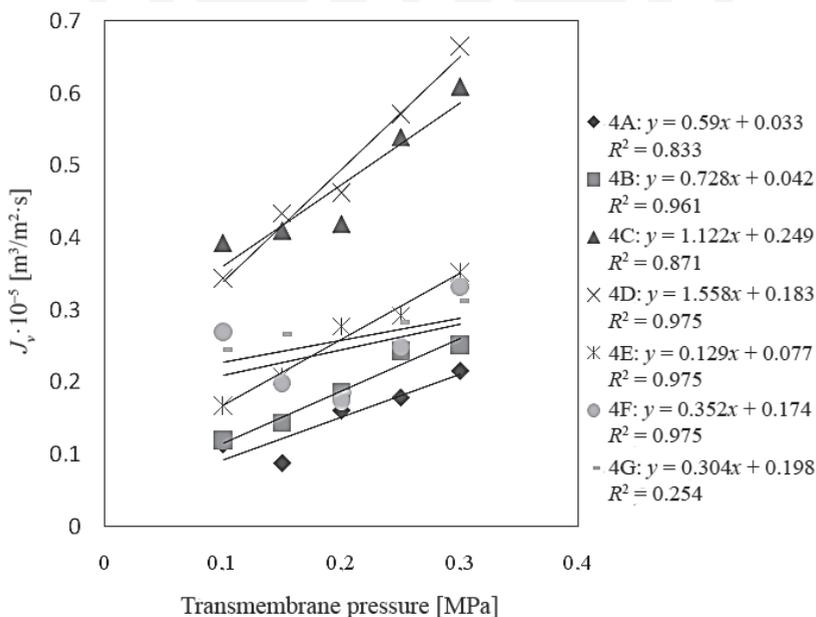
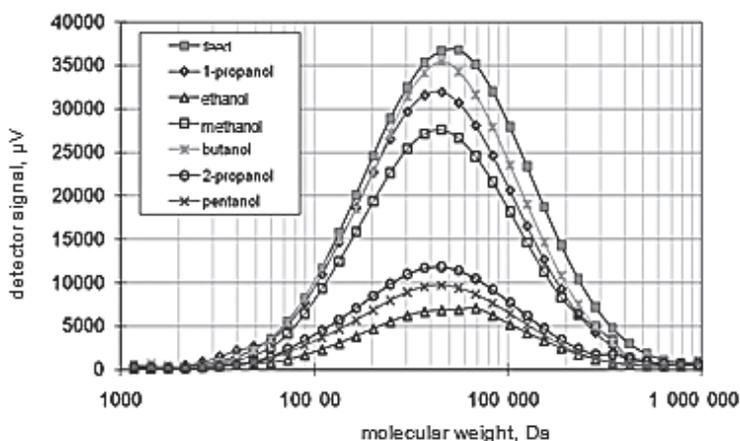


Fig. 12. The dependence of volumetric deionized water flux on pressure for membranes 4A to 4G

calculated for those membranes for $p = 0.2$ MPa) fell within the range from $0.174 \cdot 10^{-5} \text{ m}^3/\text{m}^2\text{s}$ to $0.261 \cdot 10^{-5} \text{ m}^3/\text{m}^2\text{s}$. Only for membrane 4C (gelling solution – water) the observed transport properties were similar to the most open membrane, i.e. 4D. The J_v calculated for that membrane (for $p = 0.2$ MPa) was $0.419 \cdot 10^{-5} \text{ m}^3/\text{m}^2\text{s}$.

a)



b)

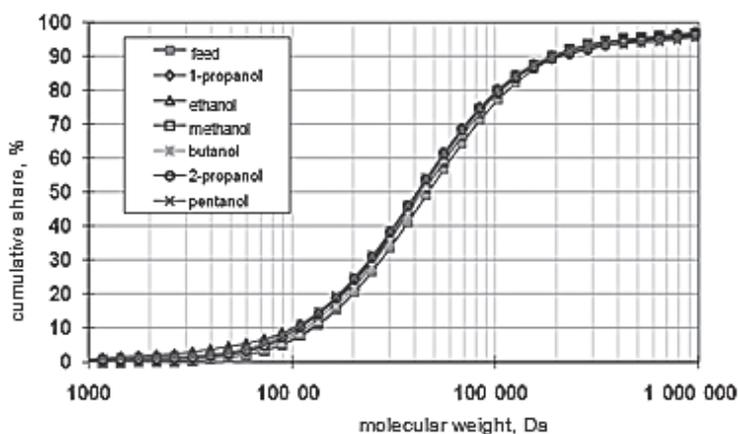


Fig. 13. Dextran molecular weight distribution curves in the feed and the permeate, obtained from the tests of membranes 4A-4G: a) correlation of the chromatogram height and dextran molecular weight, b) correlation between the cumulative share of dextran molecules and their molecular weight

Analysis of chromatograms obtained for this series of membranes (Figs. 13 and 14) indicates that, among the membranes obtained from the membrane-forming solution, containing 10% of cellulose and 10% of polyaniline, the best separation properties are observed for membrane 4G (gelled in ethanol). The membrane retained 80% of molecules with 10 kDa molecular weight. Membranes 4F (gelled in pentanol) and 4E (gelled in 2-propanol) retained 60% and 55% of those molecules, respectively. Membrane 4B (gelled in methanol) retained only 15% of the molecules. The poorest separation properties were observed in membranes

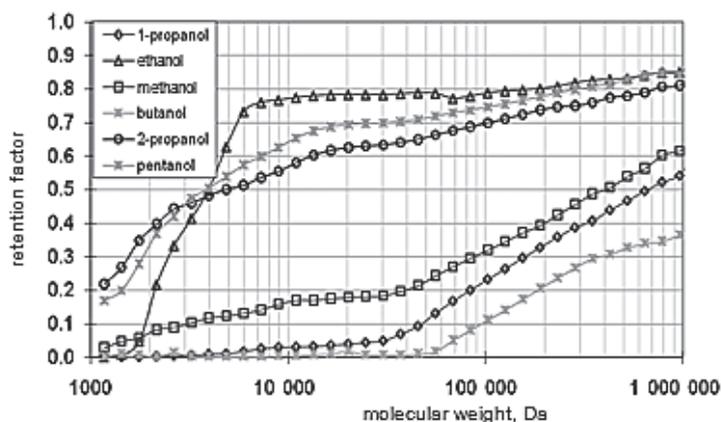


Fig. 14. Relation between the retention factor and dextran molecular weight, as determined for membranes 4A-4G

4A (gelled in 1-propanol) and 4D (gelled in butanol). Those membranes retained only several dozen percent of molecules with 10 kDa molecular weight.

8. Conclusions

The phase inversion method makes it possible to obtain UF membranes from membrane-forming solutions containing cellulose and polyaniline dissolved in ionic liquid and this process cannot be found innovative. It is difficult to clearly determine the impact of the type of gelling liquid on the transport and separation properties of the obtained membranes. Given the uniqueness of the subject, this correlation merits further research, with a reiteration of the performed cycle and expansion of the list of applied coagulants.

The highest retention level of dextran molecules was observed in the following membranes: 1C (membrane obtained from 10% solution of cellulose in ionic liquid), membrane 3G (obtained from 10% solution of cellulose in ionic liquid, with a 5% addition of polyaniline), and membrane 2A (obtained from 10% solution of cellulose in ionic liquid, with a 1% addition of polyaniline). The cut-off molecular weights of those membranes, determined for dextran with the nominal molecular weight of 200,000, were: 9 kDa, 10 kDa and 11 kDa, respectively.

The assessment of the transport properties of the membranes indicates that the water stream volume indeed depends on the transmembrane pressure. The conducted study indicated that the most “open” of the tested membranes is membrane 3F (5% addition of PANI, gelled in pentanol). Similar transport properties were observed for the following membranes: 2D (1% addition of PANI, gelled in butanol) and 3D (5% addition of PANI, gelled in butanol).

The densest membranes include: 1C (membrane without polyaniline addition, gelled in water), 1F (pure cellulose, gelled in pentanol) and 4F (10% addition of PANI, gelled in pentanol). The exact impact of polyaniline addition on the transport properties of membranes cannot be unequivocally determined. For some membranes, polyaniline increases the J_v (e.g. 3F, 2A, 2C, 3B), but for others, it has an opposite effect (e.g. 2E, 2G, 4A, 3G). In addition, it is difficult to establish some kind of relation between the type of the gelling agent and the transport properties of the obtained membranes. During the study, it turned out that the strength properties of membranes 2F (1% addition of PANI, gelled in pentanol) and 3A (5% addition of PANI, gelled in 1-propanol) were insufficient. With higher transmembrane pressure – 0.25 MPa, the membranes would burst.

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