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THE COMBINATION OF IONIC SURFACTANTS WITH POLYELECTROLYTES- A NEW MATERIAL FOR MEMBRANES?

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Abstract: The combination of two oppositely charged polyelectrolytes results in polyelectrolyte complexes. The simultaneous interfacial reaction between the different polyions leads to formation of polyelectrolyte complex membranes. Some of these have a very good performance in the membrane process pervaporation, especially for dehydration of organic liquids. The combination of a polyelectrolyte with an ionic surfactant of opposite charge results like-wise membranes but with other separation properties. The differences between the two types of membranes, formed from cellulosesulfate in combination with cationic polyelectrolytes or cationic surfactants, will be discussed.

INTRODUCTION

A characteristic feature of water-soluble polyelectrolytes is their tendency to form aggregates with suitable counterpart species. The interaction of polyions with

- low molecular inorganic counterions,
- organic dyes with ionic groups,
- ionic surfactants,
- macroions,
- colloidal particles, and
- solid surfaces

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is often described in the literature (Ref. 1).

For example the polyanion-polycation complex formation process is a phenomenon that had long been known. Especially in recent decades a rapid development in this area of polymer science can be stated, manifested in a very large number of papers, demonstrating the dominant role of this type of structure formation in the field of polyelectrolytes.

Employing suitable conditions of synthesis, polyelectrolyte complex precipitates can be obtained as films or membranes of considerable mechanical strength even in the wet state.

Already in 1961 MICHAELS (Ref. 2) started with systematic studies of preparation and application of membranes made from polyelectrolyte complexes, mainly for ultrafiltration. These membranes are formed by preparing a solution of polyelectrolyte complex in a suitable solvent medium and subsequent transformation of this solution in a membrane. The favoured components in polyelectrolyte complex formation were poly-(styrenesulfonic acid) as the anionic and poly-(vinylbenzyltrimethylammonium chloride) as the cationic part.

PHILIPP et al. (Ref. 3) describe the possibility of simultaneous interfacial reaction of aqueous solutions of two oppositely charged poly-ions in order to obtain spherical microcapsules. We used this method for the formation of flat membranes. These membranes are formed by the interfacial reaction between the anionic and the cationic polyelectrolyte supported on a glass plate. For application purposes the wet PEL complex membranes were transferred onto porous ultrafiltration membranes from polyacrylonitrile. After drying under ambient conditions easy-to-handle composite membranes were obtained.

By using sodium cellulose sulfate (CS) and poly-(dimethyldiallylammoniumchloride) (PDMDAAC) as the preferred two oppositely charged polyelectrolytes result membranes with hydrophilic properties. The hydrophilic PEL complex membrane material is very well qualified for dehydration of organics by pervaporation (Ref. 4).

The polyelectrolyte-ionic surfactant interaction can be considered as a special case in the field of polyelectrolyte complex formation.

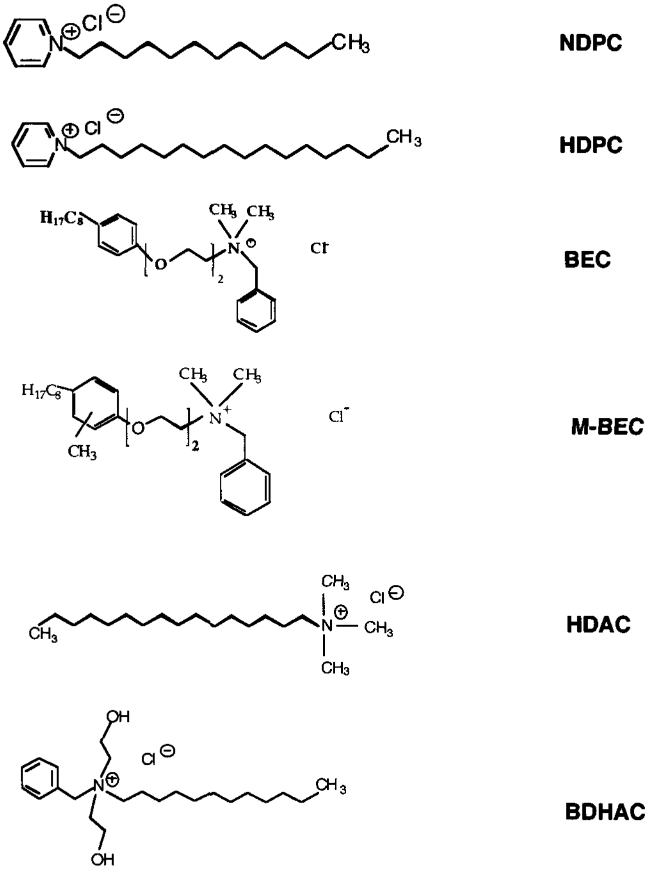


Fig. 1: Structure of ionic surfactants

The complex formation between surfactants and polyelectrolytes is additionally influenced by hydrophobic forces between the surfactant molecules (Ref. 5). However, no generally accepted model of complex formation between ionic surfactants and macroions is available today. But it can be stated that mutual ordering and binding of surfactant molecules into micelles via hydrophobic interactions and via electrostatic binding of surfactant molecules and/or micelles onto the ionic sites of the polyelectrolyte take place simultaneously.

Concerning polyelectrolyte-surfactant (PELS) complexes a comprehensive review was published some years ago (Ref. 6). Here some information about the formation and modification of membranes can be found. The aim of the work presented here was the formation of membranes due to the reaction of an anionic polyelectrolyte with different ionic surfactants, the characterization of the membrane properties and a discussion of the possible application in separation processes.

EXPERIMENTAL PART

Materials

The polyanion used for complex formation was sodium cellulose sulfate (CS) made by sulfation of cellulose acetate (Ref. 7) in all cases. The polycation poly-(dimethyldiallylammonium chloride) (PDMDAAC) was used for the formation of PEL complex membranes. The PELS complex membranes were formed with the cationic surfactants N-Dodecyl-pyridinium chloride (NDPC), Hexadecyl-pyridinium chloride (HDPC), Benzethonium chloride (BEC), Methyl-Benzethonium chloride (M-BEC), Hexadecyl-trimethylammonium chloride (HDAC) and N-Benzyl-N-dodecyl-N-bis-(2-hydroxy-ethyl)ammonium chloride (BDHAC). Fig. 1 shows the structure of the surfactants.

Membranes

An aqueous solution of CS (usually 2-6 wt%) was cast as a 0.2 mm thick film on a glass plate. On this film a layer of the aqueous counter-ion solution with a thickness of 0.2 mm was spread out immediately (Fig. 2). The simultaneous interfacial reaction between the different ions lead to formation of the complex membranes. After a reaction time of 15 minutes the glass plate with adjacent unreacted components was dipped into a water bath. The resulting membrane was loosened from the support, intensively soaked and dried after transfer on a porous UF membrane at ambient conditions.

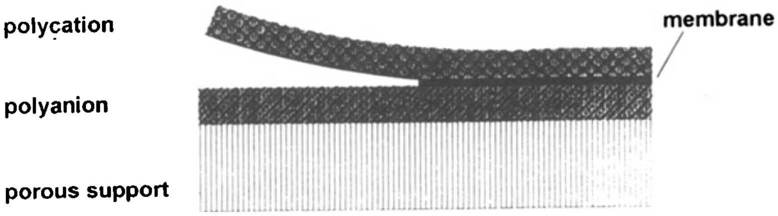


Fig. 2: Scheme of membrane formation

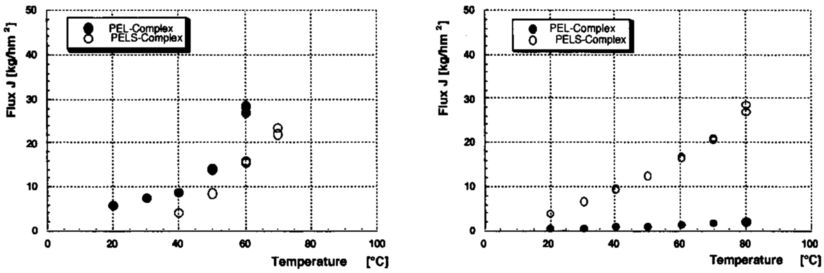
Pervaporation investigations

Pervaporation experiments were carried out with a laboratory scale apparatus using a stainless steel measuring cell P 28 supplied by CELFA AG, Switzerland, with an effective membrane area of 17 cm^2. If not stated otherwise, downstream pressure and feed temperature were kept constant below 1 mbar and 50 °C, respectively. The feed velocity was enlarged up to 40 l/h in order to minimize influence of concentration polarization. The permeate was collected in a trap cooled with liquid nitrogen. Fittings and valves between feed tank, measuring cell and cooling traps were heated in order to avoid condensation. The flux was determined gravimetrically. The composition of feed and permeate were determined by gas chromatography (H P 5890 Series II).

The membranes were characterized with methanol, water, alcohol/water mixtures, and with methanol/cyclohexane and methanol/methyl-tert-butylether(MTBE), respectively.

RESULTS AND DISCUSSION

A significant difference between the polyelectrolyte complex membranes and the polyelectrolyte-surfactant complex membranes consists in the fluxes for pure water and pure methanol, respectively (Fig. 3).



a

b

Fig. 3. Comparison of water (a) and methanol (b) flux for PEL complex and PELS complex membranes

The water flux for both membrane types is very similar in the range until to 50 °C. However, methanol shows a much higher flux for the membrane containing a surfactant in the structure. The hydrophilic PEL complex membrane is practically impermeable for the methanol molecules.

The fluxes for methanol, ethanol and isopropanol in dependence on the temperature for a PELS complex membrane are shown in Fig. 4. The fluxes for these alcohols decrease with increasing number of carbon atoms. The smallest alcohol molecules (methanol) have the highest flux. Ethanol is situated in a mean position. The flux for pure isopropanol is very low.

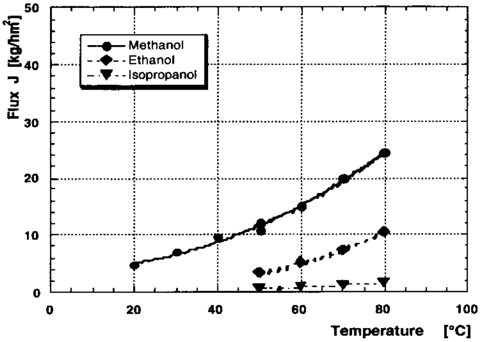


Fig. 4. Flux vs. temperature CS/HDPC membrane

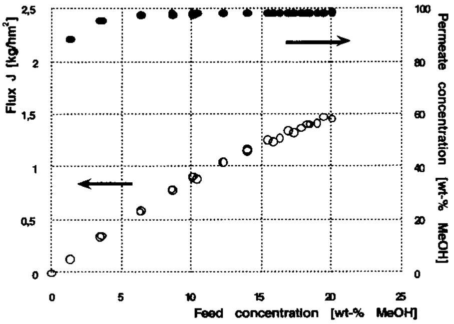


Fig. 5. Flux and permeate concentration vs. feed concentration; CS/HDAC membrane; MeOH/MTBE; T=50 °C

Fig. 5 shows the dependence of membrane performance on the feed composition for a methanol/MTBE mixture. The flux increases with increasing methanol content in the feed mixture. The methanol content in the permeate is very high in the range from 20 to 10 wt-% MeOH, at lower feed concentrations the membrane becomes permeable also for the other organic component.

The pervaporation properties for all PELS complex membranes investigated are summarized in the next two figures. Pervaporation properties for mixtures of methanol/cyclohexane and methanol/MTBE were determined. The feed concentration in the case of methanol/cyclohexane was 5 wt-% MeOH and for MeOH/MTBE 20 wt-% MeOH. In Fig. 6 the methanol concentration in the permeate (a) and the total fluxes (b) for the methanol/cyclohexane mixture are shown. The permeate concentration is high, for all PELS complex membranes between 80 and 90 wt-%, even the hydrophilic PEL complex membrane (P-DMDAAC) shows a preferential transport of methanol. But the fluxes of the membranes are significantly different. According to the nature of the ionic surfactant a differentiation of the membrane permeability is possible. Membranes with NDPC or HDPC as cationic part possess the best performance (high fluxes and high methanol content [> 97 wt-%] in the permeate). The flux of the typical dehydration membrane is nearly zero.

The results of the pervaporation experiments with MeOH/MTBE mixtures are shown in Fig. 7. The permeates contain also methanol in a concentration between 80 and 99 wt-%. The membrane with HDPC possess the highest flux. The flux of the hydrophilic membrane is very low.

CONCLUSION

1. Membranes obtained by simultaneous interfacial reaction from Na-cellulose sulfate and different cationic surfactants may be successfully used for the separation of polar from unpolar organic liquids.
2. The polyelectrolyte-surfactant complex membranes have a very high permeability for methanol.
3. In the membrane the surfactant component controls evidently the methanol permeability.

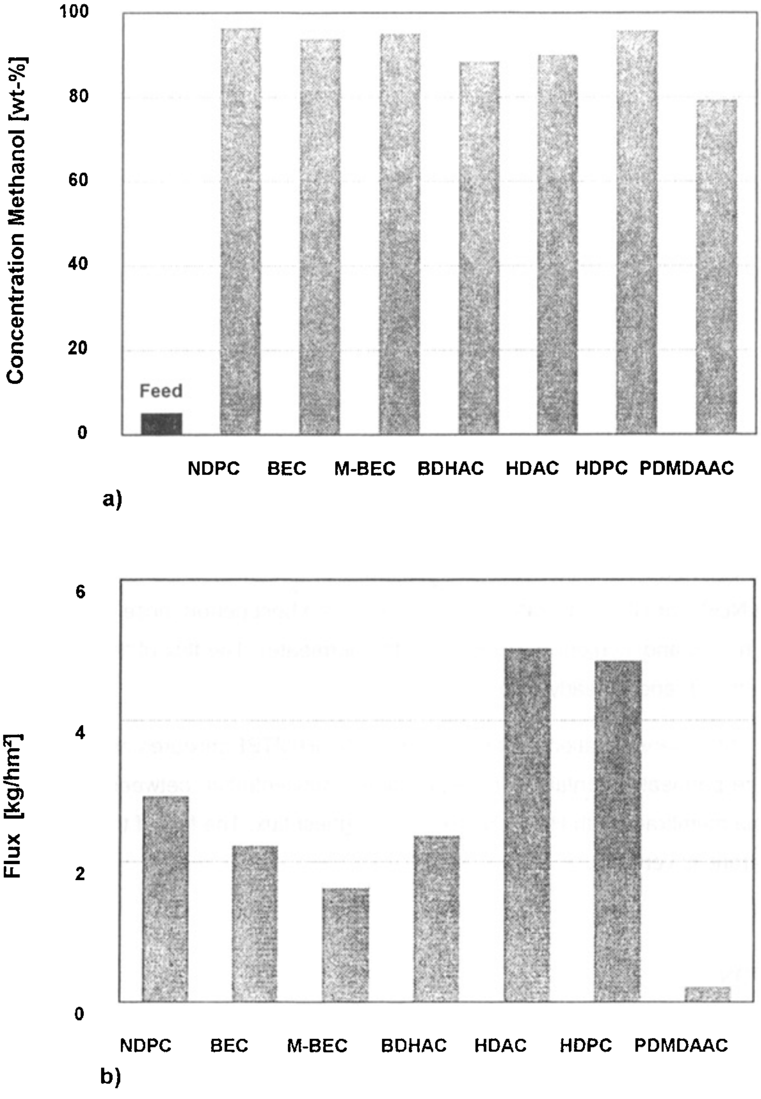


Fig. 6. Results of pervaporation experiments (MeOH / cyclohexane)
Feed: 5 wt-% MeOH; T = 50°C
a) Permeate concentration; b) Flux

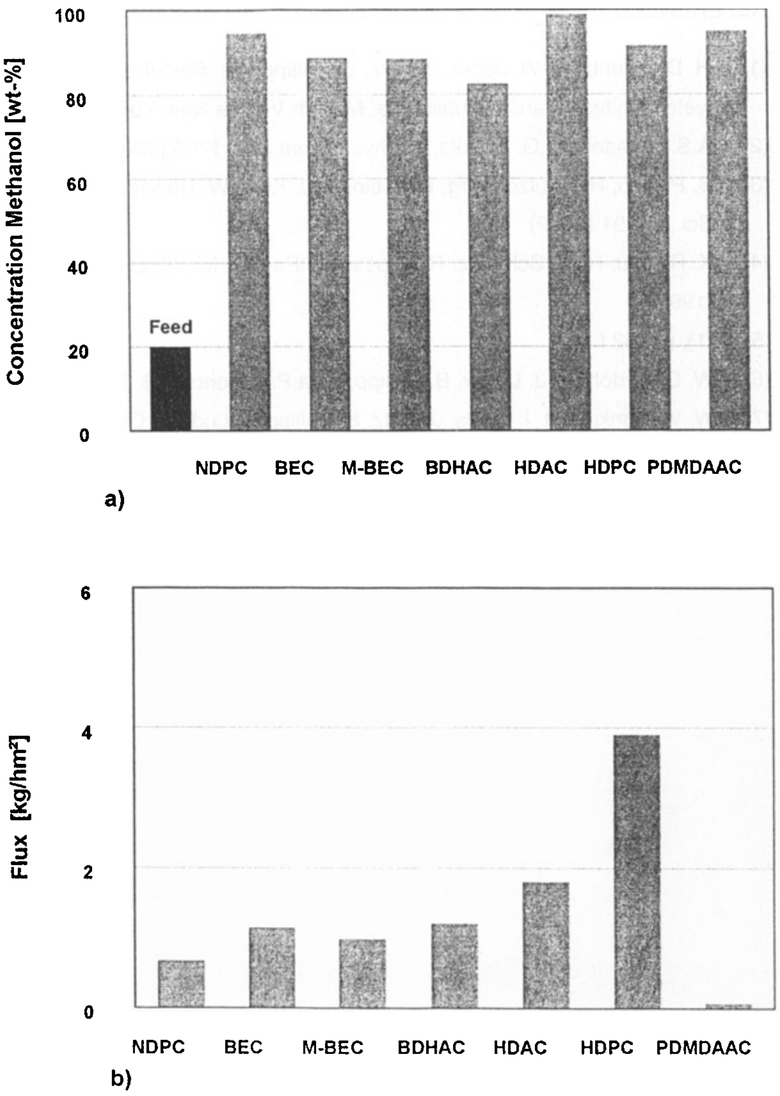


Fig. 7. Results of pervaporation experiments (MeOH / MTBE)
Feed: 20 wt-% MeOH; T = 50°C
a) Permeate concentration; b) Flux

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