EFFECT OF THE MEMBRANE POTENTIAL ON THE PERFORMANCE OF ULTRAFILTRATION MEMBRANES

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Received February 12th, 1985

In the pressure driven process the performance of membranes for ultrafiltration can be changed by incorporating charged groups into the membranes. By sulfonation of polysulfone membranes the membrane potential is varied. On interaction of the negatively charged membrane with positively or negatively charged protein molecules the formation of a concentration polarization gel layer proceeds at different rate. Thus, the performance of the membrane can be controlled by the membrane potential. The dependence of the performance on the potential is discussed and procedures for membrane cleaning are suggested.

At present, charged membranes are increasingly used in ultrafiltration processes. By contacting such membranes with solutes having the same sign of electric charges the concentration polarization is reduced as a result of repulsion and the danger of clogging decreases (antifouling effect). Thereby, the performance of the pressure driven membrane process is improved. Jitsuhara and Kimura[1] examined the properties of charged membranes for ultrafiltration made of sulfonated polysulfone. By use of a SO_3-triethylphosphate complex the sulfonation was carried out homogeneously in solution. Then the membranes were obtained from the sulfonated material by precipitation. The effect of charged groups in the membrane on ultrafiltration was analysed by measuring the flux reduction of a protein solution at different pH. The differences in the decrease of the flux rate in the alkaline or acid region allow to draw conclusions to the adsorption processes at the membrane surface.

Fane[2,3] examined the effect of pH and ionic additives on the performance of ultrafiltration membranes. They interpreted the changes observed as a result of conformational changes and charge effects in the adsorbed protein layer. Noordegraaf[4] investigated the effect of gel layer formation on the ultrafiltration of cheese whey by a negatively charged membrane at different pH. The highest fluxes were found

to occur on interaction of a positively charged whey protein (pH 2·5) with negatively charged membrane. This surprising effect is attributed to the initial stage of gel layer formation. In this initial stage a negatively charged protein in contact with the negatively charged membrane is supposed to be deposited in the gel layer, thus minimizing electrical repulsion. Contrarily, the positively charged protein will adhere to the membrane in a disordered manner. The autors suppose the negatively charged protein to block the pores at the surface of the membrane more efficiently than the positively charged protein.

Hitherto no quantitative correlation between the charged state of a membrane and their performance in the ultrafiltration process has been reported. Therefore, it is the purpose of this paper to characterize the different states of negatively charged ultrafiltration membranes by measuring the electrical potential and to suggest correlations with the membrane performance in the pressure driven process. The experiments were performed with sulfonated polysulfone membranes.

EXPERIMENTAL

Preparation of Membranes. The polysulfone membranes were produced in the Research Institute Liko Bratislava on the basis of polysulfone PL-15[5]. The membranes contain a textile support. As sulfonation proved to be impossible with wet membranes, the membranes were subjected to multistage solvent exchange, the water included in the membrane being exchanged by ethanol. After this the membranes were stored in the sulfonation medium (cyclohexane).

Sulfonation of Membranes. Analogously to the surface treatment of polysulfone films with a SO_3-triethylphosphate complex in cyclohexane described by Noshay[6] the sulfonation was carried out in cyclohexane, using chlorosulfonic acid as sulfonation agent. High concentration of chlorosulfonic acid has to be avoided to prevent destructions of the porous membrane structure.

The cyclohexane was cooled to a temperature of c. 10°C. Then 0·1 to 0·5 vol.% chlorosulfonic acid was added to the cyclohexane and mixed with it. The membrane was placed in the reaction mixture and left there at first under cooling conditions but then at room temperature for periods of two hours to several days.

The sulfonation was finished by removing the membrane sample and rinsing it with pure cyclohexane. Then the membrane was treated once with 90% ethanol and three times with 30% ethanol. After 24 hours action of 10% ethanol the membrane sample was stored in water.

Characterization of Membranes. The charged state of the polysulfone membranes was determined by measuring the concentration potentials as previously[7] described. The potential was measured with the Electrometer Keithley 610, using KCl (0·01/0·001M) as electrolyte, at 25°C. The skin layer of the membrane was oriented to higher concentration of the KCl solution. Prior to the measurements the membranes were placed in 0·2M KCl solution.

The ultrafiltration experiments were performed with an Amicon test cell model 52. The test cell has a 50 ml feed solution volume and an effective membrane area of 13·2 cm^2. Operating conditions were kept at a pressure of 0·2 MPa and a stirring speed of 600 rpm. Fresh solutions of 0·5 g/l albumine (Reanal) were prepared for each experiment. The pH was adjusted by addition of small amounts of HCl (pH 1·85) and NaOH (pH 11·37) after the addition of convenient amounts of NaCl. With 50 ml feed protein solution the tests were run until 25 ml filtrate were obtained, the filtrate flux being followed up continuously.

RESULTS AND DISCUSSION

The results of potential measurements are summarized in Table I. With membranes *A*, *B* and *C* ultrafiltration experiments were carried out. First of all the water flux J_w was measured, then the test with albumine solution was carried out at pH 1·85. After repeated rinsing with water J_w was measured anew. Then the ultrafiltration was performed with the alkaline albumine solution. Finally, after repeated membrane rinsing with water the water flux was measured once again. The temporal change of the albumine filtrate flux J_v at pH 1·85 obtained with an unmodified (*A*) and two sulfonated membranes (*B* and *C*) is represented in Table II. In the table the absolute and relative flux values are indicated. Table III presents the results for albumine solution at pH 11·37.

TABLE I
Concentration potential of membranes

Membrane	Potential (mV)
A (unmodified)	− 4·5
B	−16·3
C	−33·3

TABLE II
Filtrate flux J_v for albumine solution at pH 1·85

Time *t* (min)	*A*		*B*		*C*	
	J_v (l/hm²)	$J_v/J_{v(o)}$	J_v (l/hm²)	$J_v/J_{v(o)}$	J_v (l/hm²)	$J_v/J_{v(o)}$
1·5	43·7	1·000	37·7	1·000	40·5	1·000
3·5	41·4	0·947	35·9	0·952	38·6	0·954
5·5	42·7	0·977	36·4	0·966	36·4	0·900
7·5	40·0	0·915	33·2	0·881	35·5	0·876
10	35·7	0·817	32·7	0·867	32·0	0·791
15	35·1	0·803	30·2	0·801	30·0	0·742
20	33·9	0·776	27·9	0·741	28·6	0·707
25	33·2	0·760	27·7	0·735	27·3	0·675
30	32·9	0·753	27·3	0·724	27·3	0·675

By comparing the relative filtrate flux density ($J_v/J_{v(o)}$*) in Table II and Table III the decrease of these values is seen to be essentially smaller in the alkaline region than in the acid region, analogously with the results reported by Jitsuhara[1]. At pH 1·85 the values of J_v start to decrease continuously immediately after the onset of ultrafiltration but at pH 11·37 a 10 min. initial stage occurs being characterized by increasing filtration flux.

TABLE III
Filtrate flux J_v for albumine solution at pH 11·37

Time t (min)	*A*		*B*		*C*	
	J_v (l/hm^2)	$J_v/J_{v(o)}$	J_v (l/hm^2)	$J_v/J_{v(o)}$	J_v (l/hm^2)	$J_v/J_{v(o)}$
1·5	41·8	1·000	46·8	1·000	37·7	1·000
3·5	47·3	1·132	47·7	1·019	39·5	1·048
5·5	45·7	1·093	50·0	1·068	41·8	1·109
7·5	47·3	1·132	50·5	1·079	40·0	1·061
10	45·0	1·076	45·0	0·962	35·5	0·942
15	42·9	1·026	44·5	0·951	34·1	0·905
20	43·6	1·043	43·6	0·932	33·6	0·891
25	43·6	1·043	42·5	0·908	30·2	0·801
30	44·1	1·055	41·4	0·885	30·2	0·801

TABLE IV
Pure water permeability J_w (l/hm^2) before and after albumine ultrafiltration

	Membrane		
	A	*B*	*C*
J_w before UF	53·2	50·3	48·3
J_w after UF (pH 1·85)	37·4	30·0	29·2
J_w after UF (pH 11·37)	55·8	56·7	43·6

* $J_{v(o)}$ = filtrate flux at the beginning of measurement.

Table IV indicates the water flux through the membrane before and after ultrafiltration with albumine solution in the alkaline and acid region. After ultrafiltration with acid albumine solution the water flux decreases significantly in spite of repeated cleaning. Only after interaction with alkaline albumine solution J_w acquires again or even surpasses the initial value. The flux through the membrane is found to depend essentially on the gel layer formation at the membrane-solution interface. If back-diffusion from the membrane surface into the solution is favoured the

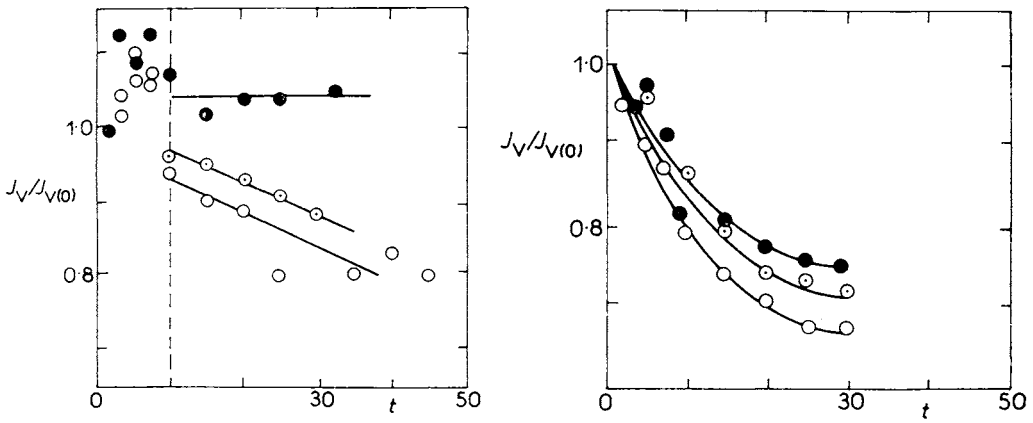

FIG. 1 *a* *b*

Dependence of relative filtrate flux $J_v/J_{v(o)}$ for albumine solution on time t for different pH and membrane potentials. ● — 4·6 mV; ⊙ — 16·3 mV; ○ — 33·3 mV; *a*: pH 11·37; *b*: pH 1·85

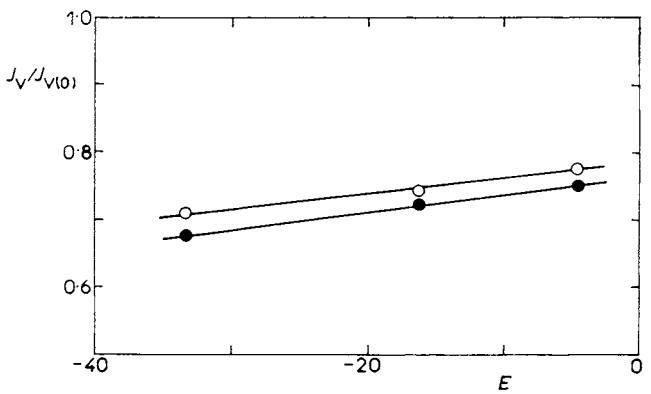

FIG. 2

Correlation between membrane potential E (mV) and relative filtrate flux $J_v/J_{v(o)} = a - bE$. ○: $t = 20$ min, $a = 0{\cdot}784$; $b = 0{\cdot}00237$; correlation coefficient 0·994; ●: $t = 30$ min, $a = 0{\cdot}766$; $b = 0{\cdot}00272$; correlation coefficient 0·999

filtration rate will increase. The results obtained in our experiments suggest a distinct relationship between the performance and the potential of membranes, the formation of the gel layer being obviously affected by the potential.

Fig. 1 illustrates the change of the relative flux with the membrane potential at both pH values considered. At pH 1·85 the flux decreases with all the three membranes investigated. The membrane having the highest negative potential shows the highest reduction of flux. On contacting a negatively charged membrane with negatively charged protein solution a 10 min. stage of increasing flux is observed. Then, with more negatively charged membranes the flux decreases, while no change of performance is observed with the unmodified membrane, the flux of which remains above the initial value. The electrostatic repulsion between negatively charged membrane and negatively charged protein molecules favours the back-diffusion into the solution. The formation of a polarization layer is retarded, the potential of $-4{\cdot}6$ mV appears to be an optimum value. No decrease of flux was detected, but at more negative membrane potentials a gel layer was observed to be formed as a consequence of the pressure driven process. Noordegraaf[4] supposes this effect to be a consequence of electrostatic repulsion resulting in higher order of the gel layer.

With positively charged protein molecules at pH 1·85 a linear correlation between membrane potential and relative flux was observed, as illustrated in Fig. 2 with measuring times of 20 and 30 minutes. The parameters of the fitting straight line are also indicated. In both cases a satisfying correlation was found to exist.

By the membrane potential also the fouling effect can be influenced. The charge reversion of the solutes results in increasing flux rate. The gel layer formation on the membrane surface is reduced due to the repulsion effect. After 30 minutes the gel formation at pH 1·85 is finished, but not at higher pH. The flux behaviour of an ultrafiltration membrane (in contact with charged solutes), therefore, can be controlled in a defined way by the membrane potential.

By the behaviour of water flux before and after ultrafiltration with differently charged protein molecules, additionally, charge reversion as a consequence of pH change provides a very good possibility for membrane cleaning and thus reestablishing the original flux values of water.

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