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Polyelectrolyte Complex Membranes – Surface and Permeability Properties

J. Lukáš[a], H.-H. Schwarz[b], K. Richau[b]*

[a]Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Heyrovského nám. 2, CZ-162 06 Praha 6, Czech Republic
[b]GKSS Forschungszentrum Geesthacht, GmbH., Institut für Chemie, Kantstrasse 55, D-14513 Teltow, Germany

Summary: In order to study, how the membrane hydrophilicity influences the pervaporation (PV) separation properties in dehydration of alcohols, two polyelectrolyte complex (PELC) membranes, based on interfacial reaction of polyanionic sodium salt of sulfoethyl cellulose (SEC) with polycationic poly[dimethyl(diallyl)ammonium chloride] (pDMDAAC), or cationic surfactant benzyl(dodecyl)dimethylammonium chloride (BDDDMAC), were prepared and tested. Contact angle measurements on membrane surfaces made in various media showed that the membrane hydrophilicity, in the sense of water wettability, had not influence neither to flux nor selectivity in the PV dehydration process. On the contrary, the membrane wettability determined by contact angle measurements in the real water/alcohol separation mixture, correlated very well with the PV experiments. These findings are confronted with the solution-diffusion PV model.

1. Introduction

In the last decade pervaporation became a very useful energy-saving and cost-effective technique for separation of industrial azeotropic, close-boiling, or aqueous organic mixtures. In particular, a big effort has been turned out in development of effective membranes for separation of water from azeotropic mixtures with alcohols, where the conventional processes fail. For this purpose, various types of membranes have been proposed [1-5] and characterized. One of the most prospective ways to prepare highly permeative and highly selective membranes for dehydration of organics by PV is using of polyelectrolyte complexes. The separation effect of PELC membranes is very often explained due to enhanced hydrophilicity of separating layer, which favours the uptake of water and hinders the uptake of more hydrophobic organic components in the feed. The high hydrophilicity of membranes is usually determined by membrane swelling experiments in water and the mechanism of selective permeation of water is commonly described by solution-diffusion model based on two steps, selective sorption and selective diffusion [6,7].

Previously, we investigated an interfacial reaction of sodium cellulose sulfate (Na-CS) and pDMDAAC solutions, forming the PELC membranes, which were found to be strongly

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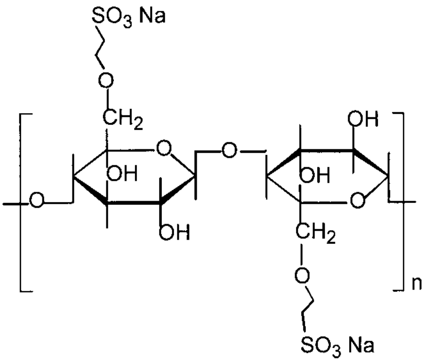
hydrophilic [8] and convenient for PV processes, enabling dehydration of alcohol/water mixtures with high selectivity [9]. On the other hand, membranes prepared from Na-CS and cationic surfactants, possessed high permeabilities for methanol [10,11].

Using the same way of interfacial reaction, new membranes from the cellulose derivative polyanion, sodium salt of SEC, with pDMDAAC polycation or with cationic surfactant BDDDMAC were prepared and studied. The aim of this work was to ascertain if and how the membrane hydrophilicity influences dehydration of organic mixtures in pervaporation process. Our investigation of these membranes should also evaluate, how the particular cationic components, pDMDAAC or BDDDMAC, influence the membrane surface wettability and separation properties. For this purpose, instead of swelling experiments, we used the contact angle measurements on membrane surfaces in various media (water, alcohols and water/propan-2-ol mixtures) and confronted the obtained results with the PV characteristics of these membranes.

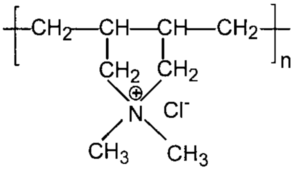
2. Experimental Part

2.1 Materials

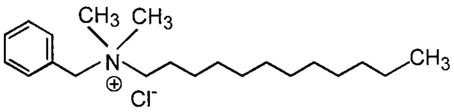
Structures of the used components



Sodium salt of sulfoethyl cellulose



Poly[dimethyl(diallyl)ammonium chloride]



Benzyl(dodecyl)dimethylammonium chloride

Sodium salt of SEC of molecular weight in the range $160{,}000 < M_w < 240{,}000$ with the degree of substitution (DS) 0.4 was purchased from Wolff-Walsrode AG (Germany). The polyanionic pDMDAAC was prepared by cyclopolymerization of dimethyl(diallyl)ammonium chloride [12] and BDDDMAC is a commercial surfactant obtained from Fluka. Methanol, ethanol, propan-1-ol and propan-2-ol (all from Merck) were used as purchased.

2.2 Membrane preparation

The membranes were prepared by reaction at the interface of two layers, one of them was polyanionic and the other one either polycationic or cationic. An aqueous solution of SEC (2 wt%) was cast on the glass plate in 0.2 mm thickness. Subsequently, a layer of aqueous counter-ion solution (pDMDAAC or BDDDMAC, in concentration of 5 wt% or 20 wt% resp.) was distributed on the film. After a reaction time of 15 minutes, the glass plate was dipped into the water bath, where the membrane morphology was formed, the unreacted components were washed out, and finally the membrane separated from the glass plate, rinsed and dried. For the practical use of these membranes in pervaporation process, a polyacrylonitrile ultrafiltration membrane from GKSS (Germany) as a supporting material was used.

2.3 Pervaporation experiments

Water/propan-2-ol mixture was used for membrane testing in the stainless steel cell type P 28 (CELFA AG, Switzerland). Experiments were performed at 50°C, permeate room pressure below 5 mbar and the feed velocity 40 L/h. The fluxes, feed and permeate concentrations of water and propan-2-ol, as well as separation factors were determined.

2.4 Contact angle measurements

Dynamic contact angles were measured using Wilhelmy-plate method by means of the Krüss K12 instrument (Germany). For this purpose the thin membrane samples were adhered on the surface of microscopical cover glasses. Measurements were carried out in various media (water, methanol, ethanol, propan-1-ol, propan-2-ol) at the plate speed 1 mm/min. The presented results are the mean values of at least two measurements.

3. Results

Two contact angles are obtained by the dynamic contact angle measurements, advancing and receding. An advancing contact angle shows the wettability of the sample in medium used by measurement, while a receding angle gives information about the roughness, morphology and other special behaviour of the sample surface. The contact angle hysteresis, expressed as a difference between advancing and receding contact angles, shows the deviation of real sample surface from an ideal solid rigid surface, which was the basic Young equation derived for. In our study, we have focused our attention particularly in advancing contact angles.

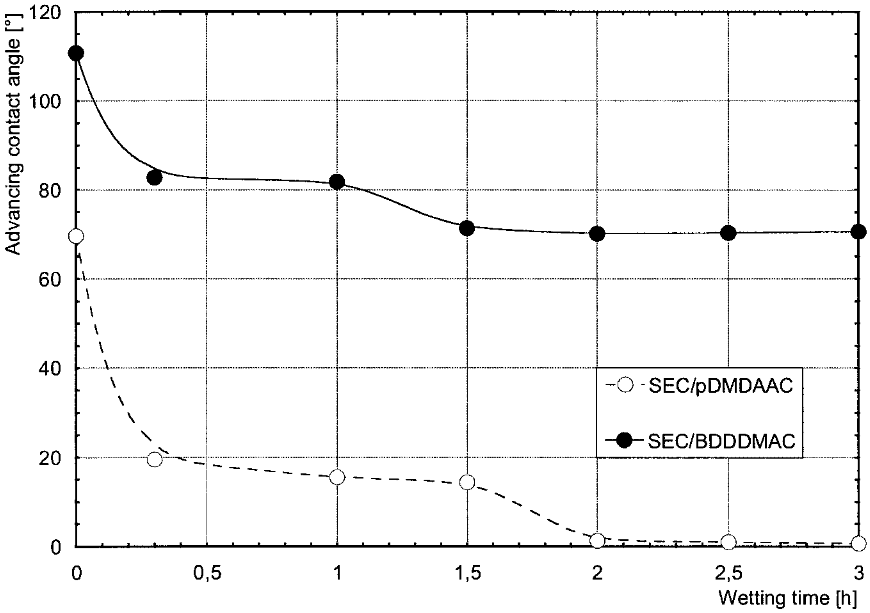


Fig. 1. Advancing contact angles measured in water as a function of wetting time of both membrane types.

Results in Figure 1 show advancing contact angles measured in water at various wetting periods. The considerably higher contact angle values at the zero time reflect the first contact of dry membranes with water. After about 2 hours of sample immersion the wetting equilibrium on both membranes was obtained. Here should be mentioned that the wetting equilibrium in all alcohols was obtained practically immediately with both membranes. Considerably higher advancing contact angles in water obtained on the membrane (SEC/BDDDMAC) give evidence about higher hydrophobicity of this membrane. The wettability of membranes in different media (Fig. 2) show that there is practically no difference between wetting ability of both membrane types in methanol, ethanol and propan-2-ol. On the other hand, in the case of propan-1-ol and mainly of water, the wettability of membrane with polycationic pDMDAAC component is substantially higher than that of membrane with cationic surfactant BDDDMAC. The wettability of both membranes in different water/propan-2-ol concentrations was found to be very close (Fig. 3). With increasing water concentration from 5 to 20 wt% the membrane wettability slowly increases, whereas in higher water content in mixture the stability of SEC/BDDDMAC membrane is getting fail.

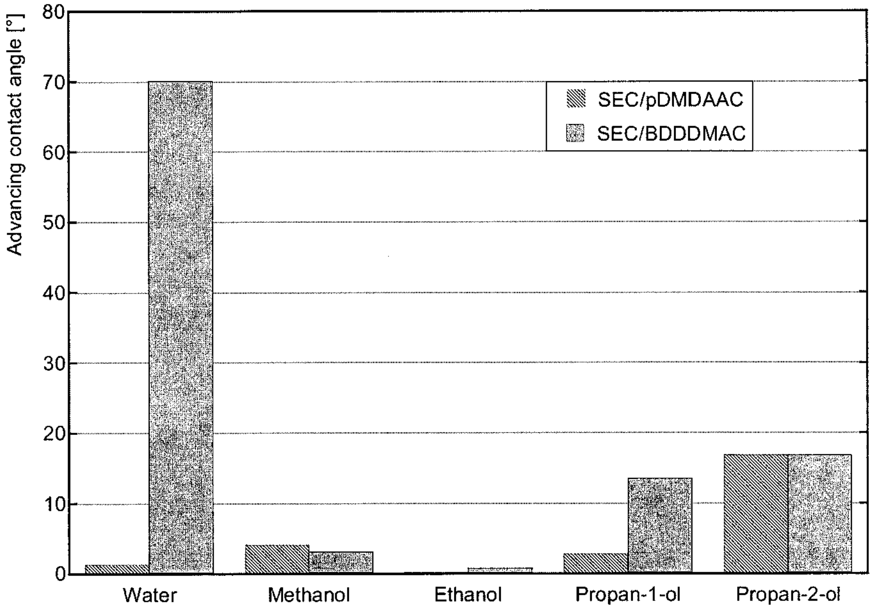


Fig. 2. Advancing contact angles measured in water, methanol, ethanol, propan-1-ol and propan-2-ol on both membrane types after 2 hours of wetting.

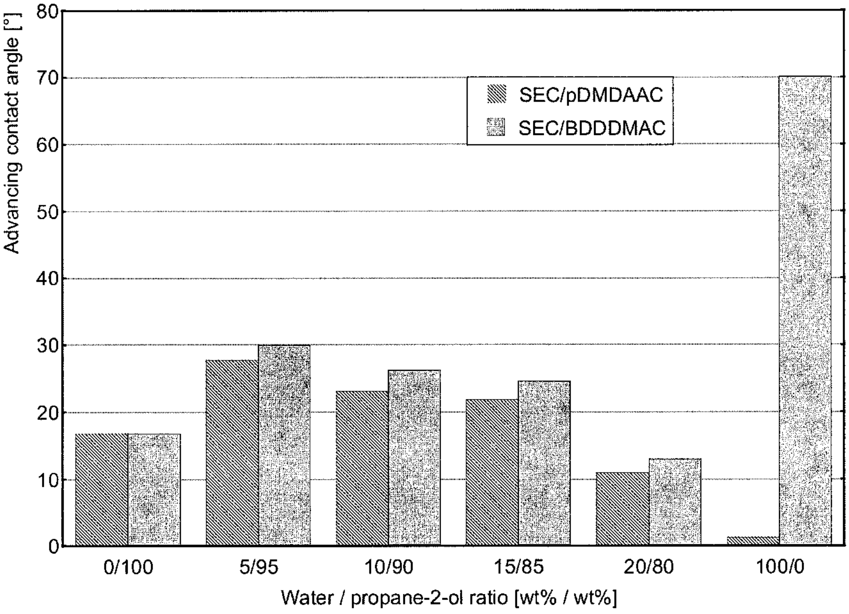


Fig. 3. Advancing contact angles measured in propan-2-ol, water/propan-2-ol mixtures and in water on both membrane types (wetting time: 2 hours).

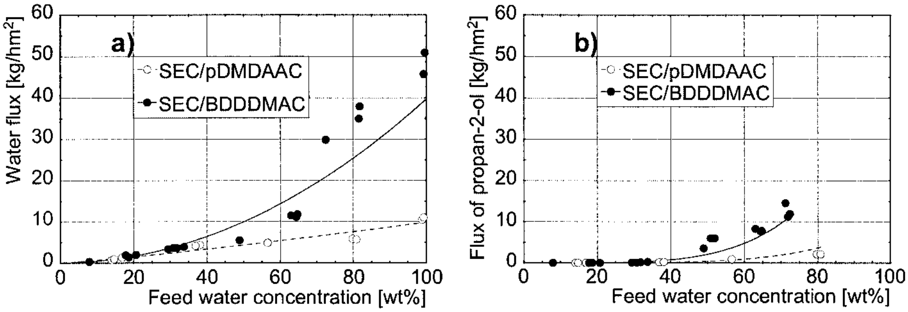


Fig. 4. Fluxes of a) water and b) propan-2-ol vs. feed concentration of water/propan-2-ol mixture, determined for both membrane types.

The pervaporation experiments carried out through the whole concentration range of water/propan-2-ol feed mixtures show that the water permeability is on both membrane types higher than permeability of propan-2-ol, but at different levels (Figs. 4). In higher water concentrations the SEC/BDDDMAC membrane possesses evidently higher fluxes for both water and propan-2-ol. Figure 5 shows the different courses of curves expressing the water separation selectivity depending on the water concentration in water/propan-2-ol feed mixtures for both membrane types. It is obvious that nearly till 40 wt% of water in the feed mixture both membranes have practically the same separation selectivity. In higher water concentrations the separation efficiency of the SEC/BDDDMAC membrane falls quickly down, whereas the SEC/pDMDAAC membrane selectivity is reasonable till about 60 wt% of water in the feed.

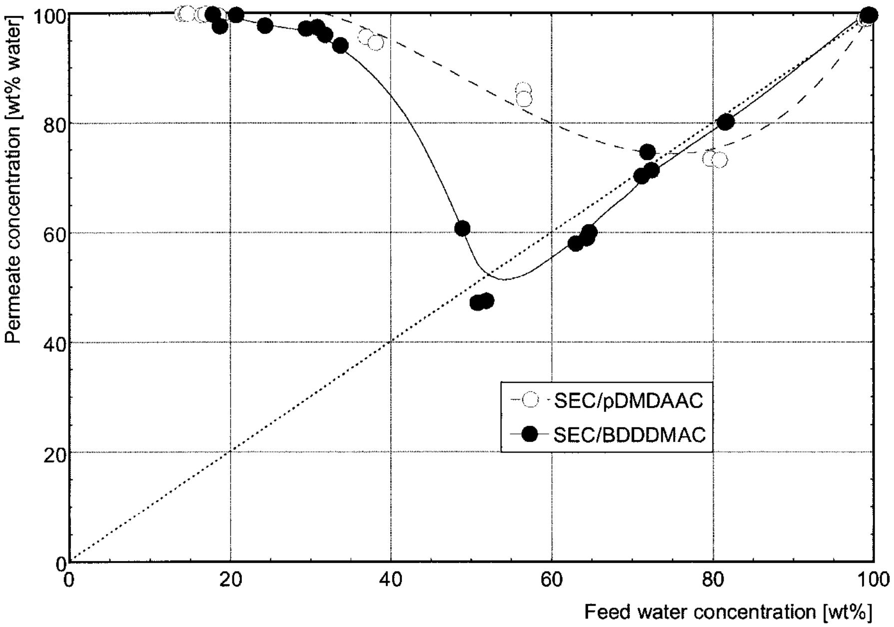


Fig. 5. Water concentration in permeate *vs* feed concentration of water/propan-2-ol mixture, determined for both membrane types.

4. Discussion

The results of contact angle measurements in water (Fig. 1) unambiguously show that the PELC SEC/pDMDAAC membrane, having an extremely high wettability in water, must be strong hydrophilic. On the contrary, the SEC/BDDDMAC membrane reveals rather a low hydrophilic behaviour. From these results can be deduced that the contribution of polycationic pDMDAAC counter-ion component to the membrane constitution should be much more hydrophilic than that of the cationic BDDDMAC. In accord with the solution-diffusion PV model we could expect much better water sorption effect on the SEC/pDMDAAC membrane. However, if we look at the contact angle values measured in alcohols and water/propane-2-ol mixtures (Figs. 2, 3), the interactions of both membranes with these media are quite different comparing with water. Regardless of much higher hydrophilicity of SEC/pDMDAAC membrane determined due to measurement in water, the both membrane behave in alcohols and water/propane-2-ol mixtures similarly. Except propan-1-ol the contact angles obtained on both membranes are very close and reveal a very good wettability. The question is, if we can in this case still speak about membrane hydrophilicity, or only about good wettability in alcohol and water/propane-2-ol mixtures. The last term seems to be more exact.

The very specific feature of water is its very high surface tension (72 mN/m), which is caused due to very strong hydrogen bindings between water molecules. This is also the reason of extremely high boiling point of water with regards to its small molecule size. On the contrary, surface tension values of alcohols we used for contact angle measurements are much lower (20.9 – 23.3 mN/m). Looking at the surface tension diagram of various water/propan-2-ol mixtures in Figure 6, it is evident that till the water concentration nearly 80 wt%, the surface tensions are much closer to those of alcohols. These findings could probably explain the differences in wettabilities of tested membranes in neat water and in water/propan-2-ol mixtures.

Therefore, classification of the PELC membranes hydrophilicity only by contact angle measurements in water would be the same mistake as to characterize the membrane hydrophilicity by only swelling experiment in water. It has been already published that the PELC membrane based on sodium cellulose sulfate or SEC as polyanion with the polycationic pDMDAAC do not swell in ethanol at all and also their swelling ratio in water/ethanol real feed mixtures is nearly four times lower compared with water [9,13]. These results are in agreement with our contact angle measurements, which confirmed the necessity to pay the main attention in characterization of membrane interactions with real water-alcohol mixture to be separated.

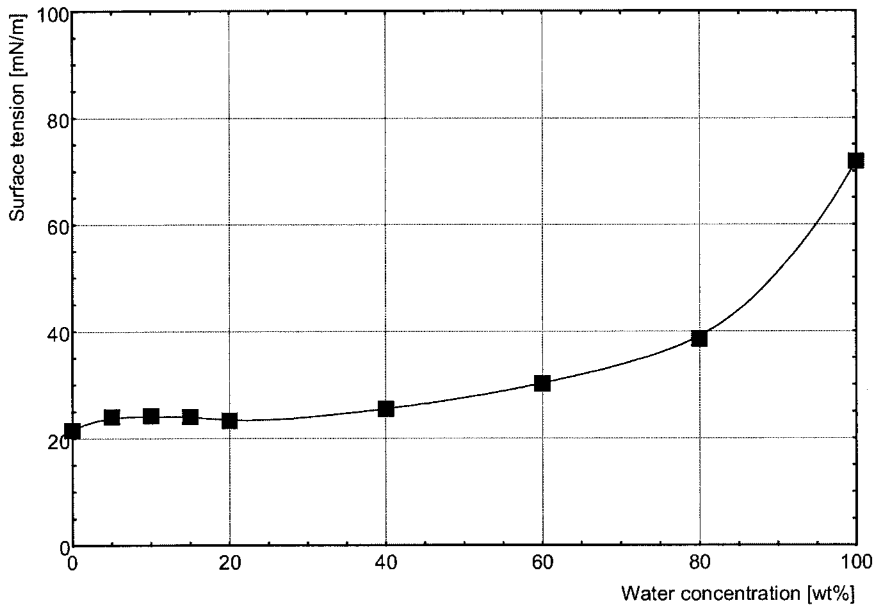


Fig. 6. Water/propan-2-ol surface tension diagram.

The dehydration PV experiments of water/propan-2-ol mixtures made on both membranes (Figs. 4,5) show that their water and alcohol fluxes (water fluxes being considerably higher), as well as their separation selectivities are till the water concentration in the feed mixture about 40 wt% nearly equal. With further increasing of water concentration in feed, the SEC/BDDDMAC membrane possesses evidently higher permeabilities, but its separation selectivity falls drastically down. The only advantage of the SEC/pDMDAAC membrane, which could be from the first sight (contact angle measurement in water) qualified as a strong hydrophilic, was found its higher chemical stability just in these higher water feed concentrations. But this stability could be explained by more compact net structure of the membrane being formed by polyanion-polycation components, compared with polyanion-cation system of the SEC/BDDDMAC membrane.

From presented results follows the conclusion that the membrane hydrophilicity (in the sense of wettability in neat water) does not influence neither flux nor selectivity in the PV dehydration process. From this point of view not even the selective sorption, which is considered in the solution-diffusion model, could play in this case an important role in PV process. Much more we incline to the vision that the fundamental phenomenon by PV is the selective diffusion through the membrane. The size of water molecule is in comparison with all organic molecules much smaller. Therefore, the diffusion channels in the membrane should have such diameter allowing water molecules movement across the membrane but closing for the organic molecules. Moreover, the strong tendency of water molecules to the hydrogen bondings must be a dominant feature in dehydration of organics by PV process. It seems that the most prospective polymer materials for this purpose are rigid chain polymers with active groups, which allow hydrogen bondings and ion-dipole interactions with water. The chemical structure of PELC membranes with polysaccharide chains on the one side (high capability to form hydrogen bondings), and polycations or cations on the other one (forming ion-dipole interactions), predetermines these materials for water separation from organics.

5. Conclusion

Two PELC membranes prepared by interfacial reaction of sodium salt of SEC, with pDMDAAC or BDDDMAC were prepared. Their investigation by means of dynamic contact angle measurement showed that the membrane wettability in neat water and alcohols or water/alcohol mixtures is quite different. From this reason the membrane hydrophilicity cannot be classified only due to swelling in water, or contact angle measurement in water.

The membrane wettability should be characterized by means of real water/alcohol mixtures. From this standpoint, the contact angles determined for water/propan-2-ol mixtures well correlated with the PV experiments, which have confirmed good fluxes and separation selectivities of both membranes.

The presented results show that the hydrophilicity of our membranes (in the sense of wettability in neat water) does not influence neither flux nor selectivity in the PV dehydration process. These findings lower the importance of selective water sorption in the solution-diffusion model. Therefore, selective diffusion should play on these membranes the fundamental role in PV mechanism in dehydration of organics.

Acknowledgement

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