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Role of membrane surface morphology in colloidal fouling of cellulose acetate and composite aromatic polyamide reverse osmosis membranes

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Abstract

Laboratory-scale colloidal fouling tests, comparing the fouling behavior of cellulose acetate and aromatic polyamide thin-film composite reverse osmosis (RO) membranes, are reported. Fouling of both membranes was studied at identical initial permeation rates so that the effect of the transverse hydrodynamic force (permeation drag) on the fouling of both membranes is comparable. Results showed a significantly higher fouling rate for the thin-film composite membranes compared to that for the cellulose acetate membranes. Addition of an anionic surfactant (sodium dodecyl sulfate, SDS) to mask variations in chemical and electrokinetic surface characteristics of the cellulose acetate and aromatic polyamide membranes resulted in only a small change in the fouling behavior. The higher fouling rate for the thin-film composite membranes is attributed to surface roughness which is inherent in interfacially polymerized aromatic polyamide composite membranes. AFM and SEM images of the two membrane surfaces strongly support this conclusion. These surface images reveal that the thin-film composite membrane exhibits large-scale surface roughness of ridge-and-valley structure, while the cellulose acetate membrane surface is relatively smooth.

Keywords: Surface morphology; Surface roughness; Membrane fouling; Colloidal fouling; Reverse osmosis membranes; Flux decline

1. Introduction

Membrane fouling is a major limitation in efficient operation of reverse osmosis (RO) plants. RO membrane foulants include sparingly soluble salts, dissolved organic substances, colloidal and particulate matter, and micro-organisms. Among these foulants, colloidal particles are considered to be the principal

cause of membrane fouling [1]. Colloids are ubiquitous in natural and process waters. Examples include clays, colloidal silica, iron oxyhydroxide, large organic macromolecules, organic colloids and suspended matter, and calcium carbonate precipitates.

During colloidal fouling of RO membranes, colloids accumulate at the membrane surface and increase the resistance to water flow through the membrane [1,2]. Attachment of colloids to the membrane surface, or to previously retained particles, is determined by an interplay between several chemical

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and physical factors, including feed water chemical composition, surface chemical properties of the colloids and membranes, and permeation rate through the membrane [1,3]. The fundamental mechanisms controlling the fouling of RO membranes are complex and not well understood.

The objectives of this communication are two-fold: (i) to demonstrate the paramount role of membrane surface roughness in colloidal fouling of polymeric RO membranes and (ii) to provide a mechanistic explanation for the lower fouling tendency of cellulose acetate RO membranes compared to that of aromatic polyamide composite RO membranes. To achieve these goals, fouling experiments with both membranes were carried out at identical chemical and physical conditions. These conditions include solution chemical composition, feed colloid concentration, initial permeate flux, crossflow velocity, and feed water temperature. Furthermore, an anionic surfactant (sodium dodecyl sulfate, SDS) was added to eliminate variations in the surface chemistry of the cellulose acetate and aromatic polyamide RO membranes, and to mask inherent surface charge heterogeneities of the membrane surfaces that might provide preferential sites for colloid attachment. Lastly, SEM and AFM images of the membrane surface were obtained to compare the physical morphology of both membrane surfaces. Based on our results, it is concluded that the vast difference in the rate of colloidal fouling of polyamide composite membranes compared to that of cellulose acetate membranes is attributed to membrane surface morphology.

2. Experimental

Thin-film composite (Fluid Systems Corp., San Diego, California) and cellulose acetate (Desalination Systems, Escondido, California) RO membranes were used in this investigation. The thin-film composite membrane (denoted TFCL by the manufacturer) is a proprietary aromatic polyamide membrane. The cellulose acetate membrane (denoted CE by the manufacturer) is a blend of cellulose diacetate and triacetate.

Commercial silica colloids (Aerosil 200, Degussa, Akron, OH) were used as a model colloidal foulant. The average diameter of the colloidal suspension, as

determined by dynamic light scattering (Nicom Model 370, Particle Sizing Systems, Santa Barbara, CA), was 0.24 μm .

The electrophoretic mobility of the silica colloids was measured by microelectrophoresis (Lazer Zee Model 501, Pen Kem, Bedford Hills, NY) and their colloidal stability was determined by light extinction measurements [4]. Zeta potential of the RO membranes was determined by a streaming potential analyzer (BI-EKA, Brookhaven Instruments, Holtsville, NY), as described elsewhere [5]. AFM images of the membranes were obtained with a NanoScope III scanning probe microscope (Digital Instruments, Santa Barbara, CA) in the tapping mode.

A plate-and-frame, closed-loop, bench-scale RO unit was used in the fouling tests. In this system, the suspension is fed to the RO membranes by a positive displacement pump (Milton-Roy Model R221, Ivyland, PA). The suspension splits into two parallel streams, feeding into duplicate membrane test cells. The rectangular cells contain membranes with dimensions of 25 by 64 mm. Temperature is controlled by circulating cooling water through a stainless-steel coil, immersed in the feed tank.

Fouling experiments were conducted with 90 mg/l silica colloids and 0.01 M NaCl as a background electrolyte. The feed solution pH in the fouling tests with cellulose acetate membranes was in the range of 5.4–5.6, whereas fouling tests with thin-film composite membranes were carried out at a feed solution of pH 7.8 by adding 1 mM sodium bicarbonate. In fouling tests with anionic surfactant, 0.3 mM SDS was added to the suspension; this SDS concentration is below the critical micelle concentration of ca. $10^{-2.5}$ M [6]. All solutions were prepared with deionized water (Nanopure II, Barnstead, Dubuque, IA) and certified grade chemical reagents.

Prior to the fouling tests, the membranes were placed in the RO test unit and equilibrated for 8 h with deionized water under normal operating pressure and temperature. Next, the membranes were further equilibrated with a particle-free solution (0.01 M NaCl or 0.01 M NaCl plus 0.3 mM SDS) for an additional 36 h. After this equilibration and stabilization period of 44 h, the permeate flux and salt rejection were found to be stable. Furthermore, SDS did not have an observable effect on the salt rejection and permeate flux of the membranes. In the last step before

initiation of fouling, the pressure was adjusted to achieve the target initial permeate flux (1.13×10^{-5} m/s) and the membrane was allowed to equilibrate for an additional 2 h. Fouling was then initiated by adding silica colloids from a concentrated stock suspension to establish the desired particle concentration of 90 mg/l. The temperature during the fouling experiments was fixed at 20°C and the crossflow velocity was kept at 53 mm/s (corresponding to a Reynolds number of ≈ 450 based on the hydraulic radius of the rectangular channel) to ensure laminar flow conditions.

3. Results and discussion

3.1. Electrokinetic properties of colloids and membranes

The isoelectric point of the silica colloids was determined from measurements of electrophoretic mobility as a function of pH [4]. An isoelectric point of 3 was obtained, consistent with previous electrokinetic studies involving silica colloids [7]. Hence, for the pH maintained during the fouling experiments, the silica colloids were negatively charged. Addition of 0.3 mM SDS caused the silica colloids to become more negatively charged due to adsorption of the negatively-charged surfactant molecules [4].

Colloidal stability measurements of the silica colloids were carried out to ensure that the silica colloids do not aggregate in the feed solution during the fouling experiments. Results showed that the silica colloids are extremely stable and do not aggregate at the chemical conditions employed in the fouling tests (0.01 M NaCl or 0.01 M NaCl plus 0.3 mM SDS) [4]. The critical coagulation concentration of the colloidal suspension was ~ 1 M NaCl. This 'anomalous' stability of silica colloids at high salt concentration is well documented in the literature and is attributed to hydration [8] and steric-like [9] repulsive forces.

The electrokinetic (zeta) potential of the composite and cellulose acetate RO membranes as a function of pH, in the presence of 0.01 M NaCl (open symbols), is presented in Fig. 1. As shown, the zeta potential versus pH curves display a shape characteristic of amphoteric surfaces containing acidic and basic func-

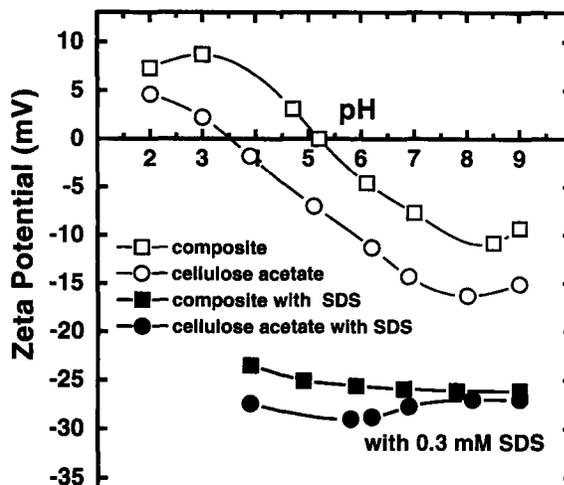


Fig. 1. Zeta potential of composite and cellulose acetate RO membranes as a function of pH. Open symbols represent experiments with 0.01 M NaCl and solid symbols represent experiments with 0.01 M NaCl plus 0.3 mM SDS.

tional groups. The difference in the zeta potential of the membranes is attributed to differences in the chemistry of the aromatic polyamide and cellulose acetate polymeric surfaces of the membranes. Extensive discussion on the electrokinetic properties of these membranes is given elsewhere [10].

Since a main objective of this investigation is to compare the fouling behavior of the cellulose acetate and composite membranes, it is imperative to eliminate the variability in the surface chemistry of the membranes. This was achieved by modifying the membrane surface through addition of an anionic surfactant (0.3 mM SDS) to the feed solution. As shown in Fig. 1 (solid symbols), the anionic surfactant has a marked effect on the charge of the membranes: zeta potentials of the membranes in the presence of surfactant are comparable to each other and are much more negative than the case with no SDS (open symbols). The striking effect of the anionic surfactant on the zeta potential of the membranes is attributable to adsorption of negatively-charged surfactant molecules on the membrane surface [4,10,11]. Surfactant molecules are readily adsorbed on the membrane surface and their negatively-charged functional groups dominate the membrane surface charge.

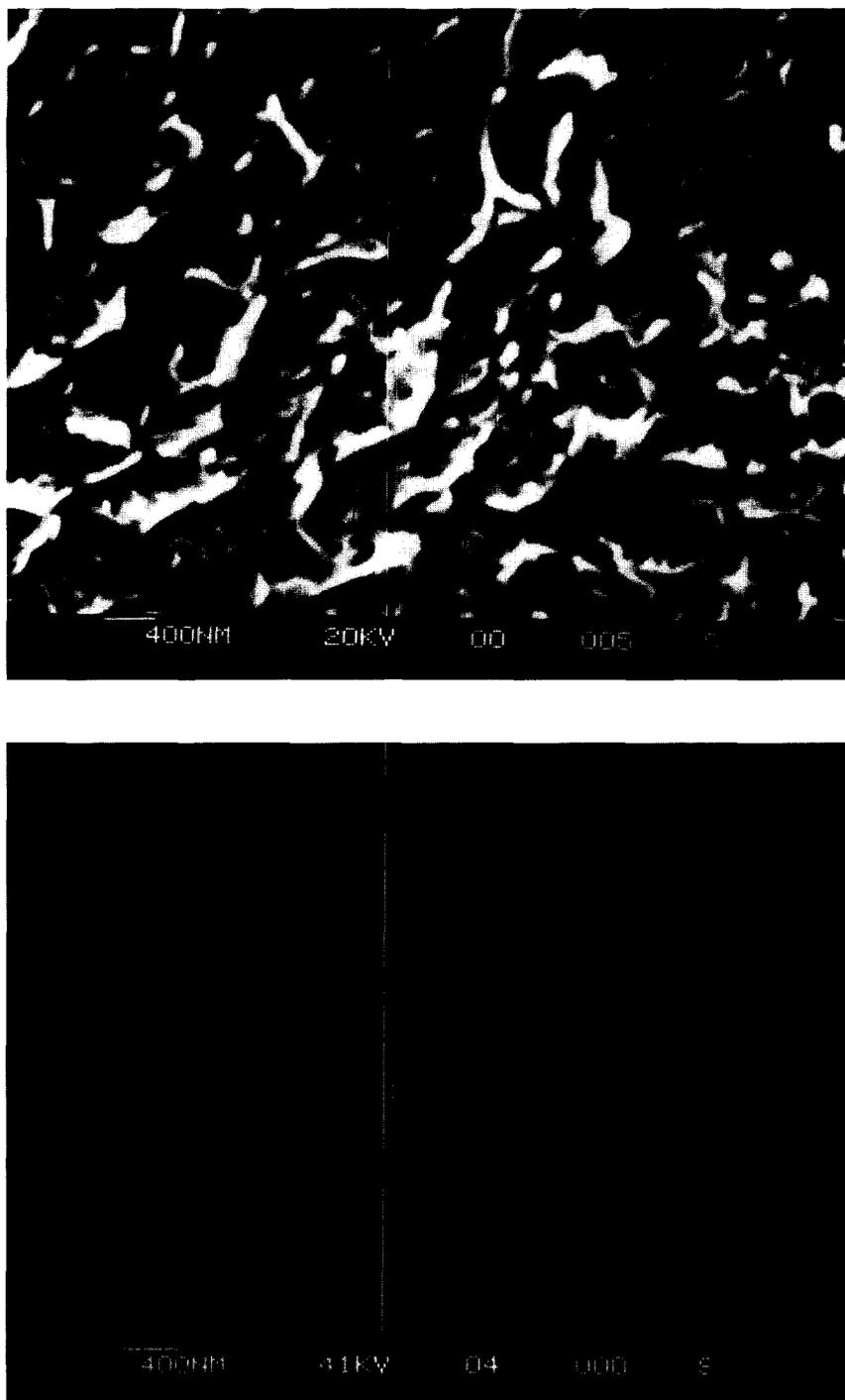


Fig. 2. SEM micrographs of RO membranes: composite membrane (top) and cellulose acetate membrane (bottom). The bar length in both micrographs is 400 nm.

3.2. Surface morphology of membranes

SEM micrographs of the active layer surfaces of the composite and cellulose acetate membranes are shown in Fig. 2. AFM images of these membranes are displayed in Figs. 3 and 4. The SEM and AFM data clearly show the striking differences between the surface morphologies of the two membranes. While the thin-film composite membrane exhibits large-scale surface roughness of ridge-and-valley structure, the cellulose acetate membrane surface is relatively smooth. The distinct roughness of the composite membranes is an inherent property of interfacially polymerized aromatic polyamide composite membranes [12]. In inspecting the AFM images, one should note that the scale of the axes (particularly of the vertical Z axis) for the two types of membranes are

quite different; a much larger scale Z axis was used for the image of the composite membrane because of its marked roughness. The roughness of the cellulose acetate membrane is of the order of a few nanometers, whereas that of the composite membrane is of the order of several hundred nanometers. It will be shown later that this remarkable surface roughness of the composite membrane has a dramatic effect on the attachment rate of colloids to the membrane surface.

3.3. Colloidal fouling of membranes

The colloidal fouling behavior of the cellulose acetate and composite membranes in the presence of 0.01 M NaCl (open symbols) and 0.01 M NaCl plus 0.3 mM SDS (solid symbols) is presented in Fig. 5. The results indicate that, in the absence of

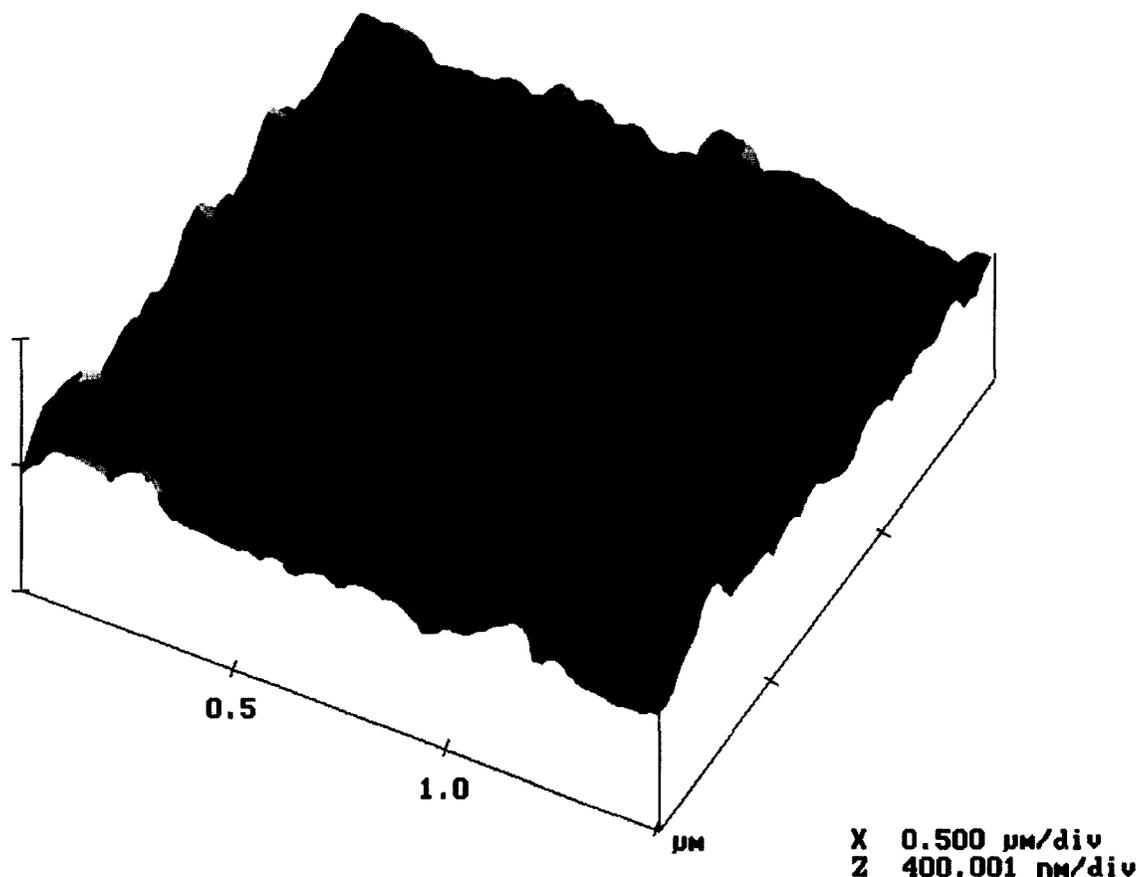


Fig. 3. AFM image of the composite RO membrane. The Z-axis scale is 400 nm per division and the X-axis scale is 500 nm per division.

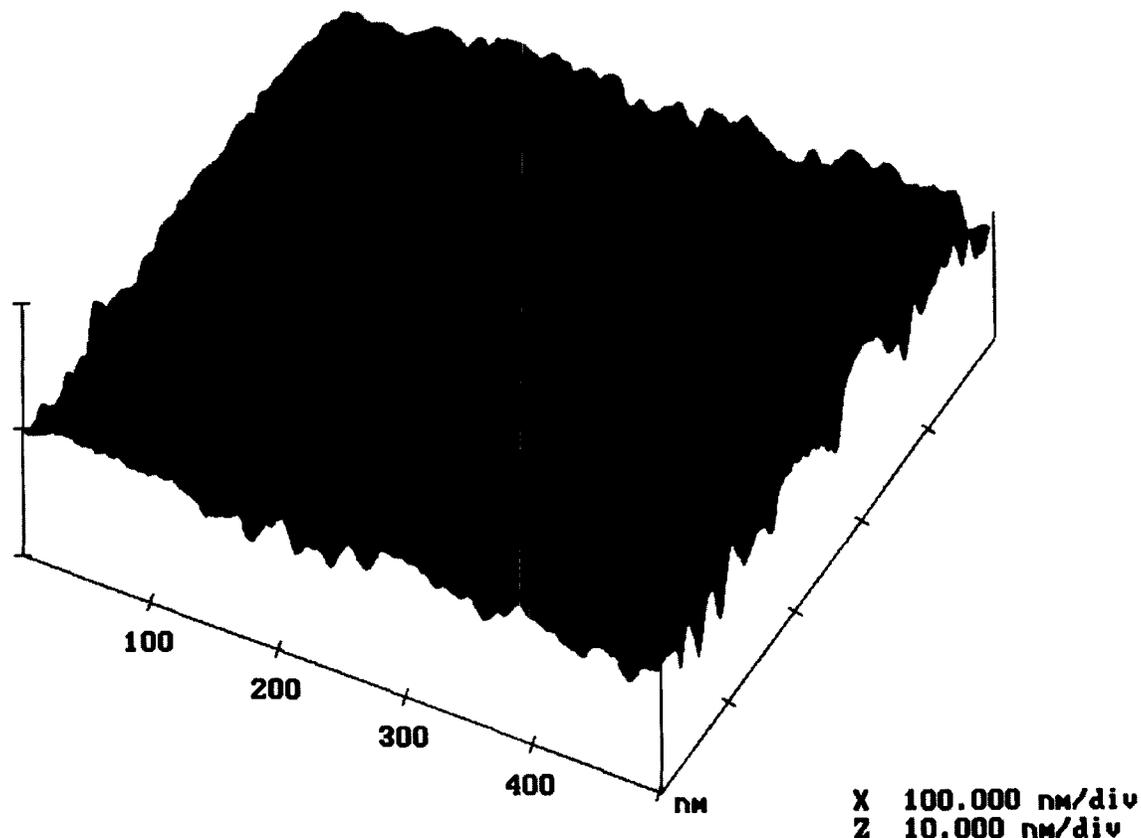


Fig. 4. AFM image of the cellulose acetate RO membrane. The Z-axis scale is 10 nm per division and the X-axis scale is 100 nm per division.

surfactant, the fouling behaviors of the two types of membranes are considerably different. The flux through the cellulose acetate membrane decreases slowly throughout the entire fouling test, whereas the flux through the composite membrane drops sharply during the first 12 h and declines more gradually later. Furthermore, the overall permeate flux reduction due to fouling is much greater with the composite membrane than that with the cellulose acetate membrane.

Previous experimental and theoretical analyses of colloidal fouling and particle deposition onto membrane surfaces indicate that the rate of colloid deposition onto a permeable surface is controlled by an interplay between double layer repulsion and the opposing hydrodynamic force resulting from the convective flow toward the membrane (the so-called 'permeation drag') [1,3]. The hydrodynamic force

can be ruled out as a cause for the different fouling behaviors of the membranes, since the initial permeate flux was identical for both membranes in the fouling experiments. Furthermore, because the ionic strength was identical and the zeta potentials of the two types of membranes were rather comparable, one may assume that the double layer repulsion force in the fouling tests was not much different for the two membranes. Hence, other explanations for the increased fouling rate of the composite membrane should be sought.

Another possible cause for the different fouling behaviors of the two types of membranes is surface chemical heterogeneity. Inherent local variations in the chemical nature of the polymer at the membrane surface can produce nonuniform distribution of surface charge and local variations in the hydrophobicity of the membranes. Theoretical analyses show that

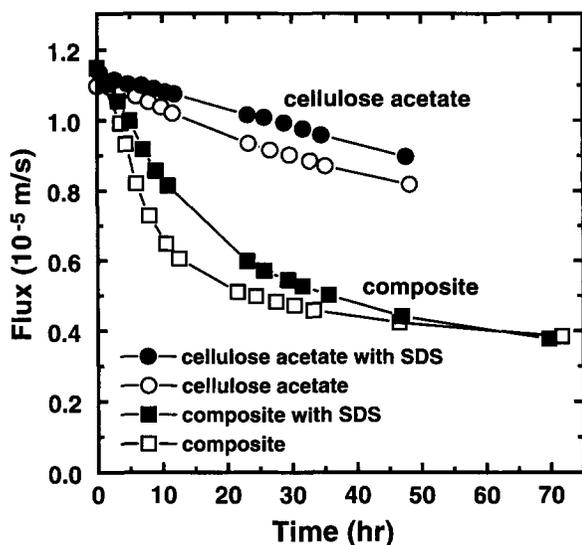


Fig. 5. Permeate flux versus time as a result of fouling for the composite and cellulose acetate RO membranes. Experiments with the composite membrane were carried out at pH 7.8, while those with the cellulose acetate membrane, at pH 5.4–5.6. Open symbols are for fouling experiments with 0.01 M NaCl and closed symbols are for fouling at 0.01 M NaCl plus 0.3 mM SDS. Silica colloid concentration was 90 mg/l and the temperature was kept at 20°C. Note that a flux of 10^{-5} m/s is equivalent to 21 gal/ft² day (GFD) or 36 l/m² h (LMH).

surface chemical heterogeneities can have a profound effect on the attachment rate of colloids onto stationary surfaces [13,14]. Surface chemical heterogeneities may provide favorable sites for attachment onto what is otherwise an unfavorable surface for colloid attachment. The rate of colloid attachment to these favorable sites may be several orders of magnitude higher than that to the unfavorable sites.

Surface chemical heterogeneities of negatively-charged surfaces can be masked by the addition of an anionic surfactant [15,16]. Adsorption of anionic surfactant molecules onto chemically heterogeneous surfaces results in a more uniform distribution of surface charge [15]. The zeta potential results (Fig. 1) indeed show that, in the presence of SDS, the membranes become much more negative and the difference between the zeta potential of the two membranes is eliminated. However, the fouling results in the presence of SDS shown in Fig. 5 (solid symbols) reveal that the marked difference between the fouling behavior of the cellulose acetate and compo-

site membranes still remains. There is a small decrease in the rate of fouling in the presence of surfactant due to increased electrostatic repulsion between colloids and the membrane surface, but fouling is still significant.

It is evident that the only major remaining factor to explain the difference between the fouling behaviors of the two types of membranes is the marked difference in their surface morphology, as shown in Figs. 2,3 and 4. In the following subsection, we discuss briefly the role of surface roughness in enhancing the rate of colloid attachment to rough surfaces.

3.4. Role of surface roughness in colloid–membrane interaction

The classical Derjaguin–Landau–Verwey–Overbeek (DLVO) theory [17] for calculating the interaction energy (sum of double layer and van der Waals interactions) between a surface and an approaching colloidal particle assumes that surfaces are perfectly smooth at the molecular level. Based on this assumption, DLVO theory predicts that colloidal forces act normal to the surfaces of the interacting bodies. In real systems, however, surface irregularities always exist and the assumption of ideal smooth surfaces breaks down. The AFM and SEM images shown earlier demonstrate that synthetic membrane surfaces can indeed have considerable surface roughness. Hence, the use of classical DLVO theory to explain experimental observations of colloidal fouling in membrane systems may not be adequate.

Surface roughness of the type shown by the AFM and SEM images of the composite membrane produces tangential colloidal forces which can immobilize colloidal particles on the membrane surface [18,19]. Furthermore, when a colloidal particle is in close vicinity of a rough membrane surface, the interaction can no longer be described by a single value of interaction energy; rather, a distribution of interaction energies should be considered [13,14,18–20]. These effects of surface roughness result in enhanced attachment of colloids onto the membrane surface (compared to the ideal case of a smooth membrane), and hence, more severe fouling. The important role of surface roughness in enhancing the attachment rate between particles (in coagulation) or between a particle and a surface (in deposition and

filtration) has been pointed out by many investigators [13,15,19–25]. These studies have direct relevance to our observation of the increased fouling rate of rough composite membranes.

Large-scale surface roughness, of the same order of magnitude as the colloids interacting with the surface, may also increase the rate of colloid attachment by providing a larger surface area and greater contact opportunities for particles with the membrane surface. This mechanism is somewhat similar to the well-known phenomenon of ‘filter ripening,’ whereby particles retained on filter grains during the initial stages of filtration significantly enhance the subsequent removal rate of particles [26].

4. Conclusion

Colloidal fouling of RO membranes is markedly influenced by membrane surface morphology. Surface roughness increases membrane fouling by increasing the rate of colloid attachment onto the membrane surface. The higher fouling rate of aromatic polyamide composite membranes compared to that of cellulose acetate membranes is attributed to the inherent surface roughness of interfacially-polymerized aromatic polyamide composite membranes.

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