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Electrical Aspects of Adsorbing Colloid Flotation. XIX. Viscosity and the Structures of Mixed Micelles

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Abstract

Viscosity measurements on mixed surfactant solutions containing the nonionic surfactant Triton X-100 and a number of other cosurfactants (dodecanoic acid, dodecyl amine, sodium dodecylsulfate, dodecyltrimethylammonium chloride, dodecyl alcohol, and sodium dodecylphosphate) indicate the presence of two quite different types of micelles. Solutions containing an electrically neutral cosurfactant exhibit very large viscosities, indicating the presence of extended micellar structures. Solutions containing a charged cosurfactant exhibit much lower viscosities, indicating that the micelles in these solutions are small spherical or ellipsoidal structures. Evidently coulombic repulsions destabilize the extended structures when charged surfactants are present in the micelles. The effects of pH and ionic strength are consistent with this interpretation.

INTRODUCTION

The use of surfactant mixtures in ore flotation has been a common practice for many years (*1*, *2*), but this has not been practiced in adsorbing colloid and precipitate flotation. We explored theoretically the adsorption of binary surfactant mixtures on surfaces (*3*, *4*), and also investigated the use of mixtures of sodium dodecylsulfate with octanoic acid and some normal alcohols for the flotation of ferric hydroxide and of mixed ferric and cupric hydroxide flocs (*5*). The experimental work indicated that very marked reductions in surfactant costs could be made without sacrificing separation efficiency.

In order to optimize these mixed surfactant systems, it would be helpful to have a good understanding of the nature of the interactions between the two species of surfactant in these solutions and in the monolayers which they form on the precipitate surfaces. One method by which the interactions of these cosurfactants was investigated was by the determination of critical micelle concentrations of the surfactant mixtures; this was done by conductimetric titrations and also by surface tension measurements (*5*). Other techniques which we have used include viscosity measurements (to be discussed here) and NMR measurements of proton longitudinal relaxation times (to be dealt with in another paper).

One of the more interesting properties of surfactants is their ability to form micellar aggregates by self-association. The resulting micelles are able to solubilize a variety of solutes, with important applications in biochemistry and physiology, micellar catalysis, enhanced oil recovery, cleaning agents, etc. Solubilization phenomena in micelles have been studied quite extensively (*6, 7*). Techniques used include quasi-elastic light scattering (*8, 9*), steady-state fluorescence quenching (*10, 11*), and NMR spectroscopy (*12–16*). These studies indicate that solubilization can be viewed as either a partitioning of the solute between the micellar nonpolar interior and the aqueous environment, or as the formation of mixed micelles, depending on the nature of the solute. Solubilizates like alkanes are mainly found in the interior of the micelles, while more polar species lie close to the surface. If the solubilizate is amphipathic, such as a long-chain alcohol, it orients with its polar or ionic group close to the aqueous solution phase and with its alkyl chain toward the interior of the micelle.

Here we shall examine the structures of mixed micelles containing Triton X-100 (henceforth denoted as TX-100, an alkylphenylpolyethoxy alcohol, approximately $(CH_3)_3CCH_2C(CH_3)_2C_6H_4(OCH_2CH_2)_9OH$ and a number of other cationic, anionic, and nonionic surfactants. Viscosity measurements provide a convenient way to detect gross changes in micellar shape and size, and turn out to yield quite useful information about the changes induced in the micellar structure by the presence of these solubilizates.

CHEMICALS, APPARATUS, AND PROCEDURES

Scintillation grade Triton X-100 was obtained from J. T. Baker. Its critical micelle concentration was determined by surface tension measurements (location of the break in a plot of surface tension versus log concentration), and found to be 0.31 m*M*, in reasonable agreement with the values reported in Rosen's tabulation (*17*) for compounds of this type. Lab grade sodium dodecylsulfate was purchased from Fisher for use in the initial experiments; in the later work, 99+% pure sodium dodecylsulfate was obtained from Sigma. The critical micelle concentrations of both samples of sodium dodecylsulfate were determined by conductimetric titration; the cmc of the sodium dodecyl sulfate from Fisher was 4.3 m*M*, substantially lower than the value of 8.2 m*M* reported in the literature (*17*). The material from Sigma yielded a cmc of 8.1 m*M*. Dodecyltrimethylammonium chloride, dodecyl alcohol, and lauric acid were obtained from Eastman Kodak. The cmc of the dodecyltrimethylammonium chloride was found to be 21 m*M*, in good agreement with the literature value of 20 m*M* given in Rosen's collection of data (*17*). Dodecyl amine of 98% purity was purchased from Aldrich, and mono-*n*-dodecyl phosphate was purchased from Alpha Products. Lab grade sodium hydroxide, sodium nitrate, and hydrochloric acid were obtained from Fisher. Deionized water was used to make up all solutions.

Viscosities were measured with Cannon-Fenske viscometers. pHs of the solutions were adjusted to the desired values with 1 *M* HCl or NaOH and a Sargent-Welch model LSX pH meter. Five milliliter portions of the solutions were taken in the viscometer tube, and the efflux times were measured after thermal equilibration in a 20 ± 0.1°C thermostat. Kinematic viscosities were calculated in centistokes by multiplying the average of three efflux times in seconds by the viscometer constant, 0.01476 cSt/s. Relative standard deviations of the kinematic viscosity were typically about 0.2%. Viscosities (η) were taken to be numerically equal to the measured kinematic viscosities, since the densities of these solutions were essentially unity, ranging from 1.0069 to 1.011 g/mL.

RESULTS

Figure 1 shows the variation of viscosity with pH for mixed surfactant systems containing 100 m*M* of TX-100 and 35 m*M* of a second amphiphile (dodecanoic acid, dodecyl alcohol, or dodecyl amine); a plot of the viscosity of a 100 m*M* solution of TX-100 alone is also shown. The behaviors of the three plots are quite different from each other and from the curve for TX-100 alone. At low pHs the solution containing dodecanoic acid shows a very high viscosity, which decreases down to that of TX-100 alone as the pH increases. The solution containing dodecanol shows an elevated viscosity over the entire range of pH, from 2.5 to 10.5. The viscosity of the solution containing dodecyl amine is

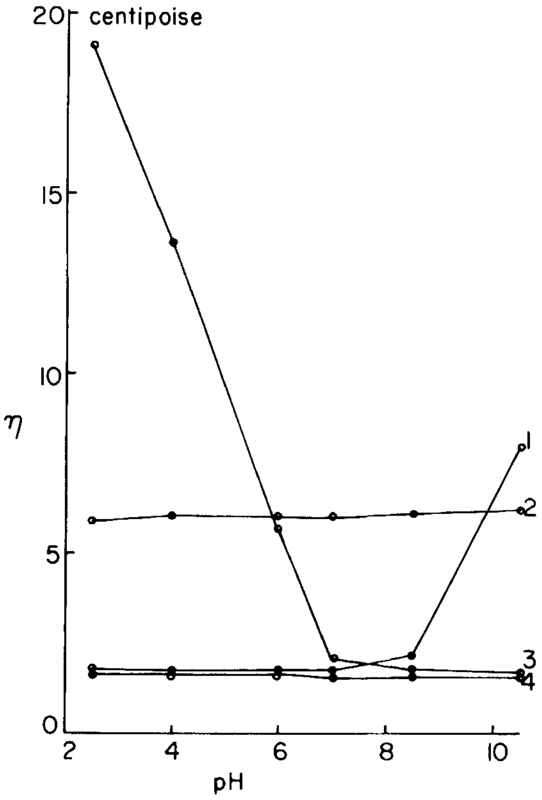

FIG. 1. Viscosities of solutions containing 100 mM TX-100 + 35 mM of a second amphiphile versus pH. (1) Dodecyl amine; (2) n-dodecanol; (3) dodecanoic acid; (4) TX-100 alone.

similar to that of TX-100 alone at low pHs, but shows a very marked increase at high pH.

The dependence of viscosity on the dodecyl amine concentration at a constant (100 mM) concentration of TX-100 is shown in Fig. 2. The pH here is 10.0. As the concentration of the amine increases above 30 mM, the viscosity increases spectacularly, reaching a value of 36.8 cP at an amine concentration of 50 mM.

The effect of varying the TX-100 concentration at a fixed concentration of dodecyl amine (40 mM) is shown in Fig. 3. The viscosity goes through a rather sharp maximum at around 80 mM TX-100. The viscosities of 100 and 200 mM TX-100 alone are shown for comparison, and establish that the large variation in the upper curve is not due to viscosity changes caused by TX-100 alone.

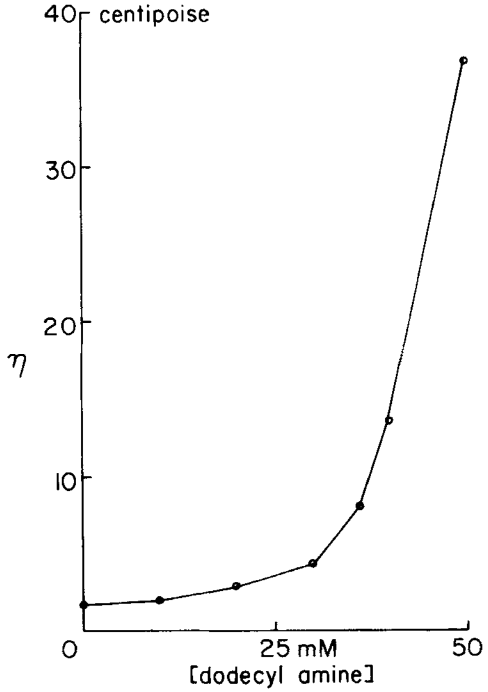

FIG. 2. Viscosities of solutions containing 100 m*M* TX-100 and varying amounts of dodecyl amine. pH = 10.0.

Figure 4 shows the effect of added salt (sodium nitrate) on the viscosity of a solution containing 100 m*M* TX-100 and 35 m*M* dodecyl amine. Runs made at a pH of 10.5 show elevated viscosities over the entire range of pH; runs made at a pH of 2.5 show viscosities which increase markedly with increasing salt concentration over the range studied.

The effects of different acid strengths of the polar or ionic heads of the second amphiphile are shown in Fig. 5; here the viscosities of solutions containing 100 m*M* of TX-100 and 35 m*M* of the second amphiphile are plotted as functions of pH. All plots show low viscosities at high pHs; dodecyl phosphate–TX-100 shows an increased viscosity at pH 2.5, and dodecanoic acid–TX-100 shows a very large increase in viscosity at pH 2.5.

The viscosities of solutions of TX-100 alone show relatively little change over the concentration range 0–200 m*M*, as illustrated in Fig. 6; the viscosity roughly doubles in size over this range. Obviously the much larger viscosity changes observed in the previous figures cannot be due to small variations in the concentration of TX-100.

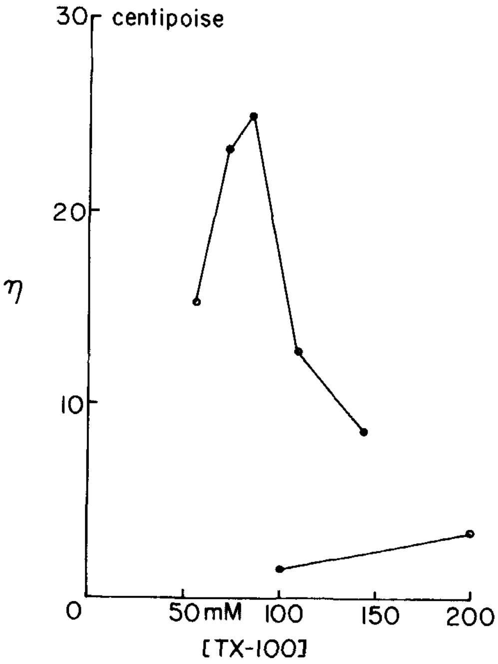

FIG. 3. Viscosities of solutions containing 40 m*M* of dodecyl amine and varying amounts of TX-100. pH = 10.5. The lower line gives viscosities for solutions of TX-100 alone.

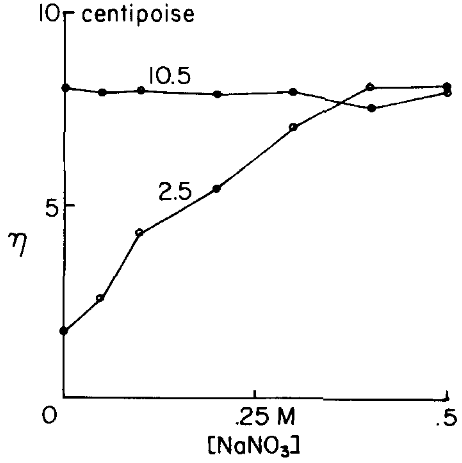

FIG. 4. Effect of ionic strength on the viscosities of 100 m*M* TX-100–35 m*M* dodecyl amine at pH 2.5 and pH 10.5. Sodium nitrate was used as the inert salt to vary the ionic strength.

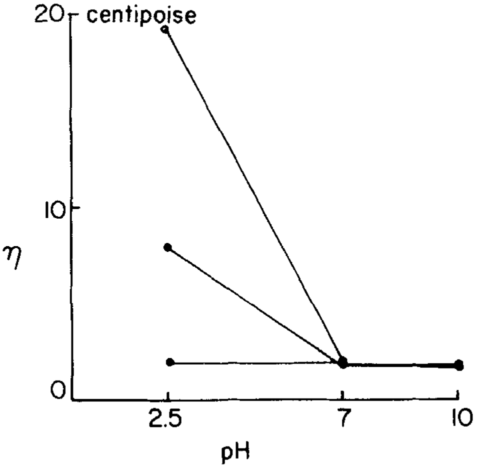

FIG. 5. Effect of pH and the identity of the polar/ionic head group on viscosity of solutions 100 m*M* in TX-100 and 35 m*M* in the second amphiphile. From top to bottom, the second amphiphile is dodecanoic acid/dodecanoate, dodecylphosphoric acid/dodecyl hydrogen phosphate ion, and dodecylsulfate.

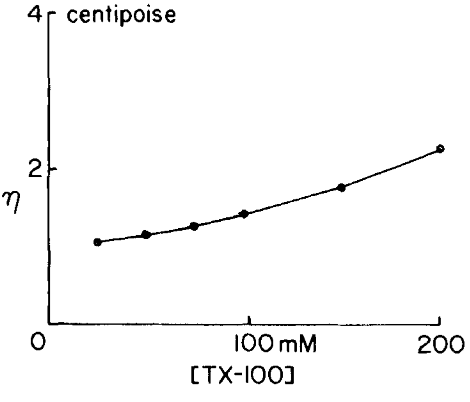

FIG. 6. Viscosities of aqueous solutions of TX-100.

The quite spectacular increases in the viscosities of both TX-100–dodecyl amine and TX-100–dodecanoic acid perplexed us, so we made six sets of measurements in which the dodecyl amine concentration was varied from 0 m*M* up to its solubility limit and the TX-100 concentration was held fixed at values ranging from 25.1 m*M* up to 200 m*M*. The plots of viscosity versus amine concentration are shown in Fig. 7. Most of the curves show a quite substantial increase in viscosity with increasing amine concentration; the solubility of dodecyl amine in those solutions which do not show a large increase is relatively small. The viscosities for two of these solutions attain values roughly as large as the maximum value found for TX-100–dodecanoic acid mixtures.

Figure 8 presents the viscosity dependence of solutions of TX-100 and *n*-dodecanol at pH 7.0. The behavior of this second amphiphile is very similar to that of dodecyl amine and that of dodecanoic acid under conditions where these compounds are not ionic. The viscosity shows quite large increases with increasing dodecanol concentration. Again, some of the curves at lower TX-100 concentrations are limited by the solubility limit of dodecanol in the TX-100 solution.

The behavior of the viscosity of dodecyltrimethylammonium chloride (DTAC) in TX-100–DTAC mixtures is shown in Fig. 9. The pH was 7.0. DTAC, the salt of a strong acid and a strong base, is completely ionized at any pH in aqueous solution. The dependence of viscosity on DTAC

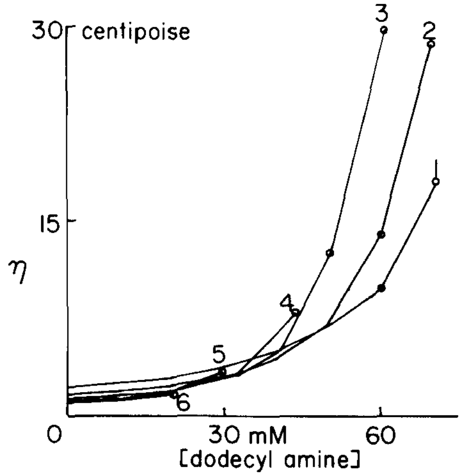

FIG. 7. Dependence of viscosity on dodecyl amine concentration in TX-100 solutions of various concentrations. TX-100 concentrations are as follows: (1) 200; (2) 150; (3) 100; (4) 74.3; (5) 50.2; (6) 25.1 m*M*. pH = 10.0.

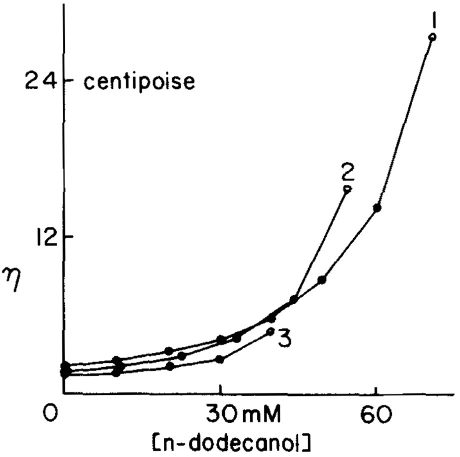

FIG. 8. Dependence of viscosity on *n*-dodecanol concentration in TX-100 solutions of various concentrations. TX-100 concentrations are as follows: (1) 200; (2) 150; (3) 100 m*M*. pH = 7.0.

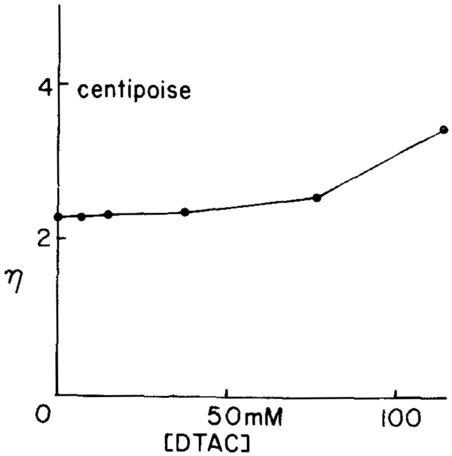

FIG. 9. Dependence of viscosity on DTAC concentration in 200 m*M* TX-100 solutions. pH = 7.0.

concentration in 200 m*M* TX-100 is very weak, increasing from slightly over 2 to slightly over 3 cP.

Figure 10 shows that the behavior of solutions of TX-100 and sodium dodecylsulfate is very similar to that of TX-100–DTAC solutions. In 200 m*M* TX-100 the viscosity increases only by about 50% as the dodecylsulfate concentration increases from 0 to 104 m*M*.

DISCUSSION

It has been suggested that TX-100 micelles are spherical or ellipsoidal in shape (*18, 19*), with molecular weight ranging between 8.6 to 9.0 × 10^4. The micelles are presumed to be hydrated; the oxyethylene groups closest to the phenyl ring pack closely, thereby shielding the inner hydrocarbon core from water, while the rest of the oxyethylene chain is in the form of a hydrated random coil.

It is evident that the cosurfactants used to form mixed micelles with TX-100 can be classified into two groups: those which cause little or no increase in the viscosity of the solution and those which cause quite large increases in the viscosity. It is evident that the former group includes all charged surfactants investigated, and the latter group includes all the electrically neutral surfactants investigated. This conclusion is also supported by the pH dependences of the viscosities of mixtures of TX-100

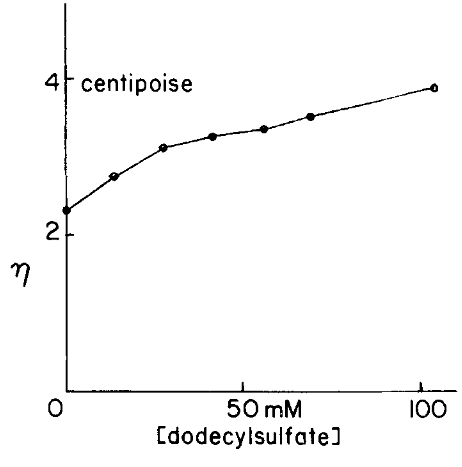

FIG. 10. Dependence of viscosity on sodium dodecylsulfate concentration in 200 m*M* TX-100 solutions. pH = 7.0.

with dodecanoic acid, dodecyl phosphate, and dodecyl amine; in these solutions the viscosities are high under conditions causing the cosurfactant to be electrically neutral, and they are low for pHs at which the cosurfactants are charged. Lastly, increasing the ionic strength of the solution causes a charged cosurfactant–TX-100 solution to increase in viscosity, becoming more like the neutral cosurfactant–TX-100 solutions.

An approach similar to that of Yedgar et al. (*20*) leads to an ellipsoidal or spherical shape for the mixed micelles. This cannot be correct for the cases in which we observe high viscosities, since globular micelles are not known to affect the rheological properties of solutions in such a low concentration range. There is a limit to the size of a spherical or ellipsoidal micelle set by the length(s) of the hydrocarbon chains in the amphiphile(s). Excessive expansion of the micelle results in exposure of the hydrocarbonlike portion of the micelle to water (*21*). We therefore assume a spherical or ellipsoidal shape and a relatively low micellar "molecular weight," comparable to that of TX-100 micelles, for mixed micelles of TX-100 with ionic amphiphiles at relatively low ionic strengths. These mixed micelles presumably have the two amphiphiles coexisting together, with the charged head group of the second amphiphile extending into the polar region of the micelle, which is occupied by water and by ethylene oxide groups of the TX-100.

The high viscosities for the mixed solutions with uncharged second amphiphile point to a radical modification of the micellar structure. Some studies on tetradecyltrimethylammonium bromide (*22*) and sodium dodecyl sulfate (*23*) have indicated a change in the size of these micelles in the presence of alcohols of medium to long chain length. In our system, however, the very substantially increased viscosities appear to indicate a change in the micellar structure, perhaps to a long sphero-cylindrical shape. In this structure the micelles have a large aggregation number. The hydrophilic nature of the surface of this cylinder would tend to cause some uncoiling as the polar heads of both amphiphiles hydrogen bond to water. This type of sphero-cylindrical shape was originally proposed by Debye and Anacker (*24*) for cationic micelles. In this structure the micelles have $n/2$ molecules (n is the aggregation number for a spherical micelle) in each spherical end cap. Additional molecules are incorporated into the cylindrical portion which extends between the end caps.

The presence of ionic heads in the micelle results in electrical repulsions which tend to keep the spherical micelles from coalescing to form long cylindrical structures (*25*). These repulsions can be reduced by increasing the ionic strength of the solution, which increases the screening of the charged amphipaths from each other by their ionic atmospheres. This then permits the formation of extended micellar structures, resulting in the increase in viscosity with ionic strength reported in Fig. 4. Uncharged amphiphiles (such as neutral dodecyl amine) are, as expected, relatively unaffected by the change in ionic strength since, if the second amphiphile is the salt of a weak acid or weak base, adjusting the pH so that it becomes electrically neutral eliminates the coulombic repulsions which previously prevented the formation of the extended sphero-cylindrical micelles.

We see that all of the aspects of the viscosity changes of these solutions of mixed surfactants can be accounted for by the formation of extended micellar structures which are destabilized by coulombic repulsions if the cosurfactant is a charged species and if there is insufficient screening by the ionic atmosphere of the micelle.

Acknowledgment

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