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Ann-Sofi Jönsson[a]; Bengt Jönsson[b]
[a] DEPARTMENT OF CHEMICAL ENGINEERING I, LUND UNIVERSITY, LUND, SWEDEN [b] DEPARTMENT OF PHYSICAL CHEMISTRY 1, LUND UNIVERSITY, LUND, SWEDEN

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Colloidal Fouling during Ultrafiltration

ANN-SOFI JÖNSSON*
DEPARTMENT OF CHEMICAL ENGINEERING I
LUND UNIVERSITY
P.O. BOX 124, S-221 00 LUND, SWEDEN
FAX: +46 46 222 45 26

BENGT JÖNSSON
DEPARTMENT OF PHYSICAL CHEMISTRY 1
LUND UNIVERSITY
P.O. BOX 124, S-221 00 LUND, SWEDEN
FAX: +46 46 222 44 13

ABSTRACT

Colloidal fouling causes serious problems in many membrane plants. Two different kinds of flux-reducing phenomena occur when treating colloidal dispersions. When treating stable dispersions the flux is reversible and can be restored after changing the operating parameters, such as the transmembrane pressure or the crossflow velocity. The flux reduction experienced when treating unstable colloidal dispersions is irreversible. In this study the DLVO theory, well-known from colloid chemistry, has been used to illustrate the mechanisms underlying the difference in filtration characteristics between stable and unstable colloidal dispersions.

Key Words. Concentration polarization; Fouling; Colloid; Silica sol; Ionic strength; pH

INTRODUCTION

Colloidal fouling is a serious problem experienced in many membrane plants. Colloidal fouling is caused by the accumulation of colloidal parti-

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* To whom correspondence should be addressed.

cles on the membrane surface, followed by coagulation. The rate of coagulation depends mainly on the colloidal stability. The salt concentration and the pH are the two main factors affecting the colloidal stability. The higher the surface charge of the colloidal components in the solution, the greater the colloidal stability. Ion-exchange softening (i.e., replacing multivalent cations with Na^+) and adjustment of pH are commonly used ways of improving colloidal stability.

One well-known and serious consequence of colloidal fouling is the flux reduction experienced during ultrafiltration of colloidal dispersions. Another consequence, to which less attention has been paid, is the irreversible flux behavior of unstable colloid sols.

If the crossflow velocity is temporarily decreased during ultrafiltration of a stable colloidal dispersion, the initial flux is restored when the flow velocity is increased again, whereas when treating an unstable colloidal dispersion, the flux is not recovered. The behavior is similar if the transmembrane pressure is temporarily increased. Upon decreasing the pressure, the flux of the stable solution returns to the initial value, whereas the flux of an unstable colloid solution is lower than before.

Great care is therefore required to ensure that the operating conditions are stable when treating unstable colloidal dispersions, whereas the reversible flux behavior of stable solutions allows variations in the operating conditions.

A colloid solution is commonly defined as a system in which the size of one or more of the components is in the range 1 nm to 1 μm (1), i.e., systems containing large molecules and/or small particles. Consequently, many solutions treated by ultrafiltration are colloid systems. Ultrafiltration is also commonly used as a pretreatment process for colloid removal in reverse osmosis plants. Common foulants in these plants are iron oxides, aluminum silicates and hydroxides, humic acids, bacteria, algae, and biological debris.

In this study a well-defined colloid, a silica sol, was used to demonstrate the flux behavior of stable and unstable colloidal dispersions. It is shown how the basics of colloid chemistry can be used to illustrate the mechanisms underlying the difference in performance between these two types of colloidal dispersions.

EXPERIMENTAL PROCEDURE

Negatively charged colloidal hydrophilic silica, Ludox HS-40 from DuPont, with an average particle diameter of 12 nm, was used in the experiments. The density of silica is 2450 kg/m^3 and the molecular weight of a silica particle 1,340,000 Da. The content of sodium chloride in the "pure" silica sol was less than 10 mM.

Sodium chloride (pro analysis) and hydrochloric acid used were purchased from Merck. The conductivity of the deizoned water, used in all experiments, was <0.2 mS/m. In order to remove colloidal and macromolecular contaminants, the deionized water was filtered through a membrane with a nominal pore size of 0.2 μm immediately before usage.

Sophisticated rotating filter devices have been used in previous investigations (2–10). In this investigation a simple, commercial module manufactured by Flootek AB, Sweden, was used. A schematic sketch of the module can be found in Fig. 1. The module was equipped with one membrane above and one below a rotor blade. Each membrane had an area of 0.05 m^2. A poly(ether sulfone) membrane, PES25, from Hoechst, with a nominal cut-off of 25,000 Da, was used in the experiments. The same membranes were used throughout all tests.

During all tests the concentration of SiO_2 was 4 g/L, the operating pressure 0.1 MPa, the temperature 25°C, and the circulation flow 0.3 m^3/h. The volume of solution was 15 L. The feed concentration was maintained constant by recycling both the retentate and the permeate to the feed tank. The rotor speed was varied between 0 and 1000 rpm.

All chemicals were first dissolved in deionized water and then gradually added to the feed tank. During the addition of chemicals the water was recirculated in the system at maximum rotary speed, 1000 rpm. After each addition of chemicals the solution was recirculated, at 1000 rpm, through the module for 10 minutes in order to attain stable conditions before mea-

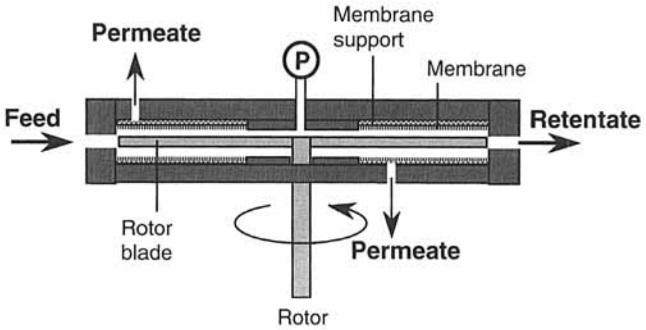

FIG. 1 Schematic sketch of the module used in the experiments. The diameter of the membrane cell is 257 mm. The length of the rectangular rotor blade is 247 mm, the width is 60 mm, and the thickness is 5 mm. The distance between the two membranes is 18 mm.

surement of the flux. The rotary speed was decreased stepwise to 800, 600, 400, 200, and 0 rpm, and thereafter increased stepwise again. After each alteration of the rotary speed, 2 minutes were allowed to elapse before measurements of the flux were made.

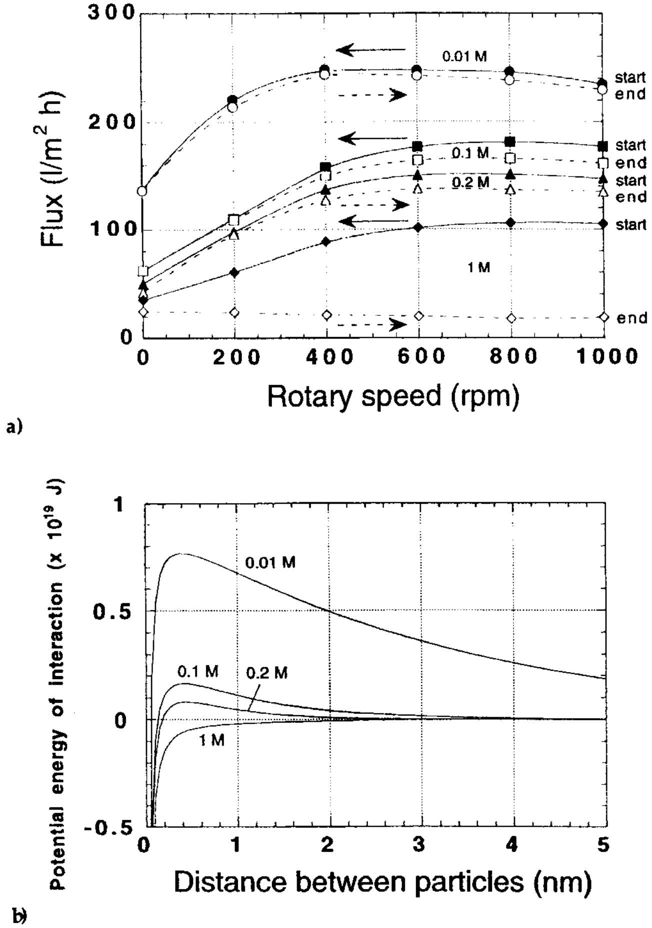

FIG. 2 (a) Ultrafiltration of a silica sol at different salt concentrations. The solid symbols denote decreasing rotary speed and the open symbols increasing rotary speed. (b) The influence of sodium chloride concentration on the total potential energy of interaction of two spherical silica particles in water: $d = 12 \times 10^{-9}$ m, $T = 298$ K, $z = 1$, $A_{\text{eff}} = 1 \times 10^{-20}$ J (13), $e/e_0 = 78.5$ and $y_d = 70$, 40, 35, and 20 mV at 0.01, 0.1, 0.2, and 1 M, respectively (14). V_A and V_R calculated using Eqs. (1)–(4) in the Appendix. As long as the total potential energy of interaction is positive, there is a net repulsive interaction between the particles.

Cleaning was performed before the beginning of the ionic strength and pH tests. A constant pure water flux for at least 12 hours was ensured before the addition of the silica sol. The membranes were cleaned with a 0.5% solution of the alkaline cleaning agent Ultrasil 10 from Henkel. The temperature during cleaning was 60°C. Before, and especially after cleaning, the system was thoroughly rinsed with deionized water.

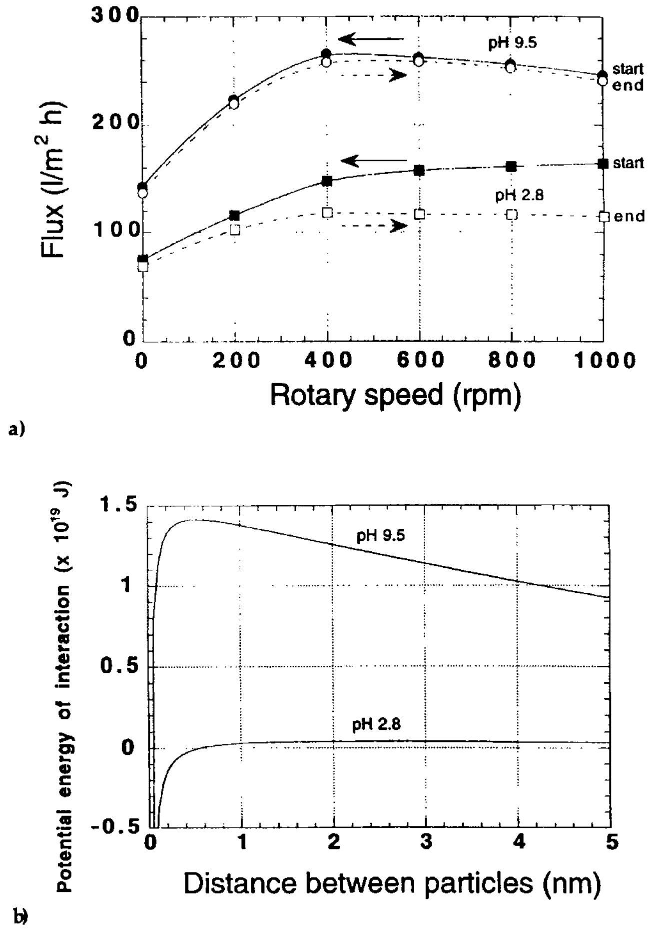

FIG. 3 (a) Ultrafiltration of a silica sol, before and after the addition of hydrochloric acid. The pH was 9.5 before addition and 2.8 after addition of the hydrochloric acid. The solid symbols denote decreasing rotary speed and the open symbols increasing rotary speed. (b) The influence of pH on the total potential energy of interaction. The surface potential of a silica sol containing 1 mM KCl is 100 mV and 15 mV at pH 9.5 and pH 2.8, respectively (14). Other parameters and coefficients in Eqs. (1)–(4) have the same values as in Fig. 2(b).

RESULTS

It is well-known that changes in ionic strength and pH affect the flux of colloidal dispersions (11, 12). The influence of the ionic strength was studied in this investigation by adding an increasing amount of sodium chloride to a silica sol. As the NaCl concentration increased, the flux decreased, but was still reversible, until, at 1 M NaCl, the flux decline became irreversible, as shown in Fig. 2(a).

When sodium chloride was added to pure, deionized water, no influence of rotary speed on the flux was detected. There was, however, a certain flux decrease. The flux at 0.1, 0.2, and 1 M NaCl was 91, 88, and 87%, respectively, of the flux of deionized water.

The influence of pH was investigated as the pH of a silica sol was decreased by the addition of hydrochloric acid. When the pH was decreased, the flux of the solution decreased considerably, as shown in Fig. 3(a). As can be seen in the figure, the flux of the low-pH solution was only partially reversible.

It was established that the low pH did not influence the membrane itself. The flux of deionized water (pH 6.5) and a hydrochloric acid solution with a pH of 2.6 was measured at various rotary speeds. The flux was not influenced by the rotary speed in either case. The flux of the acidic solution was slightly lower, 99%, than that of the deionized water.

DISCUSSION

An important property of colloidal dispersions is the tendency of the particles to aggregate, and even if the particles do not aggregate, particle–particle interactions have a considerable influence on the flux of silica sols, as shown by McDonogh et al. (15).

When treating charged particles, such as silica particles, two main types of interaction contribute to the total particle–particle interaction. One is the attractive van der Waals force and the other is the repulsive electrostatic force. These two types of interaction have been thoroughly studied in colloid chemistry, and advanced theoretical models have been presented. The most well-known theory is the DLVO theory, which gives a reliable qualitative description of these interactions. The basic expressions used in the DLVO theory are given in the Appendix. These expressions have been used to model particle–particle interactions in the solutions used in the experiments presented in this paper.

The total potential energy of interaction is very sensitive to electrolyte concentration, as added electrolyte causes a compression of the diffuse parts of the double layer around the particles. The influence of electrolyte concentration on the total potential energy of interaction between silica particles has been calculated using Eqs. (1) and (2) in the Appendix. The influence of the electrolyte concentration on the total potential energy of interaction, shown in Fig. 2(b), corresponds well with the flux results obtained during the experiments depicted in Fig. 2(a). As shown in Fig. 2(b), the electrostatic repulsion between silica particles decreases as the concentration of the sodium chloride increases. The decrease in flux obtained as the electrolyte concentration was increased is therefore probably due to a more close-packed configuration in the boundary layer as the repulsive forces between the particles decrease.

As long as the concentration of sodium chloride is less than 1 M, there remains a net repulsion between the silica particles in the boundary layer at the membrane. It is therefore possible to remove the outer particles in this layer by increasing the rotary speed. However, in the 1 M NaCl solution the attractive forces dominate and the silica sol coagulates. The increased fluid shear forces are no longer able to overcome the attractive forces between the particles and it is therefore not possible to remove the particles accumulated in the boundary layer by increasing the rotary speed.

The total potential energy of interaction is also influenced by the pH. The surface potential decreases as the pH decreases. At a high pH of the silica sol (when the surface potential is high), the repulsive electrostatic forces dominate, whereas with decreasing pH the charge density of the silica particles decreases (and thus the surface potential), and the attractive van der Waals force becomes dominant, as shown in Fig. 3(b). This is reflected in the flux behavior of the silica sol shown in Fig. 3(a), although the irreversibility of the flux decline is not so pronounced in this case as in Fig. 2(a).

CONCLUSIONS

It has been demonstrated in this investigation that there is a correlation between the flux of a silica sol and the total potential energy of interaction between silica particles, estimated by the DLVO theory. As shown in this investigation, two different kinds of flux-reducing phenomena occur when treating colloidal dispersions. If the dispersion is stable, the variation in flux with rotary speed is reversible. In this case the flux decline is due to concentration polarization. If the dispersion is unstable, the flux is not restored upon increasing the rotary speed after decreasing it. In this case the flux decline is due to fouling caused by the formation of a cake at the membrane surface. Concentration polarization and cake layer fouling are easily distinguished from one another by the use of a shear-promoting module, as shown in this investigation.

The basic colloid chemistry mechanisms underlying the reversible flux behavior of stable and the irreversible behavior of unstable colloidal dispersions is illustrated by the DLVO theory. The transition between concentration polarization and fouling occurs when the attractive particle–particle interaction becomes greater than the repulsive electrostatic forces. At this point it is impossible to remove the particles in the boundary layer at the surface of the membrane by increasing the shear forces in the system.

APPENDIX

The principal cause of aggregation is the attractive van der Waals force between the particles, whereas stability against aggregation is a consequence of repulsive interactions, such as the electrostatic interaction between similarly charged particles or the particle–solvent affinity (1).

The attractive force, V_A, between neutral, chemically saturated molecules, postulated by van der Waals, takes the following form for identical spheres (1):

$$V_A = -\frac{A_{\text{eff}}}{12}\left[\frac{1}{x(x+2)} + \frac{1}{(x+1)^2} + 2\ln\left(\frac{x(x+2)}{(x+1)^2}\right)\right] \tag{1}$$

where A_{eff} is the effective Hamaker constant and $x = y/d$ for identical spheres. y is the shortest distance between two particles and d is the diameter of a particle.

The repulsive double-layer interaction energy, V_R, for identical spheres is (1)

$$V_R = \frac{16\pi\epsilon d k^2 T^2 \gamma^2}{e^2 z^2} \exp(-\kappa y) \tag{2}$$

where ϵ is the permittivity of the dispersion medium, k is the Boltzmann constant, T is the absolute temperature, e is the unit charge, z is the counterion charge number, and γ and κ are given below:

$$\gamma = \frac{\exp(ze\psi_d/2kT) - 1}{\exp(ze\psi_d/2kT) + 1} \tag{3}$$

and

$$\kappa = \left(\frac{2e^2 N_A c_e z^2}{\epsilon k T}\right)^{1/2} \tag{4}$$

where ψ_d is the surface potential, N_A is Avogadro's constant, and c_e is the concentration of electrolyte.

The total potential energy of interaction between the particles in a sol is obtained by summation of V_A and V_R.

SYMBOLS

A_{eff}	effective Hamaker constant (J)
c_e	concentration of electrolyte ($mol \cdot m^{-3}$)
d	diameter of a spherical particle (m)
e	unit charge (A·s)
k	Boltzmann constant ($J \cdot K^{-1}$)
N_A	Avogadro's constant (mol^{-1})
T	absolute temperature (K)
V_A	force of attraction (J)
V_R	repulsive double-layer interaction energy (J)
y	shortest distance between two particles (m)
z	counterion charge number

Greek

ϵ	permittivity of the dispersion medium ($A \cdot s \cdot V^{-1} \cdot m^{-1}$)
ψ_d	surface potential (V)

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