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Polymeric Ultrafiltration Membranes and Surfactants

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ABSTRACT

Surfactants have been extensively used in ultrafiltration processes such as membrane cleaning,removal of surfactants or other organic toxic compounds and metal ions from solutions and estimation of interactions at surfactant and membrane interface. The aim of this review is to present the possibilities that arise from the data reported in the literature on the field of ultrafiltration (UF) membranes and surfactants. This data is classified into five groups and a brief description of each article is given. Pretreatment of membranes with surfactant solutions can lead to performance increase of UF process. By Micellar-Enhanced Ultrafiltration the separation of low molecular weight toxic substances and heavy metals is possible, extending the applications of conventional UF (e.g. separation of proteins). Through estimation of the type of interactions on membrane surface with surfactants the prediction of retention and removal of small size substances, the prevention of fouling, the modification of surfactant-membrane system, the design of new surfactant-membrane system could be achieved. Finally economical aspects of UF-surfactant processes are given.

Key Words: Polymeric; Ultrafiltration; Membranes; Micellar-enhanced ultrafiltration.

1. INTRODUCTION

Surfactants can be classified as the most versatile products of the chemical industry. They are basic constituents of a variety of chemical products such as

detergents, paints, dyestuffs, cosmetics, pharmaceuticals, pesticides, fibers, plastics, etc. Moreover surface active agents play a vital role in the oil industry, for example in enhanced and tertiary oil recovery. They are also occasionally used for environmental protection, e.g., in oil slick dispersions (Rosen, 1989a; Tadros, 1984).

As a consequence of their extensive use and the relative environmental and economical impacts, their removal from aqueous streams is frequently required in occasions as:

- Detergent containing process streams encountered in surfactant based manufacturing processes (Forstmeier et al., 2002).
- Laundry wastes (Bhattacharyya et al., 1974), and
- Surfactant aided processes such as micellar-enhanced separations, electroplating, cleaning procedures etc. (Goers et al., 2000; Mawson, 1997).

Membrane technology can effectively be used for separation as an alternative method friendly to the environment in terms of pollution impact and energy consumption. By membranes applications, recyclable streams to the main manufacturing process are generated (Cheryan and Rajagopalan, 1998).

The role of a membrane in separation processes is based on its action as a selective barrier. In general, separation takes place on the surface of the membrane, or in the membrane, itself, where the molecular interactions compete with one another. Thus, it is necessary to understand what goes on in the vicinity and inside the membrane. The respective mechanism of permeation is the key.

Two factors should be examined thoroughly, selectivity and total flow, in order to improve the separation efficiency of a membrane. Both factors can be studied considering the actual transport mechanism through the membrane (Kammermeyer and Hwang, 1984).

2. THEORY

2.1. Surfactants

A surface-active agent is a substance that when present at low concentration in a system has the property of adsorbing onto surfaces or interfaces with a specific orientation and of altering (usually reducing) significantly the surface or interfacial free energies. This compound is termed also surfactant, amphiphile or tenside (Myers, 1988a). One part of a surfactant's molecule has an affinity for non-polar media and the other part has an affinity for polar media. This behaviour is due to its characteristic molecular structure

(amphipathic), consisting of a structural group with little attraction to the solvent (lyophobic, hydrophobic in the case of water) and a group with strong attraction to the solvent known as lyophilic or hydrophilic group. The hydrophobic group is usually a long alkyl chain and the hydrophilic group an ionic or highly polar group. Depending of the nature of hydrophilic group surfactants are classified as anionic (−), cationic (+), zwitterionic (+ −) and nonionic (Myers, 1988a).

A fundamental property of surfactants is their capability to form micelles (colloidal-sized clusters or aggregates in solution). The concentration at which micellization occurs is called *critical micelle concentration* (CMC), below of which surfactants exist as unassociated molecules (Myers, 1988b). Changes in most physical properties of a surfactant solution are observed at the neighborhood of CMC. The existence of micelles affects a number of important interfacial phenomena, such as detergency and solubilization. Solubilization is defined as the spontaneous dissolving of a substance by reversible interaction with the micelles of a surfactant in a solvent to form a thermodynamically stable isotropic solution with reduced thermodynamic activity of the solubilized material. The importance of this phenomenon from a practical point of view is that normally insoluble substances are being dissolved.

2.2. Ultrafiltration

Ultrafiltration (UF) is one of the membrane separation processes that are grouped together under pressure—driven processes. UF is used to remove particles in the size range of 0.001–0.02 μm. Solvents and salts of low molecular weight will pass through the membrane, whilst larger molecules are retained. Thus, UF is principally used in the separation of macromolecules having molar mass in the range of 300 to 300,000. Ultrafiltration membrane performance is generally characterized by molecular weight cut-off and by notional pore size. However, cut-off values are only approximate, since the same molecules can have different radii depending on solution properties such as pH and ionic strength. In addition, a variety of physico-chemical interactions could be developed between solute and membrane surface. These interactions may be net, repulsive or attractive and lead to solute binding at the membrane surface, resulting in a reduction of permeability. Osmotic effects in UF membranes are small and the applied pressure, of the order of 1–7 bar, is primarily to overcome viscous resistance of liquid permeation through the porous network of the membrane. Commercial UF membranes are asymmetric with a thin skin 0.1–1 μm thick, of fine porous structure exposed to the feed side. This skin is supported on a highly porous layer 50–250 μm thick giving the unique requirement of high permeability and permeselectivity. Typical membrane materials are polylsulphone, polyethersulphone, polyacrylonitrile, polyimide, cellulose acetate,

polyvinylidenefluoride, aliphatic polyamides, and ceramics, e.g. zirconium and aluminium oxides. The separation mechanism of UF membranes is conceived as a sieving action, where an increase in applied pressure increases the flux rate. However, a phenomenon referred to as concentration polarization puts an upper limit on the practical flux rates. Concentration polarization arises from a build-up of solute concentration on the feed side of the membrane and this ''boundary layer'' formation results in an additional resistance to that of the membrane for overall liquid permeation. At sufficiently high pressures gelation of macromolecules can occur and a thin gel layer forms at the membrane surface acting as a secondary membrane. As well as the formation of a gel layer, another phenomenon, ''membrane fouling,'' often occurs. Fouling gives rise to a steadily declining flux with time and can be attributed to a variety of mechanisms including changes in the chemical nature of the gel layer as crosslinking and compaction (Scott, 1996).

There have been a number of different approaches used to describe solute and solvent transport through ultrafiltration membranes. Both Kedem-Katchalsky analysis and Stefan-Maxwell multicomponent diffusion equations were developed directly from the principles of irreversible thermodynamics with the solute and solvent flux related to the pressure and concentration driving forces via a set of phenomenological coefficients. In contrast, the solvent and solute flux in the hydrodynamics models are evaluated directly solving the equations of motion for a well-defined solute (assumed spherical) in a well-defined pore (typically cylindrical) (Zydney, 1996).

Permeate rates (flux) can be measured as a function of applied pressure at constant temperature. According to Hagen-Poiseuille pore model of ultrafiltration, flux is predicted by the equation:

$$J = \frac{\varepsilon \cdot d_p^2 \cdot P_T}{32 \cdot \Delta\chi \cdot \mu} \tag{1.1}$$

where J is the flow rate through the membrane, d_p is the channel diameter (in this case the mean pore diameter), P_T is the applied transmembrane pressure, μ is the viscosity of the fluid permeating the membrane, $\Delta\chi$ is the length of the channel (the membrane ''skin'' thickness) and ε is the surface porosity of the membrane. This equation can be rewritten:

$$J = \frac{P_T}{R_M} \tag{1.2}$$

where R_M is the intrinsic membrane resistance. When fouling occurs, another resistance factor (R_F) is added to the model:

$$J = \frac{P_T}{R_M + R_F} \tag{1.3}$$

An additional resistance term R_G can be added to the flux equation to account for concentration polarization, which is a function of operating parameters and physical properties (Cheryan, 1998):

$$J = \frac{P_T}{R_M + R_F + R_G} \tag{1.4}$$

3. RECENT RESEARCH ACTIVITY

Data on surfactant-membrane research field are abundant since a great variety of surfactants and membranes are available connected with UF processes. The classification of the recent literature in the field of UF membranes and surfactants into the following groups was based mainly on the role of surfactant related to UF process and on the objectives of each article:

i) Pretreatment for fouling control.
ii) Solubilization of sparingly soluble in water substances and determination of their partition coefficients by UF.
iii) Micellar-enhanced ultrafiltration where solubilized substances (mainly toxic organic substances, heavy metals) are filtered out using UF.
iv) Interaction behaviour.
v) Water management.

Recent fundamental and applied research activity focuses on problems related to UF membranes—surfactant processes (flux decline, membrane fouling, low performance, energy consumptive and cost enhancing processes, limited knowledge of mechanisms occurring at the membrane surface for the removal of organic/inorganic species in connection with the use of surfactants via UF or MEUF etc.). Investigation includes mainly determination of interactions at membrane surface, reveal of mechanisms controlling the separation, examination of factors affecting UF performance, prevention of fouling, surfactant pretreatment for performance enhancement, modeling and optimization of various processes, selection of the appropriate surfactant system, examination of selective removal of various pollutants.

An evaluation of published research on the field of separation from aqueous streams using surfactants has been done by Akay and Wakeman (1993) covering a chronological period up to 1992. It includes the following processes: ultrafiltration (UF), micellar-enhanced ultrafiltration and reverse osmosis (RO). The effect of process variables (membrane characteristics,

surfactant type, feed concentration, crossflow velocity, transmembrane pressure, and temperature) has been reviewed.

In this review, the relevant literature of the last decade is concentrated in tables and divided in five categories. Complementary data on the membranes and surfactants used are given in Appendices A and B.

3.1. Pretreatment for Fouling Control

Ultrafiltration is a very efficient process for the separation of macromolecules such as proteins, polyphenolic compounds and microorganisms. A common problem in the application of ultrafiltration membranes in separations is the decline of permeate flux. Fouling phenomena frequently are observed due to solute accumulation at the membrane-solution interface and solute adsorption onto membrane pores (Fane and Fell, 1987). It is evident that solute–solute interactions determine the surface properties and porosity of membrane and can result in irreversible flux loss (Aimar et al., 1986). Therefore, the need for flux improvement, increased membrane-life and easier cleaning led to the development of new techniques for the modification of membrane surface (Brink and Romijn, 1990). The principle of these techniques is the increase in hydrophilicity and modification of surface charge by pretreatment with specific substances. So far, the use of enzymes, carbon coating and surfactants has been proved very successful for membrane pretreatment. Recent research includes pretreatment with surfactant solutions particularly nonionic, anionic or their combinations. Surfactant pretreatment is achieved by adsorption from stagnant solution.

Pretreatment with surfactants has been applied mainly for the removal of protein BSA by ultrafiltration (Chen et al., 1992; Fane et al., 1985), for the purification of wastewaters (effluents of papermill, natural brown water) (Maartens and Jacobs, 2002; Maartens et al., 2000), and for biofouling prevention through inhibition of bacterial attachment to membrane surface (Flemming and Schaule, 1988), (Table 1). A significant contribution to this issue is Speaker's article on status of surface modification for minimizing dirt retention using organized monomolecular assemblies with a variety of hydrocarbon and fluorocarbon surfactants to counter fouling from humic substances and to reduce flux decline (Speaker, 1993). When long nonionic surfactants are used for pretreatment, the surface becomes more permeable and more hydrophilic (monomolecular layer or Langmuir-Blodgett layer) by reduction of the availability of hydrophobic sites (Speaker, 1993). In contrast, small anionic surfactants cause reduction of solute deposition by altering the electrostatic interactions between solute-membrane surface. Pretreatment with mixtures of anionic–nonionic surfactants yields to significant

Table 1. Pretreatment with surfactants.

Reference	Membrane-MWCO	Surfactant	Aim–experimental-results
Fane et al. (1985)	Dynel[1.1], 100000 PS[1,2], 30000 Reg. Cell.[1.3], 30000 Reg. Cell.[1.4], 50000 PS[1.5], 10000 PAN[1.6], 10000 PA[1.7], 100000	N5, N13, N100[2.1]	UF flux enhancement of BSA solution, through membrane pretreatment with surfactant solutions. Adsorption from stagnant surfactant solution, b-SC. Significant improvement in flux for UF of protein (20%–50%), in membrane reuse and cleaning.
Flemming and Schaule (1988)	PA, - PS, - PES, - Polyetherurea, -	Triton X-100[2.5] Dodecylguanidineacetate	A microbiological approach of biofouling on membranes. Membrane immersion in surfactant solution. Surfactants have been investigated for the prevention of bacterial adhesion to the surface. Biological affinity of different membrane materials towards different bacteria has been detected.
Chen et al. (1992)	PS[1.2], 30000 PS[1.8], 30000	Aeorosol OT[2.2] Sandopan D-TC[2.3] Gardisperse AC[2.4] N100[2.1]	Fouling reduction in UF of BSA using membrane pretreatment with anionic and mixed anionic–nonionic surfactant solutions. Passive adsorption from surfactant solution, b-SC. Flux improvement is higher when anionic–nonionic surfactants are used in pretreatment. Optimization of fouling reduction and mechanisms of surfactant pretreatment are investigated.

Nwuha and Noworyta (1993)	PS[1.60], 30000 CTA[1.61], 20000	Triton X-102[2.61] Tengitol NP-7[2.62] Tencid-HC-ST[2.63]	Improvement of UF performance by surfactant pretreatment. Membrane immersion in surfactant solutions, b-SC. The factors affecting membrane pretreatment and UF performance are examined.
Maartens et al. (2000)	PS#, 40000	Triton X-100[2.5] Pluronic F108[2.6]	Fouling prevention of UF membranes for the purification of natural brown water and humic acid solutions by membrane pretreating with surfactants. Membrane pretreatment with surfactants, Feed-and-bleed UF system. Precoating of membrane with surfactants influences foulants adsorption and retention, as well as UF flux. Cost reduction in chemical cleaning treatment and longer membrane-life are achieved.
Maartens and Jacobs (2002)	PES[1.9], -	Triton X-100[2.5] Pluronic F108[2.6]	Membrane fouling prevention and cleaning in UF of pulp and paper effluent. Membrane surface modification with surfactant solution. c-CF UF of effluent. Reduction of foulant adsorption after membrane pretreatment with surfactants and improvement of the effectiveness of cleaning methods.

#: cast from a solution of UDEL P3500 polysulfone in N-methyl-2-pyrrolidone, dried with glycerol, and stored at room temperature.
(-): no available data.

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flux improvement and fouling resistance reduction compared with that of the pretreatment with single surfactant.

In the relevant literature membrane pretreatment has been evaluated as a simple procedure with practical applications and a number of factors involved (extent of flux improvement, amount and kind of surfactant used, appropriate contact time, possibility of reuse and retreatment etc.) have been investigated.

3.2. Determination of Partition Coefficients or Equilibrium Distribution Constants in Solubilization

Ultrafiltration has been used as a method for the determination of partition coefficients of insoluble in water substances in surfactant solutions. Aboutaleb et al. (1977) applied this technique to study the solubilized system of benzoic acid in nonionic surfactant solutions. The determination of the preservative (benzoic acid) distribution coefficient between the aqueous and micellar phase is of great interest since its activity depends on the amount free in the solution. Ultrafiltration technique is fast and able to estimate the preservative activity at low solute concentration. This method is considered more convincing in comparison with the solubility method (which is one point technique) and equivalent to molecular sieve technique. The equilibrium distribution constant of phenol in aqueous solutions containing surfactant micelles has also been studied (Sabaté et al., 1999; Syamal et al., 1997), since the removal of toxic organic solutes present even in traces in aqueous streams is a serious separation problem. The determination of this constant indicates the affinity of phenol for the micelles and is proved very useful to predict the efficiency of MEUF. A mathematical mass-transfer model is introduced by Syamal et al. (1997) to describe the mobility of the solute from the surface to the center of the micelle. The model based on specific assumptions leads to an appropriate equation for the equilibrium parameter indicating the dependence of the extent of solubilization on the operating conditions. The derived equation provides a simple design criterion for the determination of the efficiency of MEUF process. Also, Sabaté et al. (1999) estimated equilibrium distribution constants of phenol between surfactant micelles and water by MEUF using commercial ultrafiltering centrifuge tubes. They suggested a phenomenological mathematical model to calculate the equilibrium parameter K_s by a simple method, which does not need expensive equipment. The obtained values of K_s were similar to those reported in the relative literature. The computed values of K_s were used to predict the permeate phenol concentration in a continuous tangential UF device. The calculated and measured concentrations were in agreement. More details on this field are given briefly in Table 2.

Table 2. Solubilization studies.

Reference	Membrane-MWCO	Surfactant	Aim–experimental-results
Aboutaleb et al. (1977)	UM-05[1.75] Pelicon 100[1.76], 1000	Tween 20[2.30] Tween 60[2.31] Tween 80[2.29] Myrj 52[2.32] Myrj 53[2.33] Emulgin C 1000[2.34] Emulgin C 1500[2.35]	Determination of benzoic acid partition coefficient by UF. b-SC Results of UF technique comparable to molecular sieving method. Partition coefficient is given by: $K_m = C_m/C_w$.
Syamal et al. (1997)	Asymmetric CA[1.30], 1000	CPC[2.12]	Quantification of phenol solubilization in cationic micelles under different operating conditions. b-SC Equilibrium parameter: $H = 1/\Phi_s(c_0/c_s - 1)$
Sabaté et al. (1999)	Reg. Cell.[1.31], 5000, 10000, 30000	SDS[2.10] CPC[2.12] C16E20[2.36] C12E23[2.37]	Determination of equilibrium distribution constants, K_s, of phenol between surfactant micelles and water. b-dead end UF By a set of equation K_S is obtained. Estimations of K_S have allowed to predict phenol permeate concentration in c-CF MEUF.

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3.3. Micellar-Enhanced Ultrafiltration (MEUF)

The use of micellar systems (or in a larger sense of all kinds of surfactant-based systems including microemulsion, vesicles, etc.) for separation purposes has become a field of increasing interest. These systems have proved to be extremely promising in different potential applications, the most demonstrative of which are: removal of metal ions from aqueous environments, removal of low molecular weight organic compounds, resolution of enantiomers (Hebrant et al., 2001).

Micellar-enhanced ultrafiltration can be defined as a technique that can be used to separate the micellar phase using membranes with a pore size smaller than the micelle diameter. In this process, surfactant is added to an aqueous stream containing solutes, which should be removed mainly for environmental reasons or recovery requirements and which are too small to be rejected by UF membranes. The surfactant at concentration greater than its critical micelle concentration (CMC) forms aggregates (micelles) into which the above substances are dissolved or solubilized. The stream passes through an ultrafiltration membrane with pore sizes smaller than the size of micelles. The membrane rejects the micelles containing solutes or pollutants. MEUF was first proposed by Scamerhorn (Scamehorn and Harwell, 1988) as an alternative separation method to solvent extraction, which is considered generally superior in effectiveness and efficiency from economical and environmental point of view in comparison to conventional techniques, such as distillation and adsorption. Dissolved toxic organics or heavy metals can be removed from aqueous wastewaters without in general introducing substantial toxicity from residual surfactant. Modifications of MEUF are colloid-enhanced ultrafiltration (CEUF) methods including ligand-modified micellar-enhanced ultrafiltration (LM-MEUF) and polyelectrolyte-enhanced ultrafiltration (PEUF). In using CEUF, a water-soluble colloid is added to an aqueous solution containing organic and/or inorganic solutes and the removal of colloid and solubilized or bound solute species is achieved.

In MEUF the following characteristics are common: 1) a secondary layer of surfactant in liquid crystalline form deposits on the membrane surface due to membrane polarization effects, 2) the secondary layer causes membrane fouling, therefore reducing its permeability, 3) the layer enhances the ability of the membrane to reject the target solute, 4) the permeate contains unbound solute and usually monomeric surfactant, although this statement is not true at very high surfactant concentration in the feed upstream the membrane and when interactions between monomeric surfactant-membrane are significant, 5) a maximum permeate flux is reached after some time, and thereafter the permeation flux slows down

(Talens-Alesson et al., 2001). This method is limited to transparent solutions above the Kraft point, especially of ionic surfactants but also of nonionics containing a long alkyl chain. In the latter case, the ultrafiltration can be carried out at a narrow change of temperature (between the Kraft point and the cloud point) (Szymanowski, 2000).

The binding force between surfactants and solutes to be recovered is indispensable to attain effective rejection in MEUF. By the micellar extraction of metal ions for which many examples have been reported in the literature two different types of micellar techniques have been applied. In the first case, a simple electrostatic attraction of metal ion to the surface of negatively charged micelles occurs. Multivalent metal ions have been successfully recovered through MEUF using anionic surfactants (e.g. SDS) having opposite charge (Scamehorn et al., 1994). However, the application of this method is limited, since it is very sensitive to ionic strength effects and the extent of binding of multivalent ions is controlled by the ion-exchange equilibria. In the second case, the formation of a real complex or cluster between a metal ion and a lipophilic extractant (or ligand, or chelating agent) solubilized in the hydrophobic core of micelles is formed. With this technique called ligand-modified micellar-enhanced ultrafiltration (LM-MEUF), selective rejection of metal ions having the same electric charge could be achieved (Hebrant et al., 1994; Ismael and Tondre, 1992; Klepac et al., 1991).

Organic solutes (e.g. phenols) are generally solubilized in micelles and then their removal is possible (Choi et al., 1998; Hong et al., 1994). The binding force between organic solute and micelle is determined by strong ionic or polar interactions, which are affected by a number of factors (structure of surfactant and organic solute, shape and size of micelle, presence of electrolytes and additives, pH etc.) (Rosen, 1989b).

Polyelectrolyte-enhanced ultrafiltration (PEUF) is a process in which a water-soluble polymer or polyelectrolyte, with an opposite valence to that of the ion to be removed, is added to the polluted aqueous stream. The target ion binds or adsorbs onto the polyelectrolyte (e.g. cationic polyelectrolyte-chromate ion) and the stream is subsequently treated by UF to reject the polymer (Sriratana et al., 1996). Water-soluble polyelectrolyte-surfactant complexes, involving oppositely charged species, have been used for the removal of toxic organic or inorganic ions present in contaminated aqueous streams via MEUF (e.g. tert-butyl phenol) (Guo et al., 1997). By adding surfactants in UF feed at concentration below CMC, membrane modification can occur via their absorption on membrane surface and removal of ions (chromate, nitrate, perchlorate anions) can be achieved. The use of the extended Nernst-Planck model in conjunction with Donnan equilibrium leads to prediction of the separation of mixtures of electrolytes

Table 3. Micellar-enhanced ultrafiltration, colloid-enhanced ultrafiltration, surfactant-modified ultrafiltration, ligand-modified and polyelectrolyte-enhanced ultrafiltration.

Reference	Membrane-MWCO	Surfactant	Aim–experimental-results
Ismael and Tondre (1992)	Cellulosic$^{(1.70)}$, 10000	CTAB$^{(2.8)}$	Implementation of metal-solubilized extractants in the field of metal recovery. b-SC. Total removal of Ni(II) from mixture with Co(II)
Tondre et al. (1993)	Cellulosic$^{(1.70)}$, 10000	CTAB$^{(2.8)}$ $C_{12}EO_6$$^{(2.20)}$	Selective separation of metal ions. b-SC. Removal of copper is achieved by taking into account the time parameter.
Ismael and Tondre (1993)	Cellulosic$^{(1.69)}$, 10000, 30000	CTAB$^{(2.8)}$ $C_{12}EO_6$$^{(2.20)}$	Examination of different aspects (equilibrium, kinetic conditions) of the extraction and back-extraction of metal ions in micellar systems using UF. b-SC. Micellar extraction (via C_{11}-HQ and HQ) of metal ions (Co(II),Ni(II), Cu(II)) in micellar system and possibility of their recovery is investigated by ultrafiltration. Kinetic separations can be achieved when ''micellar extraction'' is combined with ultrafiltration.

De la Guardia et al. (1993)	CA, 10000	CTAB[2.8] Brij-35[2.25]	Separation of trace amounts of aluminium from aqueous solution by the formation of a complex with LG. b-SC. MEUF was successfully employed to preconcentrate the analyte and to improve the sensitivity of its determination by flame atomic emission spectrometry.
Uchiyama et al. (1994)	-, 5000	CPC[2.12]	Separation of toxic TBP from aqueous streams. Using polyelectrolyte (PSS#)/surfactant complexes by CEUF. b-SC. Solubilization of TBP in PSS#/CPC complexes was determined by dialysis technique and the rejection of TBP from aqueous streams containing these complexes was studied and compared to MEUF. The dependence of fluxes on operating conditions and on feed concentrations of CPC and PSS# are reported.

(*continued*)

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Table 3. Continued.

Reference	Membrane-MWCO	Surfactant	Aim–experimental-results
Scamehorn et al. (1994)	CA[1.16], 1000, 5000	SDS[2.10]	Separation of divalent cadmium, zinc, copper and calcium ions from aqueous solutions using MEUF. b-SC. Removal of toxic metals and their mixtures is possible with rejections of at least 96%.
Reiller et al. (1994)	PS[1.5], 10000	SDS[2.10] STS[2.29]	Study of adsorption of uranyl ions at the surface of micelles by MEUF and laser-induced spectrofluorimetry. c-CF. The association of uranyl ion to surfactant micelles was investigated. It was observed that uranyl ion is more tightly bound to micellar surface than the d-block divalent ions (Cu(II), Co(ii)). A limited rejection rate is presented.

Premauro et al. (1994)	Hydrophilic cellulose membranes[1.64], 10000	Triton X-100[2.5]	Selective separation of transition metal ions through LM-MEUF. b-SC. The effective accumulation of Ni(II), Cu(II), Co (II) Mn(II) and Zn(II) in chelating aggregates consting of surfactant micelles and the ligands: PAN and C_4-PAN) was examined in combination with UF. A multistage process is proposed in order to improve the separation efficiency.
Huang et al. (1994a)	Anisotropic acrylanitriyl[1.63], 2000	Sodium salt of DCA[2.64] SDS[2.10] M-C-Thin lecithin[2.65] Centrolex F lecithin[2.66] Protein	Removal of heavy metals (Cd, Pb, Cu, Ni Zn) from simulated and a metal finishing plant wastewaters. c-CF. Selective and total removal of metal ions in combination with natural surfactants have been examined. The effects of surfactant types, metal types and surfactant/metal ratio on MEUF performance have been investigated.

(*continued*)

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Table 3. Continued.

Reference	Membrane-MWCO	Surfactant	Aim–experimental-results
Huang et al. (1994b)	Anisotropic acrylanitriyl[1.63], 2000	Sodium salt of DCA[2.64]	Removal of heavy metals (cadmium, lead, copper, nickel and zinc from waste streams. c-CF. Selective and total removal of metal ions is achieved. The optimal surfactant/metal ratio for substantial metal removal (rejection > 99.9%) is around 2,5 for DCA.
Hong et al. (1994)	PS[1.29], 3000, 10000, 30000	CPC[2.12] CTAC[2.24]	Continuous of separation of phenol from aqueous streams by MEUF. c-CF in.Hollow-fiber equipment. The effects of operating conditions (pressure difference, MWCO's, and molar ratio of surfactant to solute on the membrane performance have been investigated. The effects of concentration polarization on rejection efficiency have been elucidated.

Hebrant et al. (1994)	Cellulosic[1.25], 10000	CTAB[2.8] $C_{12}EO_6$[2.20]	Removal of nickel by UF through complexation with long-chain alkoxypicolinic acids and alkoxypyridine aldoximes in micellar media. b-SC. The kinetics of complexation between Ni(II) ions and complexing agents in micelles have been investigated and their application in UF separation has been studied.
Ahmadi et al. (1994)	Various membranes and the most suitable ones: RGO3[1.73], 30000-VF[1.74], 3000.5000	Elmpur N-1[2.69]	Removal of heavy metals (Cu, Cd, Zn, Ni) using lecithin by MEUF. b-SC. The binding behaviour of biodegradable surfactant in relation to the metals was investigated. Competitive binding and precipitation may occur in the presence of more than one metal.

(*continued*)

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Table 3. Continued.

Reference	Membrane-MWCO	Surfactant	Aim–experimental-results
Sriratana et al. (1996)	CA[(1.21)], 10000	MERQUAT-100[(2.70)]	Removal of chromate anions from water by PEUF. b-SC. Gel concentration and chromate rejection at high polyelectrolyte concentration was examined. In the absence of other added electrolytes, chromate rejections up to 99,8% were observed.
Singh (1996)	CA[(1.27)], 5000 CA [(1.19)], 10000 PVDF[(1.28)], 18000	SDS[(2.10)] Igepal RC-520[(2.26)] Igepal CO-660[(2.17)] Tween 80[(2.27)] Span 80[(2.28)]	Removal of toluene and trichloroethylene from water via MEUF. b-SC and c-CF. The efficacy of surfactants along with a surfactant stabilized oil emulsion for removing of volatile organic compounds by UF was investigated. A mathematical model was developed and the data provided a design of UF water treatment plant. Flux versus concentration follows the gel-polarization model.

Reiller et al. (1996)	PS, 10000	SDS[2.10]	Use of an anionic surfactant to perform MEUF separation of Cu(II) in the presence of a metal ligand (EDTA, tartrate ions) and uranyl ion. b-SC and MEUF. The ionic exchange model has been used to predict the influence of positive metal ion complexation upon MEUF. The effects of pH and ligand concentration on the metal de-extraction efficiency from micellar solution have been investigated. 98% Cu(II) recovery was achieved.
Syamal et al. (1997)	Assymetric CA[1.30], 1000	CPC[2.12]	Separation of phenol from water solutions. b-SC. Characterization of the filtration of surfactant solution in terms of permeate flux and concentration and phenol solubilization under different operating conditions have been studied. Removal of phenol is controlled by an optimum surfactant/solute ratio.

(*continued*)

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Table 3. Continued.

Reference	Membrane-MWCO	Surfactant	Aim–experimental-results
Guo et al. (1997)	-, 5000	$CPC^{(2.12)}$ $SDS^{(2.10)}$	Separation of TBP from water by surfactant-polyelectrolyte ($PSS^{\#}$) complexes. b-SC. Solubilization and ultrafiltration of organic solute in polymer-surfactant solutions and surfactant solutions have been examined. The utility of polyelectrolyte to reduce monomer leakage by collecting surfactant monomers was confirmed.
Morel et al. (1997)	$CA^{(1.26)}$, 1000	$TTAB^{(2.9)}$ $CTAB^{(2.8)}$ $CTAC^{(2.24)}$ $CPC^{(2.12)}$ $SDS^{(2.10)}$	Removal of nitrate ions from water by UF. b-C. Enhancement of nitrate ions separation through ionic repulsion by membrane modification, produced by a strong adsorption of surfactant molecules on the membrane, which acts on the Donnan potential difference.

Akita et al. (1997)	CA[1.18], 3000 CA[1.19], 10000	PONPEn[2.21] Pluronic P84[2.22] Amiet 308[2.23] CPC[2.12] SDS[2.10]	Removal of gold (III) from dilute hydrochloric acid media. b-SC. The factors (surfactant concentration, ethylene oxide number of PONPEn, MWCO and applied pressure) affecting the rejection of gold have been investigated. High selective separation of from some heavy metals can be attained by use of the nonionic surfactant without any complexing agent.
Choi et al. (1998)	PS, 10000	Pluronic P103, P85, F108[2.19]	Removal of phenol and 1-napthol from aqueous solutions using block copolymers. c-CF. The optimum conditions for MEUF process to remove these solutes from wastewater were examined. A method for recycling and regeneration of the polymer based on the concept of micellar temperature range found to be very effective.

(*continued*)

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Table 3. Continued.

Reference	Membrane-MWCO	Surfactant	Aim–experimental-results
Hong et al. (1998)	CA, 1000, 3000	DCMA-3Na[2.18]	Separation of divalent metal cations (cupric, zinc, cadmium and nickel) using biosurfactant MEUF. b-SC. The dependence of the separation performance on the MWCO of the membranes and the molar ratio of biosurfactant to metal cations has been investigated. High rejections of metals were achieved with equimolar surfactant/metal ratio. Binding affinity: Cd > Cu = Zn > Ni.
Herbrant et al. (1998)	Cellulosic[1.25], 10000	CTAB[2.8] $C_{12}EO_6$[2.20]	A systematic comparison between MEUF and solvent extraction for the removal of copper ions from aqueous solutions. b-SC. Both methods using a variety of complexing agents either solubilized in the organic solvent used or in surfactant micelles have been investigated on the basis of yield of copper extraction. The advantages and drawbacks of both techniques are reported

Tzeng et al. (1999)	$CA^{(1.22)}$, 30000 $CA^{(1.19)}$, 10000 $CA^{(1.18)}$, 3000 $PS^{(1.23)}$, 10000 $PS^{(1.24)}$, 3000	$CPC^{(2.12)}$	The recovery of thuringiensin from fermentation broths via MEUF. b-SC and scale-up by two-step MEUF. Two step MEUF process resulted in a significant improvement in thuringiensin recovery and in the insecticidal effect on fly larvae.
Fillipi et al. (1999)	Anisotropic $CA^{(1.21)}$, 5000	$SDS^{(2.10)}$ IGEPAL CO-$660^{(2.17)}$	Use of anionic–nonionic surfactant mixture to reduce surfactant usage and surfactant loss in MEUF for removal of metal ions or organic compounds (Zinc, TBP). b-SC. Adding nonionic surfactant to anionic surfactant at low concentrations proved the improvement of rejection of both zinc cations and TBP. The formation of micelles in the vicinity of CMC and near the membrane surface and the effects of concentration polarization have been investigated.

(*continued*)

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Table 3. Continued.

Reference	Membrane-MWCO	Surfactant	Aim–experimental-results
Akita et al. (1997)	CA[1.17], 1000 CA[1.18], 3000 CA[1.19],10000 PS[1.20], 10000	POENPEO10[2.16] SDS[2.10]	Separation of Co (II)/Ni (II) using organophosporous acid extractants via MEUF. b-SC. Selective separation of Co(II) over Ni(II) in the presence of a micelle-solubilized hydrophobic ligand has been investigated and the factors involved have been examined and a comparison with the conventional solvent extraction method has been attempted.
Admaczak and Szymanowski (1999)	Reg. Cell.[1.10], 10000	OMD-n[2.14] CTAB[2.8] SDS[2.10] Glucopon 215 CS UP[2.15]	The separation of phenol and 4-nitrophenol by ultrafiltration of colloidal solutions formed by various surfactants. b-SC. Oxyethylated methyl dodecanoates with a degree of oxyethylation in the range of 3–14 have been examined for organics removal in comparison with other conventional surfactants through MEUF experiments.

Jadhav et al. (2001)	CA[1.16], 1000	CPC[2.12]	Removal of a binary mixture of organic solutes (phenol, aniline) in an aqueous solution by MEUF. b-SC. Solubilization of organics in micelles was ascertained. The effect of operating parameters (applied pressure, solutes, surfactant bulk concentration) on the extent of separation of organic solutes has been studied. A mathematical model was developed.
Talens-Alesson et al. (2001)	Reg. Cell.[1.10], 10000	OMD-n[2.14]	Investigation of the resistance and permeation flux of micellar solutions of oxyethylated methyl dodecanoate of various hydrophobicity for the removal of phenol and 4-nitrophenol. b-SC. The relationships between averaged resistance and permeation fluxes and a molar ratio pollutant/surfactant to predict the efficiency of the separation have been evaluated.

(*continued*)

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Table 3. Continued.

Reference	Membrane-MWCO	Surfactant	Aim–experimental-results
			Resistances of secondary layer are calculated and it is confirmed the narrow range of oxyethylation of useful surfactants for the removal of hydrophilic solutes like phenols.
Mulligan et al. (2001)	Nitrocellulose[1.15], 50000	Biosurfactants[2.13]	Study of the association of zinc and copper to biosurfactants micelles and their removal by UF. b-SC. The technique of ultrafiltration and zeta potential measurements were used to determine the mechanism of metal removal by the surfactants.
Hebrant et al. (2001)	Cellulosic[1.25], 10000	Triton X-100[2.5] Brij 35[2.25] CTAB[2.8]	Separation of europium(III) (rare earth metal) by a series of micelle-solubilized extractants derived from 5-pyrazolone via ultrafiltration. b-SC. The efficiencies of the extractants in europium separation through MEUF have been examined. The yield of extraction was measured as a function of pH and extractant/metal ratio.

Gzara and Dhahbi (2001)	PS[1.14], 10000	CTAB[2.8] CPC[2.12]	Removal of chromate anions from aqueous solutions by MEUF using cationic surfactants. c-CF. Rejection of chromate anions has been investigated at surfactant concentrations below and above CMC of surfactants. The effect of pH, ionic strength and concentration polarization has been studied. Above CMC rejection reached 99,5%.
Sabaté et al. (2002)	PS, 5000, 50000	CPC[2.12]	Comparison of polysulfone and ceramic membrane for the separation of phenol in MEUF. c-CF The effect of operation variables (pressure and retentate flux) and membrane properties (nature and MWCO) on permeate flux, surfactant and phenol rejection have been analyzed.

(*continued*)

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Table 3. Continued.

Reference	Membrane-MWCO	Surfactant	Aim–experimental-results
Yurlova et al. (2002)	Arom. Polysulfonamide[1.12], - Arom. Polysulfonamide, -	SDS[2.10] OP-10[2.11]	Purification of contaminated waters with Ni(II) ions via MEUF. b-SC. The feasibility of using a combination of nonionic–anionic micelles and the determination of optimum values of the operating conditions on the performance of UF have been investigated.
Yoon et al. (2003)	Sulf. PES[1.11], 8000	TTAB[2.9] SDS[2.10]	Modification of a negatively charged UF membrane using cationic/anionic surfactants to enhance perchlorate rejection from various sources of water. b-SC. Perchlorate rejection was examined in terms of two fundamental mechanisms: steric/size exclusion and electrostatic exclusion. Greater than expected perchlorate rejection by UF based mostly on steric/size exclusion was observed as a result of a decrease of the membrane pore size.

Korzystka et al. (2003)	Reg. Cell.[1.10], 10000	OMD-11[2.7] CTAB[2.8]	Removal of phenols and their derivatives by UF of colloidal solutions containing the toxic solutes and mixtures of surfactants. b-SC. The effect of composition of mixed surfactant system on the permeate fluxes, on the resistance of the secondary layer and on the rejection of the phenols has been determined.
Juang et al. (2003)	GE[1.77], 1000 GH[1.78], 2500 GM[1.79], 8000. AES5[1.80], 2000 AES10[1.81], 5000	SDS[2.10]	Separation and removal of metal ions (Cu(II), Co(II), Zn(II), Mn(II), Sr(II), Cs(I) and Cr(III)) from dilute solutions using MEUF. b-SC. The influence of different factors (membrane MWCO and material, molar concentration ratio of the surfactant/metals, ionic strength, transmembrane pressure) on metal rejection (in single and binary metal systems) has been examined. The recovery and reuse of surfactant from retentate was studied.

(*continued*)

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Table 3. Continued.

Reference	Membrane-MWCO	Surfactant	Aim–experimental-results
Baek et al. (2003)	YM10$^{(1.82)}$, 10000 YM03$^{(1.83)}$, 3000	ODA$^{(2.71)}$	Surfactant based separation of anionic metals (chromate and ferriccyanide) by MEUF. b-SC. The removal of anionic metals using cationic surfactant has been investigated in the systems: chromate/ODA, ferriccyanide/ODA and chromate/ferriccyanide/ODA.

at the membrane/solution interface (Gzara and Dhahbi, 2001; Morel et al., 1997; Yoon et al., 2003).

Previous research on the removal of organic compounds from aqueous solutions by MEUF had concentrated on: n-alcohols such as hexanol, heptanol, octanol (Gibbs et al., 1987), 4-tert-butyl-phenol (Dunn and Scamehorn, 1985, 1987), aromatic compounds, chloroaromatic compounds, aromatic amines (Premauro and Prevot Bianco, 1995). As far as the application of MEUF for the removal of heavy metals is concerned, the separation of zinc (Scamehorn and Harwell, 1988) and copper from mixtures with calcium (Klepac et al., 1991) are reported.

Generally, the recent research on MEUF (Table 3) is focused on the evaluation of membrane performance by determination of optimum operation conditions and includes not only batch-type stirred cell experiments but, also, continuous separation using hollow fiber or cross-flow membrane modules. The factors considered are pressure difference, membrane MWCO, molar ratios of surfactants to solute, kind of surfactant and additives, pH, ionic strength etc. The leakage of monomeric surfactant to permeate is of great interest for the current research. The use of non toxic, biodegradable surfactants such as oxymethyldodecanoates (Adamczak and Szymanowski, 1999), biosurfactants (Mulligan et al., 2001), natural surfactants (Huang et al., 1994ab), anionic-nonionic surfactants mixtures (for the reduction of CMC) (Fillipi et al., 1999), and polyelectrolytes (poly-electrolyte-surfactant complex) (Guo et al., 1997) is suggested.

3.4. Interaction Behaviour

In principle, an ultrafiltration membrane works by the sieving effect with a pressure difference as the driving force. However, interactions developed between solutes and the membrane surface could lead to modification of the sieving effect and eventually affect substantially the performance of UF membrane. Membranes can be fouled by adsorption or deposition of some substances present in a process solution. The interactions responsible for the adsorption include the contributions of various mechanisms by which substances may adsorb onto solid substrate. Broadly, these contributions can be due to electrical interactions (ion exchange and ion pairing), to strictly dispersion and hydrophobic forces and to the dipolar and electrostatic effects (acid–base interactions, hydrogen bonding and polarization of π electrons).

Adsorption of surfactants onto membrane surface plays an important role for the characterization of membranes, their removal from solutions streams and cleaning processes. Therefore, since the characterization of membrane tendency to interact with solute due to membrane surface

Table 4. Interaction behaviour.

Reference	Membrane-MWCO	Surfactant	Aim–experimental-result
Krovvidi (1992)	Spectrapor, 500 Spectrapor, 1000 Reg. Cell.[1.10], 10000	Triton X-100[2.5]	Reveal of individual resistances to mass transport across the membrane in UF with surfactant solutions. b-SC. UF experiments with colloidal and non-colloidal aqueous solutions of non-ionic surfactant were carried out in order to understand interactions with the membrane.
Doulia et al. (1992)	CA[1.66], 20000 PS[1.65], 20000	Triton® series[2.67] Dobanol® series[2.68]	An alternative method to zeta potential and contact angle measurements for membrane characterization is suggested by the aid of surfactants. c-CF. Interaction behaviour in ultrafiltration of homologous series of nonionic surfactants has been studied through flux behaviour in order to characterize surface properties of membranes

Yamagiwa et al. (1993a)	PS, 50000 Polyolefin, 20000	DISFOAM CE-120 R[(2.48)]	Investigation of membrane fouling in UF of hydrophobic nonionic surfactants used as antifoaming agents (e.g. in fermentation broths). c-CF. Antifoam fouling was caused by hydrophobic interaction between the membrane and the surfactant.
Yamagiwa et al. (1993b)	PS, 50000 POE, 20000	DISFOAM CE-120R[(2.48)]	Effect of antifoam fouling on solute rejection by UF membrane. c-CF. Antifoam fouling has significant effects not only on flux but also on solute (glucose, polyethyleneglycols and dextrans) rejection.
Makayassi and Treiner (1993)	PSS[(1.59)], 5000	TTAC[(2.57)] TBzC[(2.59)]	Investigation of the behaviour of monomer surfactant in single and mixed cationic surfactant solutions and determination of the micellar composition in the region of the second CMC. c-CF.

(*continued*)

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Table 4. Continued.

Reference	Membrane-MWCO	Surfactant	Aim–experimental-result
			UF method is feasible to determine structural change and micellar composition in aqueous solutions of binary cationic surfactant mixtures.
Kim et al. (1993)	PS[(1.8)], 30000 PS[(1.52)], 100000 PS[(1.53)], 100000	SDS[(2.10)] CTAB[(2.8)]	Cleaning of UF membranes fouled by proteins. b-SC and c-CF. Investigation of the relationship between the membrane fouled by protein deposition and of cleaning process in order to extend membrane life, optimize cleaning and enhance UF performance.
Wakeman and Akay (1994)	PES[(1.51)], 3000, 4000, 10,000, 100000	HMWSP (I)[(2.46)] HMWSP (II)[(2.47)]	Ultrafiltration of emulsions and suspensions stabilized with anionic and cationic hydrophobically modified water-soluble polymers. c-CF. Investigation of UF behaviour of the above polymers through flux decay and rejection.
Popescu et al. (1994)	PS[(1.50)], -	CPB[(2.42)] CTAB[(2.8)]	Production of UF asymmetric membrane is affected by the addition of small amounts of surfactants. b-C UF

		DPB[2.43] NaOI[2.44] NaSt[2.45] SDS[2.10]	The influence of surfactants used in membrane preparation on the wettability of hydrophobic microporous surfaces was studied by determining the contact-angle and UF rates of membrane as well as by adsorption experiments.
Markels et al. (1994)	PES[1.49], 5000, 50000	CPC[2.12]	Determination of rejection characteristics of the UF membrane for micellar surfactant solutions. b-SC An unsteady mass-transfer model is developed for unstirred batch UF at constant flux to include a micellising surfactant solute. Repulsive electrostatic interactions and surfactant adsorption influence rejection.
Markels et al. (1995A)	PES[1.49], 5000, 50000	CPC[2.12]	Development of an efficient design procedure and a practical and reliable model for the prediction of permeate flux in UF based on relevant physical phenomena. c-CF. An osmotic pressure and fouling resistance model is used to predict flux in the cross-flow UF of micelles solutions.

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Table 4. Continued.

Reference	Membrane-MWCO	Surfactant	Aim–experimental-result
Singh (1996b)	CA[1.19], 10000 CA[1.62], 5000	Tween 80[2.27] Igepal RC-520[2.26] SDS[2.10] (limited experiments with only the CA[1.62])	Invetigation of ultrafiltration rejection of surfactant micelles by dynamic light scattering. c-CF. The absence of micelles in UF permeate using the technique of dynamic light scattering has been determined and as well as the diameter of the examined micelles.
Huang and Sornasundaran (1996)	CA[1.17], 1000 CA[1.18], 3000	TTAC[2.57] NP-15[2.58]	Investigations of changes in micelle composition and monomer concentration in mixed surfactant solutions b-SC The micellization behaviour of cationic–nonionic hydrocarbon surfactant mixtures has benn studied using UF technique and a model involving coexisting mixed micelles is proposed.
Doulia et al. (1997)	PS[1.65], 20000 CA[1.66], 20000 PVDF[1.67], 20000	Triton® series[2.66] Dobanol® series[2.67]	Characterization of UF membrane by surfactant method.

	PVDF[1.68], 20000		Batch adsorption experiments. Interactions between surfactants and membranes were examined by adsorption experiments.
Pontié et al. (1997)	PES[1.43], 3000–100000 PS[1.45], 10000 CA[1.46], 100000	Triton X-100[2.5]	Characterization of UF organic membranes based on streaming potential measurements and application to control cleaning treatments. Investigation of surface modification by surfactant adsorption includes particularly streaming potential determinations of surface charge of membranes in various conditions of pH, ionic strength, and pore size. Membrane cleaning procedures have been studied in terms of permeability, streaming potential and wettability.
Pontié et al. (1998)	PES[1.43], 3000–100000 CTA[1.44], 100000	Triton X-100[2.5] DTAB[2.42]	Control fouling and cleaning procedures of UF membranes by a streaming potential method. Surfactant adsorption on UF membranes was studied in order to model the deposition of natural organic matter on the membrane. Validation of the proposed streaming potential method in controlling the efficiency of a cleaning agent to the recovering of a membrane fouled

(*continued*)

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Table 4. Continued.

Reference	Membrane-MWCO	Surfactant	Aim–experimental-result
Ha-Tran et al. (1998)	PS[1.14], 10000	CTAB[2.8]	Examination of the relationship between membrane cleaning efficiency and water quality. b-SC. The efficiency of membrane cleaning has been studied with water containing particulates and some dissolved salts.
Kim et al. (1998)	PS[1.39], - Reg. Cell.[1.40], 3000 Reg. Cell.[1.41], 5000 Reg. Cell.[1.10], 10000 Reg. Cell.[1.42], 30000	C_nE_m[2.41]	Removal of toxic aromatic compound in aqueous solutions via micellar enhanced ultrafiltration b-SC. Investigation of interactions of nonionic surfactants and membranes through UF experiments.
Urbanski et al. (2002)	Reg. Cell.[1.10], 10000	CTAB[2.8] SDS[2.10] Glucopon 215 CSUP[2.15]	Separation of water soluble organics for recycling and reuse of industrial aqueous streams. b-SC. Examination of UF of micellar surfactant solutions in the presence and absence electrolytes and focus on the formation of additional membrane resistance.

Mizoguchi et al. (2002)	Polysaccharide [1.38], 1000	LDAO[2.40]	Development of UF process for non-ionic surfactant separation applicable to a new system of high density thermal energy transportation for local heating and cooling. b-SC. Investigation of UF behaviour of a new type non-ionic surfactant around CMC.
Kozlov (2002)	Aromatic polyamide[1.37], -	Catamine AB[2.39]	Ultrafiltration of acqueous. Catamine AB solutions. b-C. The study of micellar solutions of cationic surfactant includes the effects of initial polarization phenomena and the modification of membrane.
Kaplan et al. (2002)	PES[1.36], 100000	Tween 20[2.30]	Adsorption of lysozyme on membrane material and cleaning with non-ionic surfactant characterized through contact angle measurements. Characterization of membrane before protein adsorption and after cleaning with non-ionic surfactant gives insights in the membrane behaviour.

(*continued*)

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Table 4. Continued.

Reference	Membrane-MWCO	Surfactant	Aim–experimental-result
Byhlin and Jönsson (2002)	Reg. Cell.[1.32], 10000 Reg. Cell.[1.33], 20000 Reg. CelL.[1.34], 30000 PES[1.35], 20000	Triton X-100[2.5]	Influence of non-ionic surfactant on the performance of different types of membranes. c-CF. The effect of adsorption and concentration polarization on membrane performance was studied at surfactant concentration below and above CMC.

Table 5. Water management.

Reference	Membrane-MWCO	Surfactant	Aim–experimental-results
Ang and Abdul (1994)	CM50[1.57], 50000 XM50[1.15], 50000 PM500[1.58], 500000	Witconol SN70[2.60]	Evaluation of an ultrafiltration method for surfactant recovery and reuse from aqueous waste streams during in situ washing of a site contaminated PCBs and oils. Hollow-fiber UF. Laboratory and field feasibility studies were conducted and indicate that nonionic surfactant can be recovered from leachate mixture containing PCBs and oils by UF.
Markels et al. (1995b)	PES[1.47], 5000 PES[1.48], 50000	CPC[2.12]	Design methodology for micellar-enhanced ultrafiltration in order to reduce the concentration of organic pollutant in water streams. UF ''Feed'' and ''Bleed'' system. A systematic calculational procedure is developed for the design of MEUF to treat aqueous streams contaminated with organic pollutants (chlorobenzene, trichloroethylene, tetrachloroethylene and toluene). The design is considered to ensure good mass transfer, control of surfactant concentration at the membrane surface and meets the EPA standards in the permeate.

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Table 5. Continued.

Reference	Membrane-MWCO	Surfactant	Aim–experimental-results
Jönsson and Jönsson (1995)	PS[1.54], 8000 PES[1.55], 4000 PES[1.56], 25000	Car-washing chemicals containing various surface active agents	Removal of degreasing agents used at car washes by UF. The influence of commercial degreasing agents used at car washes on the flux and retention of membranes has been studied with the aim of replacing the petroleum-based agents with less harmful ones.
Sabatini et al. (1998)	-, 10000	DOWFAX 8390[2.54] Tween 80[2.27] STEOL CS-330[2.55] SD-4[2.56]	The role of membrane processes (UF) in surfactant decontamination and recovery to surfactant-enhanced subsurface remediation. Results of a field demonstration study illustrating the combined surfactant-enhanced contaminant extraction and surfactant regeneration and reconcentration processes are presented documenting the performance of hollow fiber and ultrafilter membranes.
Goers et al. (1998)	PS, 10000		Reduction of water consumption and wastewater in detergent production. Capillary module. An investigation was conducted in order to optimize changes of product in regard to the volumes of fresh water and waste water involved and to recover process water considering process-related technical concepts.

Fillipi et al. (1998)	Modified CA		Economic analysis of copper removal from water by ligand-modified micellar-enhanced ultrafiltration. This study provides approximate comparative economics between the LM-MEUF copper separation method and the conventional copper solvent extraction process.
Goers et al. (2000)	PES[1.54], 5000 PVDF[1.55], 10000 PVDF[1.56], 35000	SDS[2.10] Texapon N 70[2.49] Marinal paste A 56[2.50] Eumulgin ET5[2.51] Genapol UDD-079[2.57] APG Plantacare 2000[2.53]	Optimized product and water recovery from batch-production rinsing waters. Pilot-scale plant. Product concentrate can be recovered from rinsing waters of surfactant and detergent batch production processes by using UF membranes. An economic optimization of the recovery process was studied.
Fostmeier et al. (2002)	NadirPoo5F[1.70] D5k Desal[1.71] 6M Desal[1.72]	–	Management of rinsing waters in a liquid detergent production plant by UF/NF treatment. Pilot-scale plant

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properties is of great importance, a research activity has been concentrated on this issue (Table 4). Particularly, the characterization of membranes by determination of interactions involved in a specific system has been studied by the aid of surfactants solutions. Methods alternatives to contact angle and zeta potential measurements including UF and/or adsorption experiments and using various surfactant solutions at concentrations below and above CMC have been examined. By this method, the above-mentioned interactions and their influence to flux decline, flux recovery, fouling tendency of hydrophilic and hydrophobic membranes (Doulia et al., 1997; Kaplan et al., 2002) have been investigated. UF experiments have also been performed for the determination of structural change and micellar compositions of aqueous mixed surfactant solutions with the aim of examination and prediction of membrane behaviour, affecting substantially MEUF performance (Byhlin and Jönsson, 2002; Mizoguchi et al., 2002). The role of interactions in UF processes, where surfactants are present (e.g. cleaning UF membranes fouled by proteins, antifoam fouling etc) has been studied in order to extend membrane life, optimize process and enhance UF effectiveness (Kim et al., 1993; Yamagiwa et al., 1993ab). Generally, the main factors (chemical nature of surfactants and membranes, surfactant concentration, pH, ionic strength, additives etc) affecting adsorption behaviour of a solution-membrane system have been examined (Ha-Tran et al., 1998; Huang and Sornasundaran, 1996; Schott, 1964).

Previous studies on interactions of surfactants solutions with ultrafiltration membranes are mentioned in the literature. McBain et al. (1933) studied the ultrafiltration of soap solutions (potassium laureate), Schott (1964) examined the ultrafiltration of nonionic detergents as a method of their purification, Lee-Osborne et al. (1983) studied the monomer-micellar equilibrium of sodium alkyl benzene sulfonate, Krovvidi et al. (1984) investigated the transport of monomer surfactant molecules through porous membranes and Jönsson and Jönsson (1991) studied the influence of nonionic and ionic surfactants on hydrophobic and hydrophilic ultrafiltration membranes.

3.5. Water Management

The stringent environmental and ecological requirements have spurred the search for industrial waste treatment options with low energy, labor and capital cost. Surfactants are frequently present in waters or wastewaters of detergent or surfactant production plants, in cleaning and rinsing water plant networks and in effluents from processes using surfactants (metal removal in mining industry, surfactant washing method to remediate a contaminated site etc). The investigation of ultrafiltration application for the treatment of industrial effluents containing surfactants focuses mainly on the optimization

of cleaning and rinsing plant network in terms of reduction of water consumption by recycling, recovery and reuse of water (Forstmeier et al., 2002; Goers et al., 1998). The activity on this field includes applied research projects on specific industrial cases, the objectives of which are briefly given in Table 5.

4. CONCLUSIONS

It is evident that data on surfactant-membrane research field are abundant since a great variety of surfactants and membranes are available connected with different processes. The recent research activity includes pretreatment with surfactants enhancing UF performance, MEUF as a very promising method alternative to extraction, determination of interactions between surfactant and membrane (significant for improvement and prediction of membrane behaviour) and economical and environmental aspects of UF-surfactant related processes. It should be noticed that by the use of surfactants in membrane processes a new effective separation methods has been developed, equivalent or more effective than conventional separation methods and with occasionally better environmental and economical characteristics. The determination of interactions, unique for a given system, leads to a better understanding of the mechanisms involved at membrane-solute interface with beneficial impacts on practical predictions, design and improvement of UF behaviour.

5. APPENDIX A

Membrane trade names and material

Number	Membrane trade name	Membrane material
1.1	Amicon XM100	Dynel
1.2	Amicon PM30	PS
1.3	Amicon YM30	Reg. Cell.
1.4	Amicon YM5	Reg. Cell.
1.5	Millipore PTGC	PS
1.6	IRIS 3038TS	PAN
1.7	CJT 35	PA
1.8	Millipore PTTK	PS
1.9	Tubular membrane from Weir-Enving (Pty) Paarl, South Africa	PES

(*continued*)

Appendix A. Continued.

Number	Membrane trade name	Membrane material
(1.10)	Millipore PLGC	Reg. Cell.
(1.11)	GM (Desal)	Sulf. PES coated with an ultrathin polyimide
(1.12)	UPM-10 (Vladipor, Russia)	Aromatic polysulfonamide (5–20 nm)
(1.13)	UPM-20 (Vladipor, Russia)	Aromatic polysulfonamide (5–20 nm)
(1.14)	Millipore PTGC OMS10	PS
(1.15)	XM-50 (Romicon Inc.)	PVC-based plastic fiber membrane co-polymer with methylmethacrylate
(1.16)	Spectra® (Spectrum Medical Industries, USA)	CA
(1.17)	YM 1 (Amicon Co.)	CA
(1.18)	YM 3 (Amicon Co.)	CA
(1.19)	YM 10 (Amicon Co.)	CA
(1.20)	PM10 (Amicon Co.)	PS
(1.21)	Spectrum	Anisotropic CA
(1.22)	YM 30 (Amicon Co.)	CA
(1.23)	H1P10 43	PS
(1.24)	H1P3 20	PS
(1.25)	Millipore	Cellulosic disk
(1.26)	Millipore PCAC 04710	CA
(1.27)	Spectrum C-5K	CA
(1.28)	Koch HFM-181	PVDF
(1.29)	Amicon Co.	PS
(1.30)	Permionics India Ltd.	Assymetric CA
(1.31)	Millipore UFC4	Reg. Cell.
(1.32)	C10 (Hoechst)	Reg. Cell.
(1.33)	C20 (Hoechst)	Reg. Cell.
(1.34)	C30 (Hoechst)	Reg. Cell.
(1.35)	PES 20 (Hoechst)	PES
(1.36)	Orelis 3028	PES
(1.37)	UPM-50M	Aromatic polyamide
(1.38)	YM-1 (Amicon)	polysaccharide
(1.39)	Udel, P-1700 made in the laboratory	PS
(1.40)	Millipore PLBC	CA
(1.41)	Millipore PLCC	Reg. Cell.
(1.42)	Millipore PLTK	Reg.Cell.
(1.43)	IRIS 3028 Lot no. CGA: 969/3, 960/5, 969/3 (Tech-Sep)	PES

Appendix A. Continued.

Number	Membrane trade name	Membrane material
(1.44)	Provided from Lyonnaise des Eaux	CTA
(1.45)	IRIS 3026 lot no. 955/2 (Tech Sep)	PS
(1.46)	Millipore PCAPOM S10, lot no. H2PM97948	CA
(1.47)	Filtron PES 5,000 (Filtron, Danvers, MA)	PES
(1.48)	Filtron PES 50,000 (Filtron, Danvers, MA)	PES
(1.49)	NOVA™ disks (Filtron Inc., Danvers MA)	PES
(1.50)	Udel-type polysulphone made in the laboratory with various surfactacts used in casting solutions	PS
(1.51)	FLOWGEN NM/003, NM010, NM/100, OM/100, OM/994	PES
(1.52)	Millipore PTHK	PS
(1.53)	Memtec MPS	PS
(1.54)	PU608 (PCI Membrane Systems)	PS
(1.55)	ES404 (PCI Membrane Systems)	PES
(1.56)	ES625 (PCI Membrane Systems)	PES
(1.57)	CM50 (Romicon Inc.)	Polyvinyl chloride based plastic co-polymer with acrylonitrile fiber membrane
(1.58)	PM500 (Romicon Inc.)	PS
(1.59)	IRIS 3026	PSS
(1.60)	SM 14659 (Sartorius, Germany)	PS
(1.61)	SM 14549 (Sartorius, Germany)	CTA
(1.62)	Spectrum C-5K	CA
(1.63)	RGO3 (Osmonics Inc.)	Made from anisotropic acrylonitrile
(1.64)	Spectra/Por-C10	Cellulose
(1.65)	GR 61PP (DDS(Dow))	PS
(1.66)	CA 600PP (DDS(Dow))	CA
(1.67)	ETNA 2OA (DDS(Dow))	PVDF-modified
(1.68)	FS 61PP (DDS(Dow))	PVDF-hydrophobic
(1.69)	Millipore or amicon	Cellulosic disk membranes
(1.70)	P005F (Nadir)	Not specified in paper

(*continued*)

Appendix A. Continued.

Number	Membrane trade name	Membrane material
(1.71)	D5k Desal	Not specified in paper
(1.72)	6M Desal	Not specified in paper
(1.73)	RGO3	Acrylanitril
(1.74)	0-VF	Vinylidine flouride
(1.75)	UM-05 (Amicon)	Not specified in paper
(1.76)	Pellicon 100 (Millipore)	Diaflo membrane
(1.77)	GE (Osmonics Inc.)	PA-TFC
(1.78)	GH (Osmonics Inc.)	PA-TFC
(1.79)	GM (Osmonics Inc.)	PA-TFC
(1.80)	AES5 (Osmonics Inc.)	PES
(1.81)	AES10 (Osmonics Inc.)	PES
(1.82)	YM10 (Millipore)	Reg. Cell.
(1.83)	YM03 (Millipore)	Reg. Cell.

6. APPENDIX B

Chemical names and manufacturers of surfactant trade names

Number	Tradename	Company	Chemical name
Nonionics			
2.1	N5, N13, N100	ICI Australia Ltd.	Nonyl phenol ethoxylates, with average degree of ethoxylation n = 5, 13, 100
2.5	Triton X-100	BDH Chemicals Ltd., Fluka BioChemika	Octyl phenol ethoxylate, n = 9–10
2.6	Pluronic F-108	BDH Chemicals Ltd.	PEO-PPO-PEO blockopolymer with PPO/PEO ratio = 0.19
2.7	OMD-11	Kedzierzyn-Kózle institute of heavy organic synthesis	Oxyethylated methyl dodecanoate with the average degree of oxyethylation equal to 11
2.11	OP-10	Intercom, Ukraine	Monoalkylphenol polyethoxylate

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Appendix B. Continued.

Number	Tradename	Company	Chemical name
2.14	OMD-n	Institute of Heavy Organic Chemicals, Kedzieryzyn-Kozle, Poland	Homologue oxyethylated methyl dodecanoates with average oxyethylation degress equal to 7, 9, 11, 14
2.15	Glucopon 215 CS UP	Henkel, Germany	Alkylpolyglucoside
2.16	PONPE10	Tokyo Kasei Kogyo	Nonyl phenol ethoxylates, n = 10
2.17	IGEPAL CO-660	Rhone-Poulenc Corporation	Nonyl phenol ethoxylate, n = 10
2.19	Pluronic P103, P85, F108	Asahi Electrochemical	PEO-PPO-PEO blockcopolymer with PPO/PEO ratio = 1.79, 0.77, 0.19 accordingly
2.20	$C_{12}EO_6$	Nikko Chemicals (Japan)	n-dodecyl ethoxylate, n = 6
2.21	PONPEn	As (2.16)	Nonyl phenol ethoxylates, n = 10, 15, 20
2.22	Pluronic P84	Asahi Denka Kogyo K.K.	PEO-PPO-PEO blockopolymer with MW = 4200
2.23	Amiet 308	Kao Co.	Polyoxyethylene stearic amine with a total amine value of 74–89
2.25	Brij 35	Fluka Biochemika	Brij series are lauryl, cetyl ethoxylates manufacturer Atlas Chemical Industries[#]
2.26	Igepal RC-520	Rhone-Poulence	Dodecylphenol ethoxylate
2.27	Tween 80	ICI America	Polyoxyethylene(20) sorbitan monooleate
2.28	Span 80	ICI America	Sorbitan monooleate
2.30	Tween 20	Atlas Chemical Industries Inc., USA	Polyoxyethylene(20) sorbitan monolaurate
2.31	Tween 60	Atlas Chemical Industries Inc., USA	Polyoxyethylene(20) sorbitan monostearate
2.32	Myrj 52	Atlas Chemical Industries Inc., USA	Polyoxyethylene(40) monostearate

(*continued*)

Appendix B. Continued.

Number	Tradename	Company	Chemical name
2.33	Myrj 53	Atlas Chemical Industries Inc., USA	Polyoxyethylene(50) monostearate
2.34	Emulgin C 1000	Henkel International	Cetylstearyl ethoxylate, n = 20
2.35	Emulgin C 1500	Henkel International	Cetylstearyl ethoxylate, n = 30
2.36	C16E20	Sigma Co.	Cetyl ethoxylate, n = 20
2.37	C12E23	Sigma Co.	Dodecyl ethoxylate, n = 23
2.39	LDAO	–	N-Lauryl-N, N-dimethylaminoxide
2.40	C_nE_m	Nikko	Polyoxyethyleneglycol alkyl ether: $H(CH_2)_nO(CH_2CH_2O)_mH$, where (n = 10, m = 8), (n = 12, m = 5, 6, 7, 8), (n = 14, m = 8), (n = 16, m = 8)
2.48	DISFOAM CE-120R	Nippon Fat and Oil Co. Ltd	Oleyl ehoylate propoxylate
2.51	Emulgin ET 5	Henkel	Alkyl ethoxylate, C14–C18, n = 5
2.52	Genapol UDD-079	Clariant	Alkyl ethoxylate, max. C11, n = 7
2.53	APG Plantacare 2000	Henkel	Alkyl polyglucoside
2.58	NP-15	Nikko Chemicals	Pentadecyl nonylphenol ethoxylate
2.60	Witconol SN70	–	Alkyl ethoxylates, C_{10} to C_{12}, n = 5
2.61	Triton X-102	Rohm and Haas	Octylphenol ethoxylate, n = 12
2.67	Triton® Series	Rhom and Haas	Octylphenol ethoxylates, n = 8, 10, 12
2.68	Dobanol® series	Shell	Alkyl ethoxylates where (R = C9, n = 5), (R = C10, n = 6), (R = C11, n = 8)
Anionics			
2.2	Aerosol OT-100	Cyanamid Australia	Sodium di-2-ethylhexyl sulfosuccinate

Appendix B. Continued.

Number	Tradename	Company	Chemical name
2.10	SDS	Merk, BDH Gr. Brit., Katayama Chemical Industries, Fisher Scientific, Katayama Chemical Industries, Ltd., Aldrich Co., BioRad (USA)	Sodium Dodecyl Sulfate
2.13	Biosurfactants	Produced in laboratory	Surfactin from Bacillus subtilis Rhamnolipids from Pseudomonas aeruginosa Sophorolipids from Torulopsis bombicola
2.18	DCMA-3Na	Synthesized by spiculisprosic acid anhdride (Penicillum spiculisporum)	Trisodium salt of 2-(2-carboxyethyl)-3-decyl maleic anhydride
2.29	STS	Fluka Co	Sodium Tetradecyl Sulfate
2.44	NaOl	Loba Feinchemie	Sodium Oleate
2.45	NaSt	Loba Feinchemie	Sodium Stearate
2.46	HMSWP (I)	Specialty Polymers Division of National Starch and Chemical Ltd.	A copolymer of acrylic acid and a long chain ester salt
2.49	Teapon N 70	Henkel	Sodium dodecyl ethersulphate, n = 3
2.50	Marinal Paste A 56	Henkel	Sodium dodecyl sulphate
2.54	DOWFAX 8390	–	–
2.55	STEOL CS 330	–	–
2.56	SD-4	–	–
2.62	Tengitol NP-7	Union Carbide cooperation	–
2.63	Tencid-HC-ST	Henkel KGaA	–
2.64	sodium salt of DCA	Sigma	Sodium deoxycholate

(*continued*)

Appendix B. Continued.

Number	Tradename	Company	Chemical name
Cationics			
2.8	CTAB	Merk, Germany Chemapol, Czech Republic	Cetyltrimethylammonium bromide
2.9	TTAB	–	Tetradecyltrimethyl-ammonium bomide
2.12	CPC	Aldrich, Sigma Chemicals Co, Wako Pure Chemical Industries Ltd.	Cetylpyridinium cloride
2.24	CTAC	–	Cetyltrimethylammonium Chloride
2.38	Catamine AB	–	Alkyldimethylohenyl-ammonium chloride A mixture of $[C_nH_{2n+1}N(CH_3)_2$-$CH_2C_6H_5]Cl$ where n = 10–18
2.41	DTAB	–	Dodecyltrimethylsm-monium bromide
2.42	CPB	Loba Feinchemie	Cetylpyridinium bromide
2.43	DPB	Loba Feinchemie	Dodecylpyridinium bromide
2.47	HMSWP(II)	Specialty Polymers Division of National Starch and Chemical Ltd.	A copolymer of dimethyldiallyl-ammonium chloride and butyl acrylate
2.57	TTAC	American Tokyo Kasei, Inc.	n-tetradecyltrimethyl-ammonium chloride
2.59	TBzC	Aldrich	Dimethylbenzyltetra-decyllamonium chloride
2.70	MERQUAT 100	Calgon Corp.	Poly(diallyldimethyl ammonium chloride)
2.71	ODA	TCI Chemicals	octadecylamine
Anionics–Nonionics			
2.3	Sandopan D-TC	Sandoz Australia Pty. Ltd.	Carboxylate of a synthetic fatty alcohol with n = 7
2.4	Gardisperse AC	Albright and Wilson Australia Ltd.	Sodium salt of alkyl phenoxypolyethylene sulfate with n = 4

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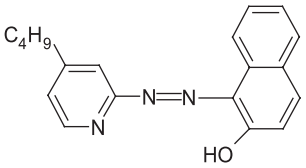
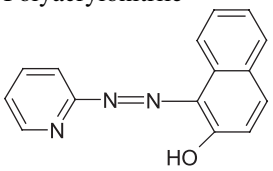
Appendix B. Continued.

Number	Tradename	Company	Chemical name
Lecithin based surfactants			
2.65	M-C-Thin lecithin	Lucas Meyer (Illinois)	Based on Lecithin
2.66	Centrolex F-lecithin	Lucas Meyer (Illinois)	Based on Lecithin
2.69	Elmpur N-1	–	Lecithin

(–): No available data;
n: degree of ethoxylation.

ABBREVIATIONS

b-C	Batch cell
BSA	Bovine Serum Albumin
b-SC	Batch stirred cell
C_{11}-HQ	7-(4-ethyl-1-methyloctyl)-8-hydroxyquinoline
C4-PAN#	
CA	Cellulose Acetate
c-CF	Continuous crossflow
CEUF	Colloid-enhanced Ultrafiltration
C_m	Concentration of the solute in the micelle (w/w)
CMC	Critical Micelle Concentration
c_o	Phenol concentration in bulk phase
c_s	Phenol concentration in micelle phase
CTA	Cellulose Triacetate
C_w	Concentration of the solute in the aqueous phase (w/w)
DCMA	2-(2-carboxyethyl)-3-decyl maleic anhydride
Dynel	Poly co(acrylonitrile/vinyl chloride)
EDTA	Ethylene-diamine-tetra-acetic acid
EO	Ethylene Oxide
H	Equilibrium parameter
HQ	8-Hydroxyquinoline
K_m	Distribution coefficient
K_s	Equilibrium distribution constant

LM-MEUF	Ligand-Modified Micellar-Enhanced Ultrafiltration
MW	Molecular Weight
MWCO	Molecular Weight Cut-Off
NPE	Nonylphenol polyethoxylate
O_m	Phenol concentration in the micellar phase
PA	Polyamide
PAN	Polyacrylonitrile
PAN#	
PA-TFC	Polyamide thin-film composite
PEO	Polyethyleneoxide
PES	Polyethersulfone
PEUF	Polyelectrolyte-enhanced Ultrafiltration
PPO	Polypropylene
PS	Polysulfone
PSS	Sulfonated polysulfone
PSS#	Sodium poly (styrene sulfonate)
PVDF	Polyvinylidenefluoride
Reg. Cell.	Regenerated Cellulose
SDS	Sodium Docecyl Sulfate
S_m	Surfactant concentration as micelles
Sulf. PES	Sulfonated polyethersulfone
Φ_s	Micelle mole fraction in the bulk

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