KATARZYNA MAJEWSKA-NOWAK*,
MAŁGORZATA KABSCH-KORBUTOWICZ*

HYDROPHILIC MEMBRANES
IN SEPARATION OF ORGANIC MACROMOLECULES

In this paper, the characteristics, methods of modification and applications of novel hydrophilic ultrafiltration membranes were discussed. The review emphasized crucial importance of hydrophilicity for the prevention of fouling and adsorption in pressure-driven membrane processes. It was supported by strong evidence that hydrophilic membranes are less susceptible to fouling than membranes made of hydrophobic polymers. Some aspects of membrane hydrophilicity evaluation (i.e., contact angle measurements) were also discussed.

The characteristics and performance of commercial hydrophilic ultrafiltration membranes (Amicon Diaflo and Nadir Intersep) with different surface hydrophilicity were compared to water droplet advancing contact angle, water flux, volume flux of dye solution, dye rejection coeffcient and foluling index. The membranes investigated can be used in ultrafiltration of organic dyes. They yielded an over 97% retention of high-molecular-weight dyes. The diminishing tendency to foul was observed for the membranes made of regenerated cellulose.

1. INTRODUCTION

Many kinds of commercial ultrafiltration membranes have been developed and used for various industrial applications. Since the membrane separation is based on the so-called sieving mechanism, they cannot separate mixtures of macromolecules of similar molecular sizes; they are also susceptible to fouling. In practical use, ultrafiltration membranes having fixed charges are better than noncharged ultrafiltration membranes. In the case of noncharged membranes, solutes are separated based on the so-called sieving mechanism, whereas charged UF membranes are characterized by three variables: sign and density of the charge and pore size. Charged membranes are able to expel charged solutes of the same sign as the sign of membrane charge. That is the reason why they are less fouled than the

* Institute of Environment Protection Engineering, Technical University of Wrocław, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland.

noncharged membranes by the gel layer formed on their surface. The charged ultrafiltration membranes can separate charged and noncharged solutes due to an electric effect even though the molecules of both solutes have the same size.

Therefore, in various industrial fields such as food, medical and biochemical industries, it is useful to apply charged ultrafiltration membranes to the separation of the constituents of proteins, enzymes, antibodies, hormones and blood proteins. They can also be applied in industrial effluent treatment (e.g., pulp and paper, cheese).

2. MEMBRANES AND METHODS OF THEIR MODIFICATION

Conventional ultrafiltration membranes (susceptible to fouling) are generally made of hydrophobic polymers (e.g., polysulfone, polyvinylidine fluoride, polyethersulfone, polyvinyl chloride, copolymers of vinyl chloride and acrylonitrile, polyvinyl acetate, cellulose acetate and cellulose nitrate). They can also be cast from water-soluble polymers (and a suitable cross-linking agent) such as polyvinyl alcohol, polyacrylamide and polyacrylic acid. Because of chemical nature of these polymers the importance of adsorption phenomena and fouling have to be taken into account. Among many industrial applications (e.g., separation of proteins) fouling is a serious problem when using these hydrophobic membranes. GREGOR [1], after fifteen years of experiments, concluded that membranes susceptible to fouling can be involved in ultrafiltration process, provided that the strong adsorption of soluble materials to the pore walls does not decrease the pore diameter sufficiently to impede transport of solvent.

Recently, different techniques enabling the transfer of hydrophilic properties to hydrophobic, highly resistant synthetic polymers have been developed. These techniques involve mainly surface modification methods combined with various chemical reactions (e.g., casting of the thin barrier layer separately followed by lamination onto a support membrane; solution coating of a support membrane by dipping it in a polymer solution; interfacial polymerization of reactive monomers *in situ* on the surface of a support membrane).

STENGAARD [2] successfully developed a method according to which a suitable ultrafiltration support obtained as a result of traditional phase inversion process is the surface coated with an aqueous solution containing a hydrophilic polymer and/or monomer having reactive groups. By rising temperature, the hydrophilic components are chemically bounded to the membrane material. The properties of the final membrane depend on the characteristics of the support membranes, the composition of the coating solution and the reaction conditions. PETERSEN et al. [3] developed a novel set of thin film composite ultrafiltration membranes consisting of ultrathin barrier layers of cellulosic graft copolymers coated on microporous polysulfone supports. Graft copolymers containing hydrophilic backbones in ionically charged side-chains were synthesized on the basis of commercial cellulosic and different vinyl monomers. These membranes were far more resistant to fouling because of their smooth surface and hydrophilicity compared to microporous polysulfone ultrafiltration membranes. Highly cross-linked thin composite ultrafil-

tration membranes are commercially available through Desalination Systems Inc. (USA) [2]. The interfacial polymerization technique (polyamide reaction) of membrane-making guarantees their different cut-off values. Filtron Corporation [4] produces ultrafiltration membranes based on polyethersulfone with chemically modified surface. One membrane series is characterized by low protein adsorption and another is resistant to anti-foaming agents.

There is a slight inconsistency in literature data relating to the hydrophobicity (or hydrophilicity) of polymers. According to GREGOR [1] such materials as cellulose acetate, cellulose nitrate and regenerated cellulose acetate are hydrophobic in nature, whereas STENGAARD [2] ascertains that membranes made of cellulosic materials exhibit hydrophilic properties, low adsorption and good separation characteristics; moreover, such materials, similarly as other different polymers, could be adopted to surface treatment procedure. In this procedure, such aromatic compounds as amines, hydroxycompounds or epoxides containing additional (hydrophilic) functional groups are the preferable co-reactants.

GREGOR [1] concluded that only sulphonic acid membranes with fixed charge were useful in fouling prevention during ultrafiltration of hydrophobic molecules and hydrophobic anions. The ultrafiltration membranes with fixed-charge groups like carboxylic, phosphorus and phosphonic are not suitable. On the contrary, NYSTRÖM and JÄRVINEN [5] applied successfully modified polysulfone membranes with hydrophilic carboxylic groups to ultrafiltration of proteins.

The problem of modifying ready-made commercial membranes by chemical treatment stems from the fact that the modification agent partly blocks the pores of the membranes. Therefore even if the membranes after modification are less apt to foul, the total flux after modification is smaller than before modification. One successful modification method seems to be that by NYSTRÖM and JÄRVINEN [5], who modified commercial polysulfone UF membranes using UV irradiation alone or together with different modification agents in liquid environment.

3. MEMBRANE HYDROPHILICITY

The importance of hydrophilicity for the prevention of adsorption has been shown by GOLANDER and KISS [6]. They stressed the fact that the hydrophilic surface attracts water so strongly that adsorption is prevented. It is generally accepted that hydrophilic membranes are less susceptible to fouling than membranes made of hydrophobic polymers. Short-time UF tests on some model foulants have been performed by STENGAARD [2]. Changes in membrane fluxes during their 2-hour exposition to a solution of the foulant (bovine albumine, dextran 4, Triton X-100) have been observed. Comparison of fouling effects (table 1) was made by calculating the relative recovery in water flux (the ratio of water flux after and before the mebrane exposure to foulant). An almost complete flux recovery for ETNA20A and RC70PP membranes is indicative of a slower flux decline and diminishing fouling tendency.

Table 1

Water flux recovery (%) for various DDS membranes [2]

Membrane		Foulant		
Symbol	Nature	Albumine bovine 0.1%	Dextran 4 50 mg/dm^3	Triton X-100 50 mg/dm^3
FS61PP[a]	hydrophobic	66	86	75
GR61PP[b]	hydrophobic	54	88	75
ETNA20A[c]	hydrophilic	97	100	100
RC70PP[d]	hydrophilic	100	100	100

[a] – polyvinylidene fluoride (PVDF).
[b] – polyethersulfone.
[c] – surface coated PVDF film.
[d] – regenerated cellulose.

The terms *hydrophilic* and *hydrophobic* are of necessity relative ones. The classical physical-chemical parameters characterizing surfaces in terms of wetting angle and the like are not applicable here. Rather a functional definition is required; it entails the actual use of a surface in a given series of environments to determine the extent of adverse reactions [1].

In terms of membrane phenomena, the definitive test of hydrophilic or non-fouling character consists in employing the membrane in a pressure driven process (as in reverse osmosis or ultrafiltration). Only under these conditions, which allow creation of a flux of both solvent and solute through the membrane, the significant differences in the ability of membranes to withstand fouling are evident [1].

Table 2

Effect of sulfonation on hydrophilicity [7]

Degree of sulfonation (–SO$_3$Na/PSF)	Ion exchange capacity (meq/g)	Water sorption (% weight increase)		Water flux (m^3/m^{2}d^a)	Advancing contact angle (°)
		5 days ambient	1 day water immersion		
1.0	2.16	11.9	61.4	45	52
0.5	1.15	5.9	24.5	6.3	–
0.1	0.3	1.0	5.0	0.41	–
0 (PSF)	–	0.5	1.9	0.005	70
Surface sulfonation					
Na salt	–	–		–	62
Free acid	–	–		–	74

PFS – polysulfone.
[a] – measured at 10 MPa.

Table 3

Measurements of contact angle (DDS membranes) [2]

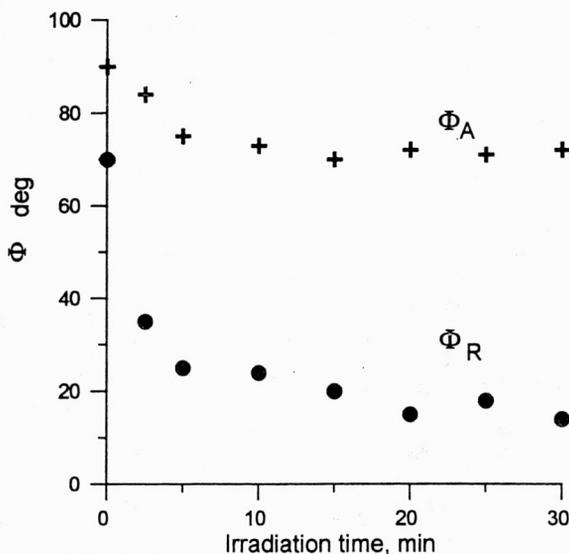| Membrane material	Membrane symbol	Water flux (m^3/m^2d)	MWCO (dalton)	Advancing contact angle (°)
Polyethersulfone	GR61PP	–	20 000	61
Polyvinylidene fluoride	FS50-U	7.2–12[a]	50 000	69
Surface-coated	ETNA20A	4.8–7.2[b]	20 000	42
polyvinylidene	ETNA10A	2.4–4.8[b]	10 000	40
fluoride film	ETNA1A	1.2–2.4[b]	1 000	43

[a] – measured at 0.2 MPa.
[b] – measured at 0.4 MPa.

Fig. 1. Change in a membrane hydrophilicity during its irradation in water without stirring after different irradation times expressed by the advancing (Φ_A) and receding (Φ_R) contact angles of the modified polysulfone surface against water [5]

Nevertheless the membrane hydrophilic properties (wettability) can be evaluated by measuring aqueous contact angle. It is a troublesome and rather unprecise method, but the data obtained via this method (tables 2 and 3) clearly show the differences in membrane hydrophilicity. The enhancement of hydrophilicity produced by sulfonation of polysulfone is illustrated by water-film contact angle data shown in table 2. Sulfonation of solution to the extent of 1.0 $-SO_3$ Na/PSF reduced the contact angle of polysulfone by about 20°. A surface-sulfonated and subsequently

neutralized membrane displayed an intermediate contact angle. A membrane, which was surface-sulfonated to the same extent but not neutralized, displayed no reduction in contact angle, suggesting that "wettability" may be mainly due to the ionic nature of the sodium salt in these systems. Table 3 clearly shows the increase in membrane hydrophilicity due to surface modification. However, it should be pointed out that at the sulfonation degree equal to 1.0 $-SO_3Na/PSF$ a membrane permeability is very high, but zero salt rejection was observed (according to NOSHAY and ROBESON [7]) due to excessively hydrophilic nature of this membrane. The intermediate degree of sulfonation (0.5 $-SO_3$ Na/PSF) gives a membrane of high salt rejection and good permeate flux.

Table 4

Water flux after membrane modification (J_m)
compared to flux before modification (J_0)
after different irradiation times (IT) [5][a]

IT (min)	Modification agent	J_m/J_0 (%) measured at 0.15 MPa
5	–	89
10	–	225
15	–	432
20	–	616
5	45 vol. % ethanol	50
10	45 vol. % ethanol	315
15	45 vol. % ethanol	488
20	45 vol. % ethanol	627
15	BSA[b] 2 ppm	423
15	BSA 5 ppm	176
20	BSA 5 ppm	485
10	PEOB[c] 10 ppm	293
15	PEOB 10 ppm	1120

[a] – membrane before modification: polysulfone membrane made by DDS (GR type).
[b] – bovine serum albumin.
[c] – block copolymer of polyethylene oxide and vinyl acetate monomer.

Figure 1 shows the change in hydrophilicity as described by the contact angles of the polysulfone membrane material modified with UV irradiation [5]. UV irradiation increased the hydrophilicity of membranes. NYSTRÖM and JÄRVINEN [5] found that at the same time an increase in flux was registered. The irradiation process favours the formation of carboxylic and sulfonic acid groups on the membranes. These are dissociated and negatively charged at neutral pH values of the water and a state of internal repulsion in the pores is developed. This repulsion causes an enlargement of the pores, which results in an increase in water flux (table 4). According to NYSTRÖM and JÄRVINEN [5] when the modification is made

a)   b)   c)

Fig. 2. Hydrophilic chains protruding from pores in solutions of different types of solvents [5] (a) hydrophilic chains in "good" solvent, (b) hydrophilic chains in "poor" solvent, i.e. inappropriate pH, high ionic strength or hydrophobic solvent, (c) hydrophilic, negatively charged chains in "good" solvent forming internal electrostatic repulsion and englargement of the pore without loss in retention

in aqueous solutions of different hydrophilic substances, the resulting membrane permeability can be controlled by changing the amount of modification agents. Examples of the behaviour of hydrophilic chains in different types of solvents are given in figure 2.

4. APPLICATION OF HYDROPHILIC MEMBRANES

4.1. PERMEATION OF DEXTRANE MACROMOLECULES THROUGH UF MEMBRANES

KOBAYASHI et al. [8] studied the ultrafiltration permeation of nonionic dextran and anionic dextran sulfate through the charged membranes in aqueous solution. The charged ultrafiltration membranes were prepared from polyacrylonitrile grafted with ionic monomer. The ultrafiltration experiments were carried out in an Amicon stirred cell at the pressure of 0.1 MPa. The results obtained obviously supported the conclusion that electrostatic interaction between charged membranes and charged polymer solutes (i.e., anionic dextrans) controls permeation of

Table 5

Properties of uncharged and charged ultrafiltration membranes [8][a]

Membrane polymer	Fixed charge (meq/g polymer)	Water content (%)	Water volume flux[b] (m^3/m^{2}d)
PAN-Br	–	12.6	14.11
PAN-g-DAEM	–	65.3	3.34
PAN-g-DAEM$^+$	0.12	81.6	1.56
PAN-g-DAEM$^+$	0.40	85.2	1.42
PAN-g-DAEM$^+$	0.59	90.6	0.79
PAN-g-DAEM$^+$	0.75	90.8	0.72
PAN-g-DAEM$^+$	0.22	88.2	1.24

[a] – membranes were prepared from 8 wt.% of poly(acrylonitrile-graft-N, N-dimethylaminoethyl-methacrylate) solution containing poly(vinyl alcohol) in various amounts.
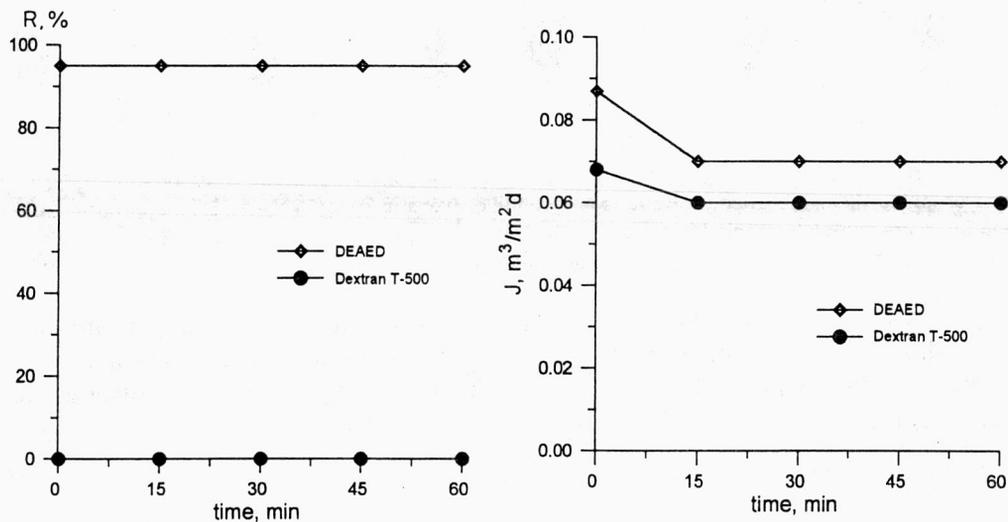[b] – measured at 0.1 MPa.

Fig. 3. Rejection coefficient and volume flux of charged and noncharged dextran solutions
for positively charged ultrafiltration membrane [9]

charged polymer solutes. They found that when increasing the number of fixed charges
in the membrane, the volume flux of water decreased (table 5) and the rejection of
dextran increased despite the higher hydrophilicity of the charged membranes.

NAKAO et al. [9] investigated the effect of the membrane charge on the rejection of
dextrans. As illustrated in figure 3, the positively charged DEAED (di-
ethylaminoethyl dextran) of molecular weight equal to 500 000 was strongly rejected
by the positively charged ultrafiltration membrane (MWCO 2 000 000) with fixed
ammonium groups. The rejection of nonionic dextran T-500 was almost zero, so it is
obvious that electrical repulsion occurs in the case of positively charged particles.

4.2. ULTRAFILTRATION OF PROTEINS

In ultrafiltration of proteins, one of basic problems is the fouling of the membranes,
which causes a considerable flux decline. Fouling often occurs when small divalent ions
like calcium ions are present or when the protein solution contains small amounts of
lipides. Also the proteins themselves seem to adsorb tightly onto the membranes,
especially if the membranes are hydrophobic in nature. The resulting fouling can be
either reversible or irreversible.

In fouling and adsorption of proteins on membranes, the strength of the hydro-
phobic interaction between the proteins and the membranes seems to be an important
factor determining adsorption. The proteins consist of both hydrophilic and hydro-
phobic parts, and their ratio is different for different proteins. This type of membranes
can also be applied in sewage treatment, in pulp and paper, or cheese industries.

In ultrafiltration, both adsorption forces and dynamic experimental conditions determine the degree of fouling and flux reduction. In ultrafiltration, even when the proteins seem to be hydrophilic and charged and no fouling is expected because of electrostatic repulsion between molecules and membrane, it still appears that fouling takes place. When changes of the charges of the protein and membrane induced by pH control do not improve the ultrafiltration efficiency, modification of commercial membranes or manufacturing of new types of membranes seems to be an effective way of improving conditions of protein UF.

One of the practical application of charged ultrafiltration membranes is macromolecular fractionation of particles of similar molecular sizes and different charges. In various industrial fields such as food and medical industries and bioindustry, it becomes particularly important to separate solution constituents such as proteins, enzymes, antibodies, hormones and blood proteins. It is well known that those constituents are positively charged, noncharged and negatively charged according to the pH of the solution. Therefore it could be possible to separate the neutral particles from the charged ones by means of charged membranes. KIMURA et al. [10] applied successfully the sulfonated polysulfone membranes (of nominal molecular cut-off about 10 000), which had negative charge, to separation of amino acids, whose molecular weights ranged from 75 to 200. An amino acid is electrically neutral at its isoelectric point and has a negative or positive charge at lower or higher pH, respectively. Therefore, the amino acid permeates through the charged membrane at its isoelectric point, and is rejected because of charge effect at higher or lower pH.

NAKAO et al. [9] studied the separation of protein mixture consisting of myoglobin and cytochrome C with the use of charged polysulfone membranes. Negatively charged membranes were obtained by sulfonation of polysulfone, and positively charged membranes were synthesized by chloromethylation of polysulfone and then by quaternization of the amino group. The ion exchange capacity of the membranes ranged from 0.9 to 1.2 meq/g-polymer. When the protein mixture was passed through negatively charged membrane at the isoelectric point of cytochrome C, the rejection of myoglobin approached 80% (at this pH value this macromolecule has a negative charge). At the same time, cytochrome C permeated completely through the membrane. Conversely, at the isoelectric point of myoglobin, cytochrome C had a positive charge and thus it was rejected in about 20% by the positively charged membrane. The rejection of myoglobin in this case was close to zero.

As it has been already mentioned, the irradiation procedure is one of the methods allowing us to increase the membrane hydrophilicity. The effect of irradiation of the polysulfone membrane (GR 81) on permeate flux and separation efficiency during ultrafiltration of 0.5% whey solution is given in table 6. At pH = 6 the whey proteins are slightly negatively charged and the irradiated membrane should be more negatively charged than the unmodified membrane, therefore the state of electrostatic repulsion between the membrane and the molecules in solution keeps the retention high even when flux is increased. Table 7 gives the permeate fluxes and

retention coefficients for unmodified and modified polysulfone membranes during ultrafiltration of BSA. It should be emphasized that the retention observed is very high in all cases. If flux increases considerably a slight loss in retention occurs.

Table 6

Membrane permeability (J_0 – flux before modification; J_p – flux after modification) and the measured retention (R) during ultrafiltration of 0.5% whey solution; pH = 6 [3]

Irradiation time (min)	J_p/J_0 (%)	R (%)
–	38	99.4
10	36	99.4
15	83	99.2
20	144	99.0

Table 7

Permeate flux (J, m^3/m^{2}d) and retention (R, %) after one hour of ultrafiltration of BSA at different pH values through unmodified and modified polysulfone membranes. $\Delta P = 0.15$ MPa [3]

Modification agent	IT[a] (min)	pH = 3		pH = 5		pH = 7		pH = 9	
		J	R	J	R	J	R	J	R
–	–	0.96	96.8	0.54	98.8	0.41	98.5	0.84	99.0
PEOB[b]	15	2.18	99.7	0.98	99.1	0.67	99.4	2.40	99.9
PP[c]	15	2.62	99.4	1.46	97.1	1.27	97.0	2.88	99.9
DEAE[d]	15	2.49	99.7	0.98	99.1	0.96	98.8	2.56	99.9
DEXSU[e]	15	1.84	98.8	0.84	98.9	0.88	99.4	3.12	99.9

[a] – irradiation time.
[b] – non-ionic copolymer.
[c] – polypeptide.
[d] – positively charged polymer.
[e] – negatively charged polymer.

The results confirm the critical importance of fouling in membrane phenomena invariably connected with the presence of polyanions in natural systems along with hydrophobic molecules and, particularly, hydrophobic anions. They reveal that sulfonated polystyrene membranes have enormous advantages over quarternized membranes in their resistance to fouling. It is also obvious that anionic molecules of intermediate and high-molecular weights are responsible for fouling.

4.3. THE EFFECT OF IONIC NATURE OF SOLUTE ON SEPARATION EFFICIENCY

GREGOR [1] determined the properties of those ultrafiltration membranes of graded porosity which had sulfonic acid groups on their outer surfaces and inner pore surfaces. GREGOR [1] explained the non-fouling character of sulfonic acid membranes by electrostatic repulsion between the fixed groups and the particles of negative charge present in the solution being permeated. He also proved that no metallic or other cations are adsorbed on these membranes and they retain their hydrophilic nature. Figure 4 [5] shows the relationship between the rejection coefficients and the molecular weights of different solutes. These solutes were present at relatively low concentrations (about 0.1% or 0.1 M) and each of them was the only solute in solution. These data were plotted for sulfonic acid membrane of intermediate porosity at 0.4 MPa.
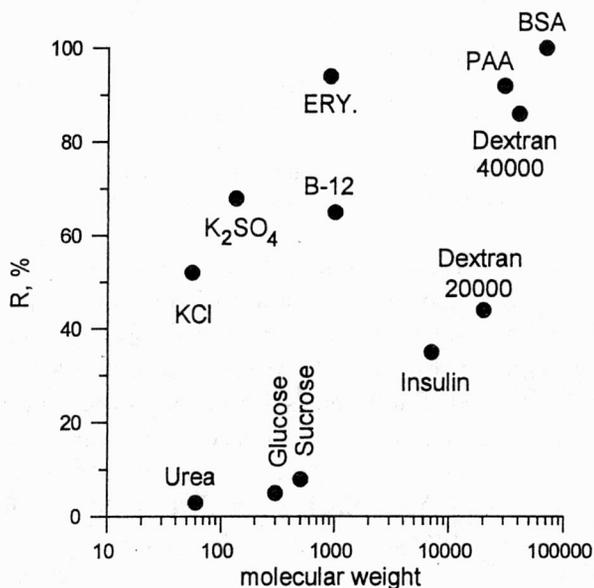

Fig. 4. Rejection coefficient versus molecular weight
of the solute for sulfonic acid fixed-charge membrane of intermediate porosity
($\Delta P = 0.4$ MPa) (PAA – polyacrylic acid; BSA – bovine serum albumine; ERY – erytrosin) [1]

It can be seen that uncharged solutes of low molecular weights (urea, glucose) passed through the membrane as readily as the solvent. In the case of ionic solutes, the rejection of sodium chloride was approximately 60%, while that of sodium sulfate reached 80% because the membrane has a character of fixed sulfonic acid and therefore the selective rejection of doubly charged anions prevails over monovalent ones. The rejection of erythrosin (MWCO 800) was satisfactory, while that of vitamin
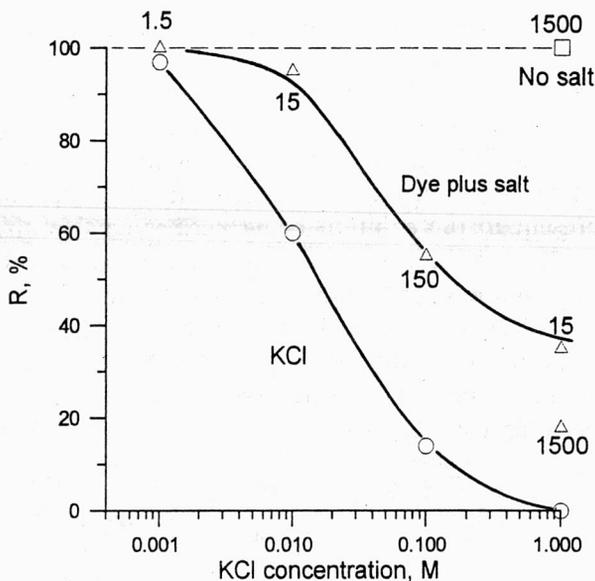
Fig. 5. Dye and salt rejection as a function of the concentration of each
of them for sulfonic acid fixed-charge membrane

B_{12} (MWCO 1300) was not as high because the latter molecule was not charged. Since these membranes were characterized by high concentration of fixed charges, it was found by Gregor that their rejection to ionic solutes was crucially dependent on the ionic strength of the solution. Figure 5 shows the rejection of KCl and the negatively charged erythrosin by a given membrane as a function of the concentration of each of them. When the dye was present in the absence of salt, its rejection was virtually complete, but when the same dye was present in 1 M salt solution, an appreciably lower dye rejection was found. Accordingly to the results obtained by Gregor it can be stated that sulfonic acid membranes rejected solutes on the basis of charge, size and the nature of the charge itself. Negatively charged dyes were rejected more firmly than those charged positively; high salt concentrations lowered the rejection of all charged species, while low ionic strength favoured the rejection of charged species.

5. EXPERIMENTAL

5.1. MATERIALS AND METHODS

Commercially available asymmetric ultrafiltration membranes were used. Of the variety of UF membranes the following types have been chosen: Amicon Diaflo membranes (YC, YM, PM and XM series) and Intersep Nadir membranes (PES, C, CA, PS and PA series).

Aqueous contact angles were determined for each membrane type. In the case of Amicon Diaflo membranes, the polymer samples were prepared as follows: the polymer was extracted from the membrane by dimethylformamide, the solution was poured onto microscopic glasses, the samples were dried at ambient temperature and then in vacuum at 50 °C. Water droplets of 0.05 cm³ volume were deposited on the prepared films and advancing contact angles of liquid droplets were measured by means of TM 50 system (Technicome SA, France) [11]. For Intersep Nadir membranes the procedure of contact angle measurements was similar, except that water droplets were deposited directly on the membranes.

Preliminary studies of membrane transport and separation properties were also performed. An Amicon UF stirred cell was used in those experiments. Volume flux and retention coefficient were determined for organic dyes of anionic nature. The pressure applied was equal to 0.1 MPa. Dye concentration in aqueous solutions amounted to 100 g/m³.

5.2. MEMBRANE CHARACTERIZATION

Table 8

Characteristics of Amicon UF Diaflo membranes [12]–[14]

Membrane type	Membrane polymer	Description	MWCO
YC	regenerated cellulose or cellulose acetate	A high-flow hydrophilic membrane for concentrating low-MW peptides, nucleotides, carbohydrates and antibiotics. Designed for maximum solute recovery.	500
YM	regenerated cellulose	Advanced hydrophilic membranes with exceptionally low non-specific protein binding properties. Recommended where maximum solute recovery is of utmost importance. Outstanding resistance to common biochemical solvents. Oxidizing agents such as chlorine are not required for flux restoration. Most YM membranes used in centrifugal devices are unblocked by substrate. This minimizes adsorption of permeating solutes, enhancing recovery.	1000–100 000
PM	polysulfone	A high-flow hydrophobic membrane, negatively charged below pH = 8. Do not adsorb ionic or inorganic solutes but may adsorb steroids and hydrophobic macromolecules. Compared with YM, they give somewhat more rapid flow.	10 000–30 000
XM	poly(acrylonitrile-co-vinyl chloride)	Moderately hydrophilic (intermediate between YM and PM series), negatively charged. Recommended for concentration of large macromolecules or for separation of particulate from macromolecular material. Excellent resistance to detergents and phosphates.	50 00–300 000

Amicon Diaflo membranes. Amicon's UF membranes are characterized by a very thin (0.1–0.4 μm) dense skin with a controlled pore structure which opens to a much thicker (50–250 μm) spongy layer. Most membranes are cast on porous substrates in order to improve their handling qualities and to allow their reuse. Amicon membranes are inert and non-cytotoxic; moreover, they do not denature biological materials. They are available as YC, YM, PM and XM types varying in hydrophilicity/hydrophobicity and molecular weight cut-off (MWCO). The characterization of Amicon UF Diaflo membranes (constructed mainly according to manufacturer data) is given in table 8 [12]–[14].

Table 9

Characteristics of Intersep Nadir ultrafiltration membranes [15]

Membrane type	Membrane polymer	Description	MWCO
PES	polyethersulfone	Modified PES membranes are moderately hydrophilic, have a broad chemical resistance and can be used over a wide pH range. They have high fluxes and display low fouling characteristics when applied to chemical streams. They are ideally suited to the concentration and purification of a wide range of products, particularly antibiotics.	1000–100 000
C	regenerated cellulose	The C membranes are the most hydrophilic available membranes. They maintain relatively high flow rates when applied to biological streams, but show relatively slow water fluxes. The low-biological fouling characteristics are ideally suited to the concentration and purification of a wide range of biological solutions, particularly where high product recovery is required.	1000–100 000
CA	cellulose acetate	Cellulose acetate membranes are the third most hydrophilic membranes offered in the Nadir range. They have high product fluxes due to low fouling characteristics and are very uniform with narrow cut-off range. CA membranes are often applied to peptide desalting/concentration and where precise MWCO is required.	1000–100 000
PS	polysulfone	The PS membranes are chemically modified to be hydrophilic, have broad chemical resistance and wide pH range compatibility. Also with high water flow rates, PS membrane is the product of choice in the fine prefiltration of enzymes and antibiotics.	1000–100 000
PA	aromatic polyaramide	The modified PA membrane range is hydrophilic, having a very broad chemical resistance which can be also used over a wide pH range. PA membranes can be used with particularly aggressive solvents.	1000–100 000

Intersep Nadir membranes. Intersep offers five types of membrane series with superior performance and stability which allow them to meet the challenges of each specific application. Intersep Nadir membranes are cast on a tough, very porous substrate of polypropylene enabling their improved handling and reuse. Industrial manufacturing of those membranes offers dependably controlled retention characteristics, water permeability and solute transport. Each type of a membrane differs in polymer material, hydrophilicity and environmental resistance. Each series of a given membrane type is characterized by different MWCO. The characterization of UF Intersep Nadir membranes is given in table 9 [15].

6. RESULTS

6.1. MEASUREMENTS OF ADVANCING CONTACT ANGLE: MEMBRANE HYDROPHILICITY

The contact angle is a measure of wettability of a surface. An ideal hydrophilic surface is characterized by a contact angle of $0°$.

The measurements of the contact angles of the Amicon and Intersep Nadir membranes are presented in table 10 and table 11, respectively. Among the Amicon membranes the YM and PM membranes are the most hydrophilic, since their con-

Table 10

Advancing contact angle of water droplet on Amicon membranes

Membrane polymer	Membrane symbol	Contact angle (deg)
Cellulose derivative	YC	67.36
Regenerated cellulose	YM	0
Polysulfone	PM	0
Poly(acrylonitrile-co-vinyl chloride)	XM	50.65

Table 11

Advancing contact angle of water droplet on Intersep Nadir membranes

Membrane polymer	Membrane symbol	Contact angle (deg)
Polyethersulfone	PES-1	50.01
Regenerated cellulose	C-1	54.76
Cellulose acetate	CA-1	53.8
Polysulfone	PS-1	67.6
Polyaramide	PA-1	66.2

tact angles amount to 0°. This observation is partly consistent with literature data
(table 12) [14]. JUCKER and CLARK [14] found that the YM10 and YM30
membranes had very small contact angles, which is conformable to general
expectation that membranes made of regenerated cellulose are relatively hydrophilic.
On the contrary, polysulfone is considered as a polymer hydrophobic in nature and
the measured value of contact angle (0°) for the PM membranes is rather doubtful.
The only explantation is that the polysulfone was modified (prior to membrane
casting) by manufacturer to be hydrophilic. On the other hand, the values of contact
angle measured in the case of the Intersep Nadir PS membranes (table 11) are much
higher that those expected. The manufacturer clearly ascertains that these memb-
ranes are chemically modified to be hydrophilic.

Table 12

Contact angle of water droplet
on Amicon membranes [14]

Membrane	Contact angle (deg)
PM30	42.5
XM50	40.0
YM10	6.5
YM30	7.0
YM1	96.0
YM100	31.0

The XM Amicon membranes are relatively hydrophobic as can be concluded
from the results of static adsorption reported by LAINE et al. [13], and the results
obtained (table 10) are in quite good agreement with literature data (table 12). It can
also be observed that the YC Amicon membranes are the most hydrophobic in this
membrane series.

The Intersep Nadir membranes, according to the manufacturer information,
should be hydrophilic. They can only differ in degree of hydrophilicity. As it can be
seen from data in table 11 the membranes made of polyethersulfone, cellulose acetate
and regenerated cellulose (PES-1, CA-1, C-1, respectively) are most hydrophilic. This
is only partly consistent with manufacturer's suggestion – the most hydrophilic are
the CA and C membranes. The contact angle measurements for the PA membranes
indicate that these membranes are the least hydrophilic, which is consistent with the
general expectation.

Taking into account some inconsistency of the results obtained with the
expectation and literature data, it should be stated that the contact angle measure-
ment is rather unprecise method of surface wettability determination. It is known
that surface roughness and porosity can cause the increase in the values of contact
angles. JUCKER and CLARK [14] observed that the surface of the YM1 membrane
(table 12) was macroscopically more rough than the other membranes and they

presumed that this was the cause of the high value of contact angle. The above method of hydrophilicity determination should be supported by adsorptive fouling tests.

6.2. TRANSPORT AND SEPARATION PROPERTIES

The volume fluxes of dye solutions and rejection coefficients for selected Amicon and Nadir Intersep membranes are given in table 13 and table 14, respectively. It has been found that the retention coefficient for high-molecular-weight dyes (helion grey, direct meta black) exceeds 97% for all membranes tested. The efficiency of organic dye separation from aqueous solutions is surprisingly high, particularly in relation to MWCO of the membranes investigated (1000 or 10000). Even the rejection of low-molecular-weight dye (methyl orange) approaches 50% for all membranes of MWCO equal to 1000. The results obtained indicate that the molecular sieve-mechanism alone is insufficient to explain the separation of organic dyes by hydrophilic UF membranes. The electrostatic interaction between the membrane and anionic macroparticle can be regarded as a factor supporting the efficiency of ultrafiltration process.

Table 13

Transport and separation properties of the selected Amicon membranes*

Dye	Membrane YM-1 (MWCO 1000)			Membrane PM-10 (MWCO 10000)		
	J_d (m^3/m^2d)	J_d/J_w –	R (%)	J_d (m^3/m^2d)	J_d/J_w –	R (%)
Methyl orange (m.w. 327)	0.13	1.0	47.0	1.62	0.89	12.7
Helion grey (m.w. 617)	0.13	1.0	97.4	1.27	0.69	98.8
Direct meta black (m.w. 781.2)	0.13	1.0	99.5	1.26	0.69	99.5

* – transmembrane pressure 0.1 MPa.
J_d – volume flux of dye solution.
J_w – water volume flux.

In order to compare the fouling effects, the so-called fouling index is given in tables 13 and 14. It has been calculated as the ratio of volume flux of dye solution to water flux before ultrafiltration process. It was suggested that mainly adsorption and deposition (gel layer) of the dye particles on the membrane surface or their adsorption in pore interior were responsible for flux decline. The highest the value of fouling index, the less fouling tendency of a given membrane. The YM-1 Amicon membrane is characterized by a fouling index equal to 1.0, which is consistent with the measured values of contact angle (table 10). Among the Nadir Intersep

Table 14

Transport and separation properties of the selected Nadir Intersep membranes*

Dye	Membrane PES-1 (MWCO 1000)			Membrane C-1 (MWCO 1000)			Membrane CA-1 (MWCO 1000)			Membrane PS-1 (MWCO 1000)			Membrane PA-1 (MWCO 1000)		
	J_d (m^3/m^2d)	J_d/J_w –	R (%)	J_d (m^3/m^2d)	J_d/J_w –	R (%)	J_d (m^3/m^2d)	J_d/J_w –	R (%)	J_d (m^3/m^2d)	J_d/J_w –	R (%)	J_d (m^3/m^2d)	J_d/J_w –	R (%)
Methyl orange (m.w. 327)	0.19	0.95	58.5	0.1	1.0	73.7	0.11	0.71	69.6	0.13	1.0	41.6	0.6	0.85	46.1
Helion grey (m.w. 617)	0.15	0.75	99.8	0.1	1.0	99.4	0.11	0.71	99.8	0.09	0.7	99.4	0.41	0.59	99.3
Direct meta black (m.w. 781.2)	0.17	0.85	99.7	0.09	0.9	99.5	0.11	0.71	99.5	0.1	0.78	99.7	0.28	0.4	99.6

* – transmembrane pressure 0.1 MPa.
J_d – volume flux of dye solution.
J_w – water volume flux.

membranes only C-1 membrane exhibits the fouling index equal almost to 1.0, which is also in good agreement with the data in table 11. On the other hand, the polysulfone and polyaramide Intersep Nadir membranes (PS-1 and PA-1, respectively) are characterized by rather low fouling indexes, so they are less hydrophilic as it has been indicated by the measurements of contact angles.

7. CONCLUSIONS

1. Hydrophilic ultrafiltration membranes are less susceptible to fouling than membranes made of hydrophobic polymers. The importance of hydrophilicity for the prevention of adsorption is based on the fact that hydrophilic surface attracts water particles.

2. In practical use, ultrafiltration membranes having fixed charges are better than noncharged membranes. They are characterized by three variables: sign and density of the charge and pore size, so they are less fouled than noncharged membranes due to the gel layer formation.

3. In terms of membrane phenomena, the conclusive test of hydrophilic or nonfouling character is based on employing the membrane in a pressure driven process. The contact angle measurement is rather unprecise method of surface wettability determination and should be always supported by adsorptive fouling tests.

4. Membrane manufacturers offer a wide spectrum of hydrophilic ultrafiltration membranes characterized by different retention characteristics, water permeability and solute transport. Commercial Amicon and Intersep Nadir membranes can be used in the ultrafiltration of organic dyes. The membranes yielded an over 97% retention of high-molecular-weight dyes. The volume flux of dye solutions at a pressure of 0.1 MPa ranged from 0.1 to 1.6 m^3/m^2d. The membranes made of regenerated cellulose are less capable of fouling.

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MEMBRANY HYDROFILOWE DO SEPARACJI ORGANICZNYCH MAKROCZĄSTECZEK

Scharakteryzowano metody modyfikacji i przedstawiono zastosowanie nowych hydrofilowych membran ultrafiltracyjnych. Zwrócono szczególną uwagę na istotne znaczenie hydrofilowości w zapobieganiu niekorzystnym zjawiskom (*fouling*, adsorpcja) w ciśnieniowych procesach membranowych. Wykazano, że membrany hydrofilowe są mniej podatne na *fouling* niż membrany wykonane z polimerów hydrofobowych. Omówiono również pewne aspekty określania stopnia hydrofilowości (tj. pomiary kąta zwiłżania).

Przedstawiono porównawczą charakterystykę handlowych membran hydrofilowych (Amicon Diaflo i Nadir Intersep) o różnym stopniu powierzchniowej hydrofilowości. Określono takie parametry membran jak: kąt zwiłżania wodą, strumień wody, objętościowy strumień roztworu barwnika, współczynnik retencji barwnika i indeks *foulingu*. Testowane membrany mogą być wykorzystane do ultrafiltracji barwników organicznych. Membrany te są zdolne do zatrzymywania 97% barwników o dużej masie cząsteczkowej. Najmniej podatne na *fouling* były membrany wykonane z regenerowanej celulozy.

ГИДРОФИЛЬНЫЕ МЕМБРАНЫ ДЛЯ СЕПАРАЦИИ ОРГАНИЧЕСКИХ МАКРОЧАСТИЦ

Проведена характеристика модификации и представлено применение новых гидрофильных ультрафильтрационных мембран. Особенное внимание было обращено на существенное значение гидрофильности в предохранении перед бесполезными явлениями (*fouling*, адсорбция) в мембранных процессах с использованием давления. Было обнаружено, что гидрофильные мембраны являются менее податливыми к *фулингу*, чем мембраны, выполненные из гидрофобных полимеров. Обсуждены также некоторые аспекты определения степени гидрофильности (т.е. измерения угла увлажнения).

Представлена сравнительная характеристика торговых гидрофильных мембран (American Diaflo и Nadir Intersep) разной степени поверхностной гидрофильности. Определены такие параметры мембран, как: угол увлажнения водой, струя воды, объемная струя раствора красителя, коэффициент ретенции красителя и индекс *фулинга*. Тестируемые мембраны могут быть использованы для ультрафильтрации органических красителей. Эти мембраны могут задерживать 97% красителей большой молекулярной массы. Наименее податливыми к *фулингу* были мембраны, выполненные из регенерируемой целлюлозы.