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Rajindar Singh[a]
[a] M.A.E. ENVIRONMENTAL TECHNOLOGIES, AMHERST, MA, USA

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TECHNICAL NOTE

Investigation of Ultrafiltration Rejection of Surfactant Micelles by Dynamic Light Scattering

RAJINDAR SINGH
M.A.E. ENVIRONMENTAL TECHNOLOGIES
P.O. BOX 3261, AMHERST, MA 01004, USA

ABSTRACT

The absence of nonionic surfactant micelles in ultrafiltration membrane (molecular weight cut-off = 10,000) permeates is verified with the aid of a dynamic light-scattering (DLS) technique. DLS is also used to determine the hydrodynamic radii of micelles at concentrations above the critical micelle concentration. An empirical relationship between the micelle diameter, diffusion coefficient, and a pseudomolecular weight is plotted. The relationship can be used to screen high molecular weight cut-off membranes for surfactant-based UF applications.

INTRODUCTION

Surfactant-based ultrafiltration (SBUF) has been studied for possible use in removing dissolved organic compounds from hazardous wastewater (1, 2). The basis of SBUF is that at concentrations above the critical micelle concentration (CMC), surfactant molecules attach to each other to form organized aggregates or micelles (3). These large aggregates, which average 30–200 monomers, are easily rejected by UF membranes (4). The aggregates form in such a way that the hydrophobic portions of the molecules align toward the center, away from the surrounding hydrophilic aqueous solution. These aggregates are able to solubilize volatile organic compounds and hydrocarbons (3, 5). Generally speaking, the more hydrophobic the organic compound, the higher the degree of solubilization in a micelle.

BACKGROUND

The size of micelles is an important parameter for selecting a membrane with the largest molecular weight cut-off (MWCO) in order to achieve both a high flux and a high rejection. Since only micelles are rejected by UF membranes, a high CMC value (as is the case with ionic surfactants) means large quantities of surfactant monomers would leak through the membrane. Nonionic surfactants, by contrast, usually have large aggregation numbers and low CMC values (3). Therefore, nonionic surfactants would be ideally suited for SBUF applications in hazardous wastewater treatment (6).

The rejection of micelles has been determined in SBUF studies by measurement of the surfactant concentration in the permeate. No direct measurement of the presence or absence of micelles in the UF permeate has been reported in the literature. In this study we investigated the absence of micelles in UF permeate using the technique of dynamic light scattering (DLS) (7). The diameter of micelles was also determined.

The micelle diameter is calculated from the value of the diffusion coefficient measured by DLS. If one assumes that all micelles are spherical in shape, the radius of a micelle in solution may be calculated by using the Stokes–Einstein relation:

$$D = kT/(6\eta R)$$

where D is the diffusion coefficient, k is Boltzmann's constant, T is the absolute temperature, η is the solvent viscosity, and R is the hydrodynamic radius of the micelle. The DLS technique for measuring D is rapid, precise, requires only small volumes, and is nondestructive (7). It is currently the technique of choice for measuring the diffusion coefficients of relatively small particles (<1 μm).

EXPERIMENTAL

Materials

The nonionic surfactants Tween 80 (Rhone-Poulenc) and Igepal RC-520 (ICI America) were used in UF experiments. Tween 80 is a polyoxyethylene sorbitan monooleate with a molecular weight (MW) of 1326 and a CMC equal to 450 mg/L. RC-520 is a dodecylphenoxy polyethyleneoxy ethanol (MW = 526, CMC = 15 mg/L). Limited tests were also conducted with an anionic surfactant, sodium dodecyl sulfate, SDS (Aldrich Co., MW = 288, CMC = 2360 mg/L). All surfactants were used as received. Regenerated cellulose acetate membranes (Amicon, YM-10) were used in nonionic surfactant UF experiments. The average pore size of the membrane is 29 Å and the MWCO is 10,000. A Spectrum C-5K cellulose acetate

membrane (MWCO = 5000, pore diameter = 15 Å) was used for SDS runs.

Ultrafiltration

Ultrafiltration (UF) tests were conducted in a cross-flow cell (Molecular/Por, Spectrum) at 2.75 bar·g and 20 ± 1°C. The system consisted of a UF cell with an effective membrane area of 14.52 cm^2, a 600-mL feed vessel, and a variable speed positive displacement pump. The feed flow rate was 1100 mL/min. The flow rate could be varied by controlling the pump speed and the backpressure control valve. The retentate was recycled back to the feed tank.

Prior to each run, distilled water flux was established at the operating conditions by taking data over a 1-hour period. After each run the membrane and cell were washed with a biodegradable detergent (Fisher Brand) and the pure water flux was measured again. Permeate samples were collected in 20 mL vials for measuring surfactant concentration and for light-scattering analysis.

Surfactant Measurements

The concentration of nonionic surfactants was measured using a Perkin-Elmer UV-VIS spectrophotometer at a wavelength of 223 nm. The concentration of SDS was measured with a Myron LDS conductivity meter.

Light-scattering measurements (7) of surfactant micelles were made at the University of Massachusetts, Amherst (Ford-Langley Instruments, Amherst). All samples were filtered through a 0.45-μm Millpore filter (Millex-HV, polyvinylidene difluoride membrane, polyethylene housing) to remove "dust" or other solids. All measurements were made at ambient conditions.

RESULTS AND DISCUSSION

Hydraulic radii of Tween 80 and RC-520 micelles are given in Table 1. The data show that the at concentrations above CMC, the micelles diameter was much larger than the average pore diameter of YM-10 membrane which is 29 Å. Light-scattering data show that no micelles were observed in the permeate samples. This is also evident from the surfactant concentrations in the permeate; all concentrations were below the CMC values. Thus, all micelles were rejected by the membrane even under high flow conditions. One would anticipate that micelles would deform under high shear conditions, resulting in possible leakage through the membrane. The concentration of SDS in the permeate, for example, was 1270 mg/L, which is one-half its CMC value. Except for RC-520, permeate surfactant con-

TABLE 1
Nonionic Surfactant Micelles Size Analysis Data

Surfactant	UF sample[a]	Surfactant concentration (%)	Hydrodynamic radius (Å)	Diffusion coefficient (cm^2/s)	Remarks
Tween 80	Feed	0.436	37–39	5.5×10^{-7}	—
" "	Permeate	0.004	No micelle	n/a	No scattered light
" "	Retentate	4.5	37–39	5.5×10^{-7}	—
RC-520	Feed	0.0061	400–600	4.5×10^{-8}	—
" "	Permeate	0.0015	No micelle	n/a	No scattered light

[a] Amicon YM-10 membrane, MWCO = 10,000 dalton, pore diameter = 29 Å.

centrations were considerably lower than their CMC values. There are two possible explanations for this behavior: 1) surfactant is adsorbed on the membrane, and 2) it is not possible to generate a clean separation with a UF membrane.

The diameter of SDS micelles was 48 Å, which is in good agreement with the values of 45–50 Å reported in the literature (8). The micelle diameter increased from 48 Å at CMC to 180 Å when the SDS concentration was four times its CMC. Generally speaking, micelles grow in size with concentration, the structure often changing from spherical at low concentrations to rodlike at high concentrations (3, 8, 9). In the case of certain surfactants, however, structure appears to be independent of concentration (10). The data in Table 1 show that the micelle size of Tween 80 also remains constant (75–80 Å), even when the concentration increases 10-fold.

The size of micelles of RC-520 and Tween 80 is compared with data for a few selected proteins as obtained from the literature in Table 2 (11).

A plot of the protein molecule diffusion constant as a function of its molecular weight is shown in Fig. 1. The diffusion coefficients of Tween

TABLE 2

Protein	Molecular weight	D (cm^2/s)
Albumin	65,000	6×10^{-7}
γ-Globulin	170,000	4×10^{-7}
Collagen	345,000	0.7×10^{-7}

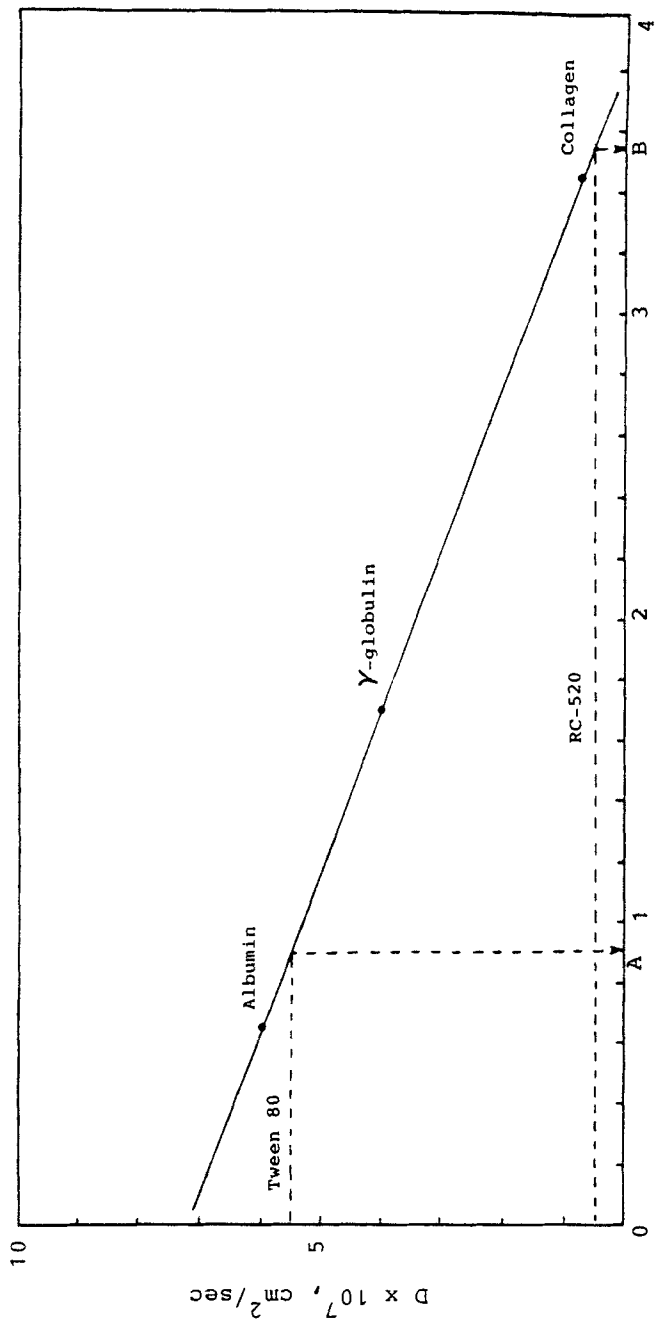

FIG. 1 Diffusion coefficient vs molecular weight plot for macromolecules. Diffusion coefficients for Tween 80 and RC-520 are from Table 1. Points A and B refer to pseudomolecular weights of Tween 80 and RC-520, respectively.

80 and RC-520 are also plotted. Corresponding points of pseudomolecular weights of Tween 80 and RC-520 micelles, based on their diffusivities, are determined as 92,000 and 346,000, respectively.

The rejection of macromolecules depends upon the size and shape of the solute, e.g., globular proteins have a higher rejection than linear polymers for the same molecular weight. As a rule, it is best to select a membrane with a MWCO about half of the solute to be separated. Thus, UF membranes with MWCOs of 30,000 and 100,000 for Tween 80 and RC-520, respectively, could achieve both high flux and high rejection. In an earlier study it was shown that in the case of some polyethoxylated nonionic surfactants, complete rejection of micelles was achieved with 50,000 MWCO membranes when CMC was exceeded by at least one order of magnitude (9).

In conclusion, dynamic light scattering has been shown to be a valuable technique for confirming the absence of micelles in a UF permeate. The relationship between the micelle diameter, diffusion coefficient, and a pseudomolecular weight can be used to screen high MWCO membranes for SBUF applications.

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