Polymer/Surfactant Interaction—Its Relevance to Detergent Systems[1]

E.D. Goddard*
Haworth, New Jersey 07641-1311

The field of polymer/surfactant interaction is reviewed in this work. Results from two investigative methods, *viz.*, dialysis and surface tension, are discussed, illustrating the main behavioral patterns and outlining the principles of the interactions. Next, aspects of the interaction phenomena that appear to have relevance to detergent formulation are presented. These include solution rheology, solubility control and surface conditioning. Lastly, the importance of surface activity of the polymer itself is stressed, culminating in a discussion of the properties of hydrophobically modified water-soluble polymers ("polymeric surfactants"), both alone and in the presence of conventional surfactants.

KEY WORDS: Cloudpoint, dialysis, gels, interaction models, rheology, solubilization, surface conditioning, surface tension, surfactants, water-soluble polymers.

In recent years, there has been an upsurge of interest in the subject of polymer/surfactant interaction. The 1940s and 1950s saw much research into the properties of combinations of proteins and surfactants, and since then the systems studied have generally comprised mixtures in which both the water-soluble polymer and the surfactant are of synthetic origin. There are a number of reviews carried out in this area (1–3), and the whole field has recently been reviewed in depth by Goddard and Ananthapadmanabhan (4).

As pointed out in these reviews (1–4), a large number of physicochemical techniques—about two dozen—have been employed to examine the interaction patterns of mixtures of aqueous solutions of polymers and surfactants. It is the purpose here to describe only a few of the techniques to develop a picture of the principles behind the interaction patterns. A second purpose is to examine the relevance of the information to contemporary detergent systems and to suggest areas for possible exploitation. Finally, attention is drawn to the unusual reactivity in the above connection of a relatively new class of water-soluble polymers, namely those that are hydrophobically modified.

PRINCIPLES

One concept, popular among early investigators and still employed today, was to consider the interaction as one in which the surfactant molecules are bound by the polymer. This view is understandable in the case of protein as the polymer because, in this case, well-defined sites on the macromolecule for attracting the surfactant molecules could be identified. Indeed, a popular method of measuring the extent of interaction was to directly determine the degree of binding by means of dialysis techniques.

Direct binding studies: phase diagram. In dialysis, the protein (or other macromolecule) is contained in a dialysis bag with a pore size small enough to restrict the polymer molecules, but large enough to allow the smaller surfac-

tant molecules to pass freely. Then, under each set of conditions—generally holding the amount of polymer fixed but varying the amount of surfactant—the system is allowed to come to equilibrium, and binding curves are constructed by analysis of the "internal" and "external" liquors. Such curves illustrate the concepts and characteristics of polymer/surfactant interaction.

Typical dialysis equilibrium results are presented in Figure 1 for the binding of sodium dodecyl sulfate (SDS) by polyethylene oxide (PEO). It is important to note that these measurements were carried out in the presence of salt (0.1 M NaCl) to minimize the Donnan membrane effects (5). The equilibrium binding curve of SDS has a typical sigmoidal shape. At low concentrations of SDS, no binding is registered. Binding starts at a fairly well-defined concentration, variously referred to as the "T_1" concentration (explained later) or the "CAC" (critical aggregation concentration). Above the CAC, binding increases sharply and ultimately levels off when the polymer is saturated. T_1, or CAC, is almost invariably less than the CMC (critical micelle concentration) of the surfactant (*i.e.*, binding, when it occurs, is energetically more favorable than simple self-aggregation of the surfactant), and saturation generally occurs at a (total) surfactant level that exceeds the CMC. The steep increase in binding, which occurs just above the CAC, is a strong indication that the process is cooperative, *i.e.*, initially bound surfactant ions assist the binding of subsequent surfactant ions, probably by formation of micelle-type clusters or aggregates. As with the CMC, the CAC of a (polymer-bound) surfactant decreases progressively when salt is added to the system and, at the same time, the extent of binding increases. For example, with PEO as the binding polymer,
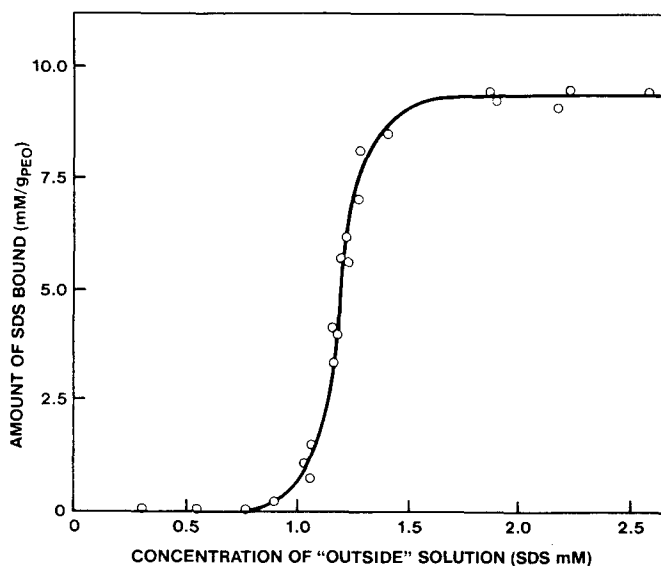

FIG. 1. Binding isotherm of polyethylene oxide/sodium dodecyl sulfate (PEO/SDS) system in 0.1M NaCl: Solid line from Hill equation (Ref. 34). [Reproduced from Shirahama, K., *Colloid Polymer Sci.* 252:978 (1974), with permission.]

saturation binding of SDS is of the order of 0.3 mol SDS per base mol of polymer in a salt-free system, and rises to ca. 1 mol SDS in the presence of 0.1M NaCl (1).

A phase diagram that illustrates the binding behavior has been given for an SDS/PEO [molecular weight (MW) 20,000] system by T. Sasaki et al. (6). Although it is based on measurements in a salt-free system with a gel filtration technique, the results are directly applicable to the present discussion. (Fig. 2). With no interacting polymer present, the area labelled "PS" (the complex) would disappear, i.e., points C and B would coincide, and only the single surfactant ion field and the micelle field would exist. In the presence of the polymer, point A corresponds to the CAC, and B to the condition where all polymer molecules are saturated with surfactant. Further addition of surfactant would then merely result in the creation of more simple micelles.

The discussion so far has involved an interacting nonionic polymer and an ionic surfactant. As will be elaborated upon later, one can expect much stronger interaction when the polymer is a polyion with charges opposite in sign to that of the surfactant. Interaction in such systems usually becomes manifest in the formation of precipitates, i.e., insoluble complexes, over certain concentration ranges and ratios of the two species. Normally, if the polyion bears the same sign of charge as the surfactant, no interaction is observed except in special circumstances, which will be discussed later. Because polycationic conditioning polymers are often incorporated into liquid anionic surfactant systems, it is helpful to construct simple, qualitative phase diagrams in which the appearance of the systems is recorded, i.e., to construct crude solubility diagrams. Such a diagram for the cationic cellulosic Polymer JR*(Union Carbide, Danbury, CT)/SDS system is shown in Figure 3 (7). It is seen that clear systems can be formulated at relatively low or high concentrations of added surfactant for a given concentration
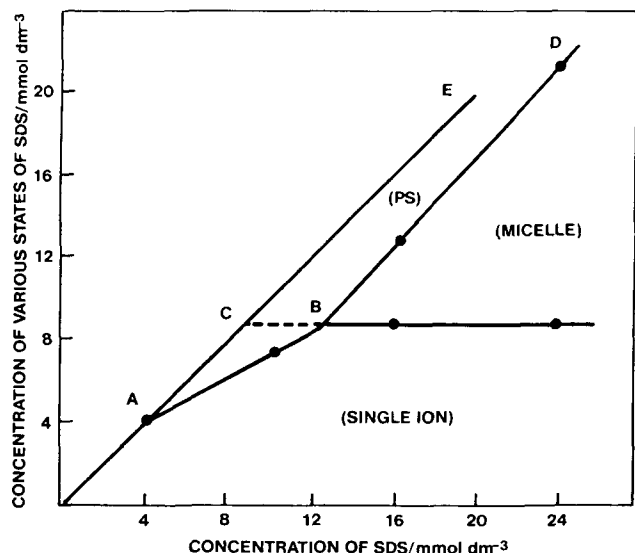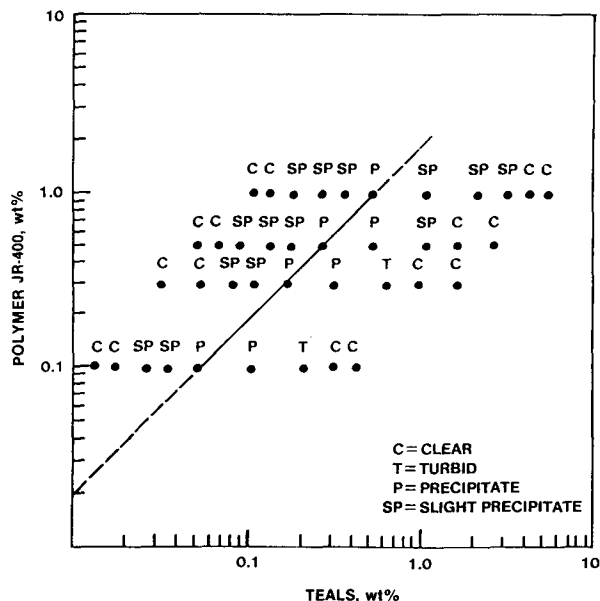

FIG. 3. Solubility diagram of Polymer JR 400/triethanolamine lauryl sulfate system (Ref. 7).

of polymer. In this "log-log" diagram, the fact that the line of maximum precipitation has a 45° slope signifies that the complexes formed under these conditions have a constant composition, actually 1:1 stoichiometrically based on charge. Viewed another way, for a series of systems of constant polymer content and increasing surfactant concentration, the "complexes" pass from being soluble (polymer-rich), through 1:1 stoichiometry, to the soluble region in which the compositions are surfactant-rich. In recent years, considerable work aimed at determining complete phase diagrams of various combinations of polyion/oppositely charged surfactant pairs has been undertaken by Lindman, Thalberg and their co-workers (8). These diagrams considerably refine the simple concepts referred to above. Furthermore, these workers (8) have successfully modelled the behavior by using Flory-Huggins concepts.

In the last two decades, a convenient analytical tool for determining the concentration of ionic surfactants has been available, viz., the specific surfactant ion electrode. This tool has the great advantage that it allows the binding of such an ion by a polymer to be studied in the absence of the added salt that is required for the simple dialysis membrane method. Several authors (9–11) have employed the electrode method to study the binding of sodium alkylsulfates by nonionic polymers, such as PEO, polyvinylpyrrolidone (PVP) and polyvinylalcohol (PVA). In general, the results obtained are similar to those seen with the dialysis technique. Hayakawa and Kwak (3) seem to have been the first to employ the electrode method to study interactions involving ionic polymer systems, a series of polyanions of both synthetic and natural origin, and the cationic surfactants alkyltrimethylammonium (RTAB) and alkylpyridinium halides. In the calibration procedure, excellent (Nernstian) responses of the electrodes employed were obtained to concentration changes of these surfactant ions. Representative results of Malovikaya et al. (12) for the polyanion, sodium
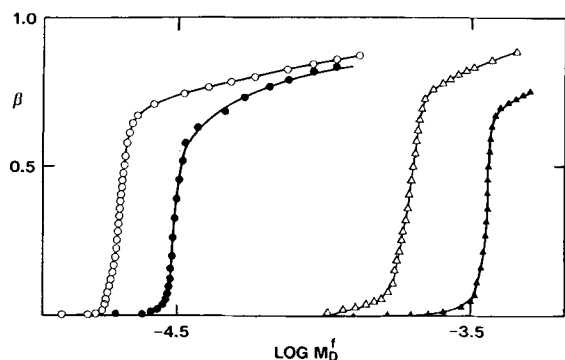

FIG. 2. Phase diagram of PEO/SDS system (0.05% PEO); PS, polymer/surfactant complex. [Reproduced from Satake, T., et al., Bull. Chem. Soc. Jap. 53:1864 (1980), with permission.] Abbreviations as in Figure 1.

FIG. 4. Binding isothems of polyacrylate (5×10^{-4}M). Comparison of alkylpyridinium and alkyltrimethylammonium ions. $\triangle$, DPyCl; O, TPyBr; $\blacktriangle$, DTABr; $\bullet$, TTABr. [Reproduced from Malovikova, A., et al., ACS Symposium Series 253:225 (1984), with permission].

polyacrylate, are given in Figure 4. Several important conclusions can be drawn from these data: (i) The binding curves are sigmoidal, again indicating that a cooperative process, i.e., clustering of the bound surfactant ions, is operative. (ii) The initial concentration for binding (CAC) is relatively low—appreciably less than the CMC of the surfactant. This means that the presence of the polyion renders binding and cluster formation of the surfactant ions energetically much more favorable than in self-clustering of the surfactant when present alone (simple micelle formation). Undoubtedly, the strong electrostatic attraction of the ionic sites on the polymer promotes the adsorption of surfactant ions, which then nucleate and promote clustering. (iii) As for simple micellization, there is a major reduction in critical aggregation concentration as the chainlength of the surfactant is increased from dodecyl, D (C_{12}) to tetradecyl, T (C_{14}). (iv) Other data (3) of Hayakawa and Kwak (3) demonstrate that added simple electrolyte has a strong influence in the sense of increasing the CAC, i.e., weakening the interaction. This result unequivocally demonstrates that electrostatic forces are a primary driving element in the adsorption/nucleation process of the surfactant ions onto the polymer and that shielding, by added electrolyte, diminishes the electrostatic potential for adsorption. Kwak (13) also showed that, as for simple micellization, there are specific ion effects in the added electrolyte, but these effects will not be elaborated upon here.

The above data were obtained on clear systems, i.e., below the stoichiometric equivalent concentration of the surfactant. An important corollary is that, in these oppositely charged systems, extensive interactions and formation of intermolecular complexes can occur even with no formation of insoluble species. Recent work on the binding of C_{14}TAB by polyacrylate and polymethacrylate polyanions suggests that binding can be influenced by other factors in addition to electrostatic forces, such as polymer conformation and hydrophobicity (14).

The surface-tension method. In an aqueous mixture of two solutes, one highly surface-active and the other surface-inactive or feebly surface-active, it is to be expected that interaction between the two species would be readily evident in the surface behavior of the mixed solution. This approach was pioneered by Cockbain (15), who used interfacial-tension measurements on protein/surfac-

tant combinations, while Jones (16) was the first to apply the surface tension method to a study of mixtures of a nonionic polymer (PEO) and an anionic surfactant (SDS). The technique is favorable in this case because PEO is only moderately surface-active. He was able to show unequivocally that interaction occurs between these two species. Thus, in the presence of polymer, there was an arrest—labelled "T_1" (the CAC)—in the surface-tension lowering caused by added SDS. This was a well-defined concentration which represents the commencement of interaction. With increasing SDS concentration, there followed a surface-tension plateau (the interaction region) and, finally, a second arrest at a higher concentration (labelled "T_2"), which represents saturation of the polymer and, after that point, the surface-tension curve rejoined that of SDS alone. Jones' analysis (16) of the data was thus in line with that of interaction patterns established earlier by the dialysis method. Although there have been subsequent refinements, Jones' interpretation (16) has remained a basic building block for such developments. The surface-tension technique has since been employed by many other workers to obtain further insight into the interaction phenomenon. Schwuger (17), for example, showed in the PEO/SDS system that the interaction pattern is largely independent of PEO molecular weight, unless it falls below about 4,000 daltons. Below 1,500 there is no interaction. Lange (18) extended the studies to the PVP/SDS system. His results (Fig. 5) illustrate the basic concepts of Jones (16) well and, in this case, they also illustrate the effect of polymer concentration on T_1 (little effect) and T_2 (increases with concentration). Further discussion of the method and results obtained are given elsewhere (4).

Turning now to charged polymer/oppositely charged surfactant systems, Goddard and co-workers (7,19), in their studies of mixtures of a cationic cellulosic polymer and SDS, showed that a strong synergistic reduction of surface tension occurred. This behavior is quite different from that observed in systems with nonionic polymers. The effect is evident at low concentrations of SDS, and implies
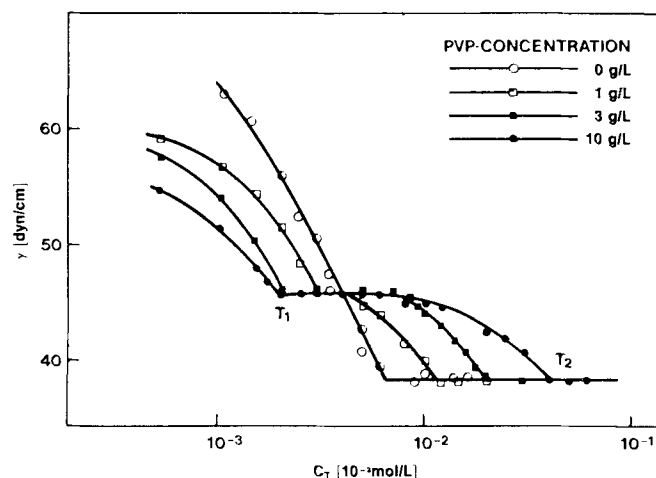

FIG. 5. Surface tension(γ)/concentration plots of SDS in the presence of PVP at various concentrations; "T" assignments follow Jones (16). [Reproduced from Lange, H., Kolloid Z. Z. Polym. 243:101 (1971), with permission].

that the cationic polymer of normally feeble surface activity is transformed, on addition of small amounts of SDS, into a much more hydrophobic complex by virtue of the hydrocarbon chains of the bound surfactant. Figure 6 depicts the changing conditions in the solution and surface of the system as the concentration of added SDS is increased. Even under conditions of maximum precipitation, when most of the polymer and added surfactant are out of solution, the surface tension is still low. This implies that the stoichiometric complex, with all positive charges of the polymer neutralized by bound surfactant anions, has a hydrophobic character, i.e., the hydrophobic chains of the bound surfactant point "outwards." There is no doubt that the polymer itself is part of a highly surface-active complex. Independent confirmation of these conclusions came from a different experiment in which the insoluble alkylsulfate (behenylsulfate) was confined to the surface as an insoluble monolayer (19). As little as 10 ppm of Polymer JR (Union Carbide) introduced in the subphase resulted in a pronounced expansion of the monolayer and provided presumptive evidence of a newly formed surface-active species, namely a polymer/surfactant complex similar to that depicted in the "surface zone" of Figure 6 at intermediate surfactant concentration.

The above results pose an important question: In the nonionic polymer/ionic surfactant complex systems, is the polymer also one (or part) of the species that adsorbs? The weight of evidence, supported by recent experimentation (20), suggests that this is the case: (i) A reactivity series of the polymers (toward ionic surfactants) can be set up on the basis of the hydrophobicity of the polymers (21). (ii) The surface activity of the polymer on its own in aqueous solution is a measure of its hydrophobicity and, hence, reactivity (22). (iii) Polymers like polyacrylamide and dextrose, which do not lower the surface tension of water, are not reactive toward surfactants (23). Conversion of the former polymer to poly N-isopropylacrylamide creates a polymer that is both reactive (24) and surface-active (22). (iv) Depictions of polymer/surfactant com-

plexes involving association of the polymer at the periphery of the surfactant clusters (Fig. 7) suggest that similar association can take place when the surfactant assembly is in the form of an adsorbed monolayer at the air/water interface, i.e., present as a semi-infinite hemi-micelle (Fig. 8).

If the above reasoning is correct, when the surfactant is present in excess and the concentration of micelles is relatively high, the micelle/water interface can be expected to compete progressively and successfully with the air/water interface for the polymer, i.e., the polymer will be stripped progressively from this latter interface. This is in line with the observations that the surface tension eventually attains the value of micellar, polymer-free solutions (Fig. 5). This mechanism also is implied in the case of polyion/oppositely charged surfactant systems and the highly surface-active complexes that form (Fig. 6).

Why do polymers and surfactants interact? The original image of polymer/surfactant interaction was based on the
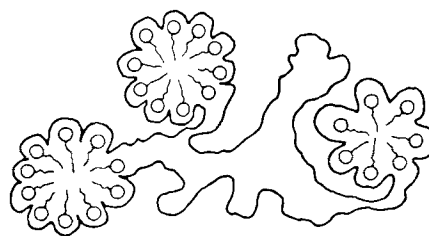
FIG. 7. Schematic diagram of polymer-surfactant complex. [Reproduced from Nagarajan, R. and B. Kalpakci, B., *Polymer Prepr. Am. Chem. Soc. Div. Polym. Chem. 23*:41 (1982), with permission].
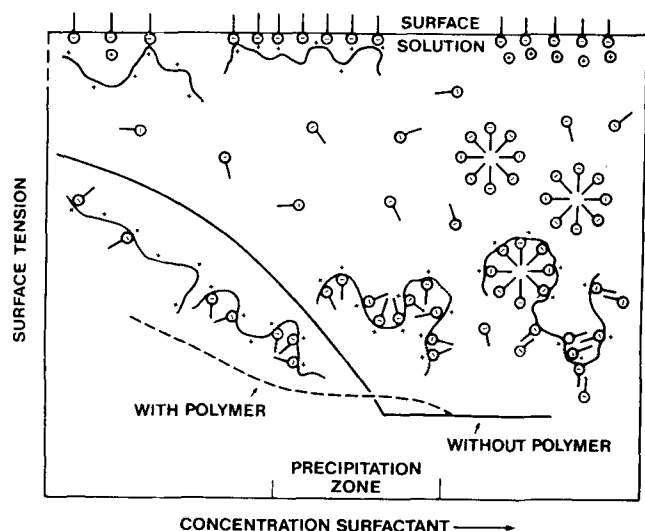
FIG. 6. Conditions in the bulk and surface of solutions of a polycation (fixed concentration) and anionic surfactant. Full line is the hypothetical surface tension concentration curve of the surfactant alone; dotted line is that of mixture with polycation. Simple gegenions are depicted only in surface zone (1).

FIG. 8. Schematic diagram of a draining lamella in a foam prepared from a mixed solution of a polymer and a surfactant.

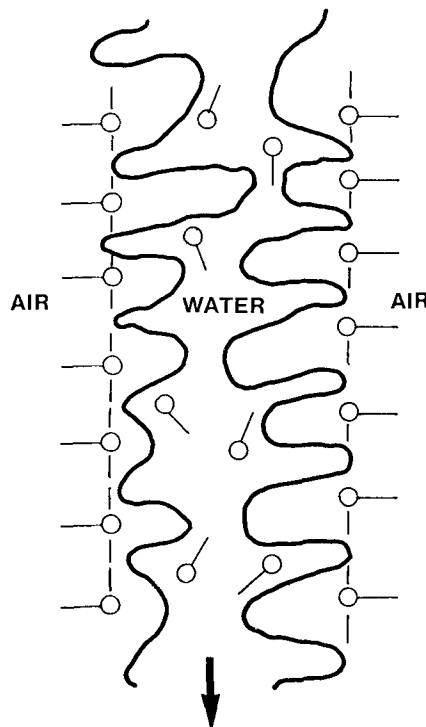notion that the polymer presents adsorption sites along its backbone for the surfactant. To appreciate the driving forces that promote polymer/surfactant interaction according to the current image, it is appropriate to consider (i) the molecular structure of a typical ionic surfactant and (ii) the driving forces for self-aggregation (micellization) and adsorption at the air/water and oil/water interfaces. These processes allow the unfavorable free-energy condition of the alkyl chains of the dissolved surfactant, which are in contact with water, to be relieved. This is demonstrated in the two-dimensional representation of a (Hartley) micelle in Figure 9. The new state is a delicate compromise—aggregation creates a strong electrostatic repulsion of the ionic headgroups which prevents their close approach. This situation, relieved to some extent by counterion binding, explains why micellization is so sensitive to the addition of salt, which, in general, reduces the CMC. The net result is that the first few peripheral carbon atoms of the aggregated hydrocarbon chains are still in contact with water.

The current image of a polymer(nonionic)/surfactant (ionic) complex was ushered in by Cabane's nuclear magnetic resonance (NMR) measurements of these systems (25). According to his model, segments of the polymer are "wrapped around" clusters of the surfactant. His ideas elaborate and refine the "string of beads" structure suggested earlier by Shirahama et al. (26). From the diagram of this type of proposed structure (Fig. 7) for the complex, it is easy to see how polymer associated with the surfactant aggregate relieves the two stresses referred to above; viz., the ionic head groups are now more insulated and the extent of contact of the peripheral hydrocarbon chain segments with water is diminished. Furthermore, it becomes easy to understand why water-soluble polymers with a higher level of hydrophobicity (and interfacial activity) have a stronger interaction tendency toward the surfactant aggregates.

Regarding charged polymer/oppositely charged surfactant systems, it is appropriate to think of each charge of the polyion as a potential adsorption site for surfactant ions, in contradistinction to the hydrophobic sites in the

uncharged polymers considered above. Electrostatic forces are among the most potent of physical forces and are involved, for example, in the adsorption of cationic conditioning surfactants onto negatively charged surfaces, like cotton, and minerals such as quartz. In all those situations, one adsorbed surfactant ion can act as a nucleating site for cluster formation of additional surfactant ions. In conditioning, this leads to the formation of hemimicelles. The energetics of these processes are so favorable that even the formation, during adsorption, of a modified solid or polymer interface that is more hydrophobic, can be tolerated. (This phenomenon is utilized in flotation of minerals, and it can result in eventual precipitation in the case of a polyion.) In virtually all cases, however, further addition of surfactant leads to hydrophilization of the surface and solubilization of the complex, and this can be viewed simplistically as the adsorption of a second layer of surfactant, with ionic headgroups pointing outwards.

This image provides an explanation of why polyions do not interact with surfactants of like charge, e.g., carboxymethyl-cellulose with anionic surfactants. In this case, the potent electrostatic forces are repulsive.

We can now devise a tabular scheme that illustrates the reactivity in polymer/surfactant systems in a general way. This scheme is presented in Table 1. Several points can be made. (i) Conventional nonionic surfactants based on ethylene oxide are either not reactive or are only weakly reactive. One reason is that for these surfactants, self-aggregation is not opposed by potent electrostatic forces that are operative in ionic surfactant systems. Indeed, the CMC values of nonionic surfactants are about two orders of magnitude lower than for their ionic counterparts. Furthermore, the relief of residual hydrocarbon/water contact in a nonionic surfactant micelle by physical looping of a surrounding polymer would be hampered by the relatively thick polar layer of the micelle, at least in conventional nonionic surfactants with a bulky PEO headgroup. In fact, on the basis of principles of mixtures of polymers in solution, a repulsive force could well exist (27). However, some reactivity has been reported recently (28) for a nonionic surfactant of unconventional structure—namely one based on a (thio)glucopyranoside headgroup, which is significantly different from a bulky PEO moiety. These aspects will be referred to again in the section on hydrophobic water-soluble polymers. Conventional nonionic surfactants do interact with one particular polymer, namely polyacrylic acid (29,30). This reactivity is closely linked to the well-known association reactions that occur between PEO and polyacrylic acid, and it probably involves hydrogen bonding between individual ether and carboxyl groups.

(ii) Cationic surfactants are noticeably less reactive toward nonionic polymers than are anionic surfactants
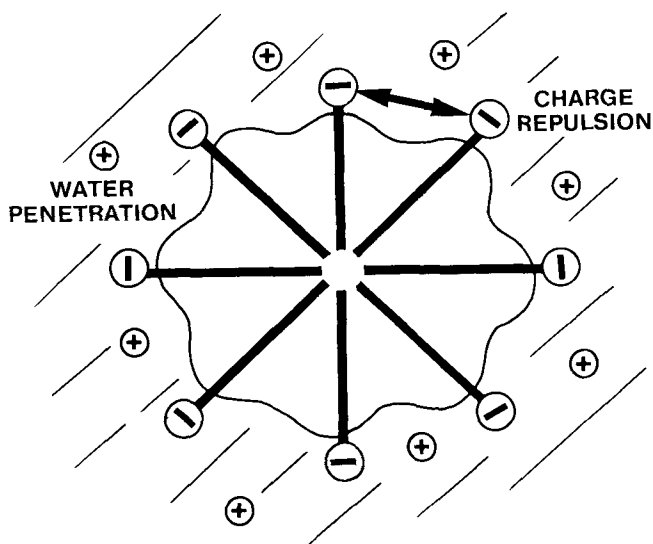

FIG. 9. Schematic diagram of an anionic surfactant micelle.

TABLE 1

Table of Surfactant (SA) Reactivity

Type of polymer	Degree of reactivity[a]
P°, uncharged polymer	SA⁻ > SA⁺ >> SA°
P⁺, polycation	SA⁻ >> SA° >> SA⁺
P⁻, polyanion	SA⁺ >> SA° >> SA⁻

[a]SA⁻, anionic surfactant; SA⁺, cationic surfactant; and SA°, non-ionic surfactant.

(18). This difference has never been satisfactorily explained, but may be due to a combination of the large size of their ionic head groups and the different water structure around them. Saito and Yukawa (31,32) have pointed out that their reactivity can be altered substantially by changes in the counterion.

(iii) As implied in the discussion to this point, the strongest interaction occurs in the combination of polyelectrolyte/oppositely charged surfactant, the weakest in a polyelectrolyte/like-charge surfactant combination.

Expanding the listing beyond the contents of Table 1, we can add two more points: (iv) Flexibility in the polymer, *i.e.*, the ability to orient component interactive groups appropriately, can be expected to increase reactivity. Until now, this aspect has been inadequately addressed.

(v) Hydrophobicity in a polymer promotes its interaction with ionic surfactants. The reactivity series, set up by Breuer and Robb over 20 years ago (21), shows the following order: PVA < PEO, MeC < PVAc ≤ PPO. This series, ranging from PVA to polypropyleneoxide (PPO), is also the sequence of increasing hydrophobicity and surface activity. Methylcellulose (MeC) and polyvinylacetate (PVAc) have intermediate activity.

Mathematical/thermodynamic modelling. On the basis of the traditional view that interaction of ionic surfactants with an uncharged polymer involves nonspecific interaction forces, it is easy to understand that mechanisms analogous to adsorption were considered to explain the interaction. As an example, the equation found by Shirahama (33) to fit the interaction of SDS and PEO, *viz.*,

$$\theta = KC^n/(1 + C^n) \qquad [1]$$

where θ is the degree of binding, n is an empirical exponent, C is the equilibrium concentration of "adsorbate" (SDS) and k is a constant, bears a striking similarity to Langmuir's equation (in which the exponent n is unity). Equation 1 is thus a more general form of the latter, which it predated by several years. It was actually proposed by Hill (34) in 1910 and allows for the possibility that the adsorbed species will form clusters of size n molecules. Shirahama's data led to a value of n ≈ 20.

More recent models have generally considered that aggregation of surfactant is formally involved in the process because many probing methods (*e.g.*, NMR) support this view, although accumulated evidence has confirmed that the cluster size n (a measure of the degree of cooperativity) is smaller than that in regular micelles. The simple model of Smith and Muller (35) illustrates the basic approach well. Each polymer molecule comprises a number of "effective" segments of mass Ms, and total concentration [P], that act independently of each other and are able to bind n surfactant ions, D⁻, according to the equilibrium reaction:

$$P + nD^- \leftrightarrow PD_n^{n-} \qquad [2]$$

with the equilibrium constant being given by:

$$K = [PD_n^{n-}]/[P][D^-]^n \qquad [3]$$

K is derived from the half saturation condition:

$$K = [D^-]_{0.5}^{-n} \qquad [4]$$

Applying the above treatment to their data for the PEO/SF₃DS (sodium triflurododecyl sulfate) system, Smith and Muller (35) deduced the cluster size, n, to be about 15 (much smaller than for regular micelles) and Ms to be 1830, which explains the experimental finding that PEO of MW 1,500 (or less) is ineffective for binding. The free energy of binding/aggregation per surfactant molecule is given by:

$$\Delta G^\circ = -RT \ln K^{1/n} \qquad [5]$$

and the value obtained, −5.07 K cal/mole, is close to that of micelle formation of this surfactant (SF₃DS).

More complete models were developed later by Gilanyi and Wolfram (36) and by Nagarajan (37). For example, the mass balance equation of Nagarajan (37) allows the total surfactant concentration (X_t) to be partitioned into singly dispersed surfactant (X_1), surfactant in free micelles (X_f) and surfactant bound as aggregates (X_b) according to:

$$X_t = X_1 + g_f(K_f X_1)^{g_f} + g_b n X_p \left[\frac{(K_b X_1)^{g_b}}{1 + (K_b X_1)^{g_b}} \right] \qquad [6]$$

Here g_f and g_b are the aggregation numbers of free micelles and bound aggregates, respectively, the Ks are equilibrium constants and n is the number of binding sites per polymer molecule.

The relative magnitudes of K_b, K_f, g_b and g_f determine whether or not complexation with the polymer occurs. If $K_f > K_b$ and $g_b \approx g_f$, formation of micelles occurs in preference to complexation. If $K_f < K_b$ and $g_b \approx g_f$, complexation/aggregation on the polymer takes place first and, upon saturation of the polymer, free micelles form. If $K_f < K_b$ but g_b is much smaller than g_f, formation of free micelles can occur even prior to saturation of the polymer. A first critical surfactant concentration will be observed close to $X_1 = K_b^{-1}$, and a second critical concentration will occur near $X_1 = K_f^{-1}$.

Excellent verification of his analysis was obtained by Nagarajan (37) from experimental specific ion activity data of Gilanyi and Wolfram (36) for the PEO/SDS system, together with appropriate values of the constants in his equation (Fig. 10). Up to point A, in all cases, only single ions of surfactant are present. With no polymer present, a further increase in concentration leads to micelle formation. In the presence of polymer, a region AB (complex formation) occurs, followed by micelle formation at point C, *i.e.*, when the polymer concentration is not too high. If the latter condition is not met (*e.g.*, with 4 g of polymer/L), virtually all the added surfactant is bound within the concentration range of surfactant studied.

Further refinements to the models continue to appear, one being the inclusion of a surface term in the free energy equation term for aggregation, as in the equations of Ruckenstein *et al.* (38), in Nagarajan's newer model (39) and in the dressed micelle theory of Evans *et al.* (40) and Brackman (41). A summary of these developments has been given by Lindman and Thalberg (8), who also discuss the computer simulation approach to polymer/surfactant interaction developed by Balazs and Hu (42).

As a footnote to this section, we emphasize the results of fast-kinetics studies by Wyn-Jones and co-workers (43,44), which show that the molecular processes
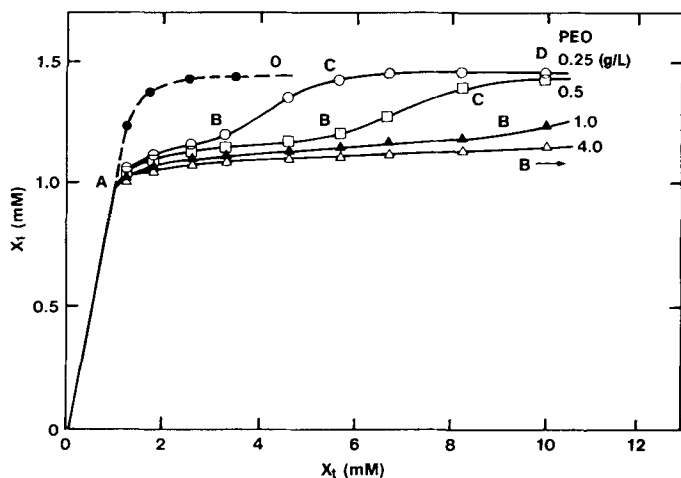
FIG. 10. Experimental data of Gilanyi and Wolfram (36) for PEO/SDS solutions containing 0.1M NaNO$_3$ for comparison with theoretical curves. [Reproduced from Nagarajan, R., *Colloids Surfaces* 13:1 (1985), with permission].

involved in the formation of polymer/surfactant aggregates are at least as fast and, if anything, more facile than those involved in simple micelle formation, possibly because the aggregates are smaller than regular micelles (45).

It has already been pointed out that the major differences in the above systems exist when the polymer and the surfactant are oppositely charged. Discrete binding sites for the surfactant ions are now present. However, evidence given above (and below) indicates that binding is reinforced by alkyl chain association and can again be considered a special case of surfactant aggregation. There are strong analogies between the process of surfactant adsorption, leading to complex formation of the surfactant with the polyelectrolyte, and adsorption, leading to hemi-micelle formation for ionic surfactants on the surface of oppositely charged solids, such as minerals. In both cases, an ion-exchange process is involved in which the counterion of the polyelectrolyte (or charged surface) is replaced by the surfactant ion, and binding commences at a concentration that is orders of magnitude below the CMC of the surfactant.

Goddard and Hannan (46) have pursued this analogy with charge neutralization of mineral solids by studying the solubility diagrams of a homologous series of alkyl sodium sulfates in mixtures with the cationic cellulosic polymer, Polymer JR. In each case, in the limit, the slope of the points of maximum insolubility in the plot of log polymer *vs.* log surfactant concentration changed from 45 to 90° (*i.e.*, became independent of polymer concentration if the latter were reduced below a certain value). Mathematically, the result could be expressed as:

$$C_e \exp(n\omega/kT) = \text{constant} \qquad [7]$$

where C_e is the polymer concentration-independent surfactant concentration corresponding to maximum precipitation. A value of ω of -1.1 kT was derived, suggesting that the environment of surfactant molecules in the complex also resembles that of micelles.

A differentiating factor for the polyelectrolyte over the mineral surface is molecular flexibility, meaning that its properties, such as conformation, can be substantially altered by the adsorption process and can actually reinforce it. One of the models for binding, developed by Satake and Yang (47), is based on the Zimm-Bragg theory for coil-helix transitions of polymers as adapted to the cooperative bonding by Shirahama *et al.* (48,49), who employed a statistical mechanical treatment of the binding process. This approach has been used by Hayakawa and Kwak (3) in their extensive studies of cationic surfactants to obtain estimates of their free energy of binding to various polyanions. The parameter $[(C_D^f)^{1/2}$: concentration of surfactant corresponding to half saturation of the polymer] was employed to assess this free energy. The surfactants used were families of alkyl-pyridinium and alkyltrimethylammonium salts. For a variety of binding polyions, ΔG had values in the range of 1.20–1.30 kT per CH$_2$ group, again somewhat higher than that of simple micellization.

Delville (50) has presented a model to describe the process based on two additive effects, one due to Poisson-Boltzmann condensation of the surfactant ion and the other to a contribution due to cooperative bonding. At high surfactant concentration, in the post-precipitation or resolubilization zone, "string of beads" structures have been invoked in which the beads are surfactant clusters and the polyion is the string. Possible structures are depicted in Figure 6, which links the surface and bulk behavior with compositional changes in the system. Lastly, we recall the Flory-Huggins approach that was used by Lindman, Thalberg and their co-workers (8) to describe the overall phase behavior.

PROPERTIES AND OPPORTUNITIES RELEVANT TO DETERGENTS

The many changes that occur when polymer is incorporated in a surfactant solution, or *vice versa*, have a relevance to detergent formulation and utilization. Those that appear to have opportunities are highlighted below.

Viscosity enhancement. Uncharged, flexible polymers tend to adopt a random-coil configuration in solution; polyelectrolytes, on the other hand, because of charge repulsion effects, tend to be linear and thus promote viscosity, unless the ionic strength of the solution is high. When a nonionic polymer acquires charges by binding an ionic surfactant, an increase in viscosity is to be expected on the basis of the "polyelectrolyte effect." Jones (16), and subsequently Francois *et al.* (51), demonstrated such an effect for PEO/SDS systems, which sets in at concentrations (T$_1$) of SDS below the CMC. With further addition of SDS, increases in solution viscosity of as much as fivefold were observed. Results obtained by the latter authors for a series of PEOs of MW from 7 × 10^4 to 2 × 10^6 daltons are given in Figure 11. Recently, the influence of SDS on the rheological behavior of a PEO specimen of even higher MW (5 × 10^6 daltons) was examined by Brackman (52). While confirming viscosity enhancement effects, she reported a marked incidence of viscoelasticity in these systems, as manifested in the development of normal stress effects.

Ethylhydroxyethyl cellulose (EHEC), like MeC, is a practical, interesting polymer in the sense that, depending
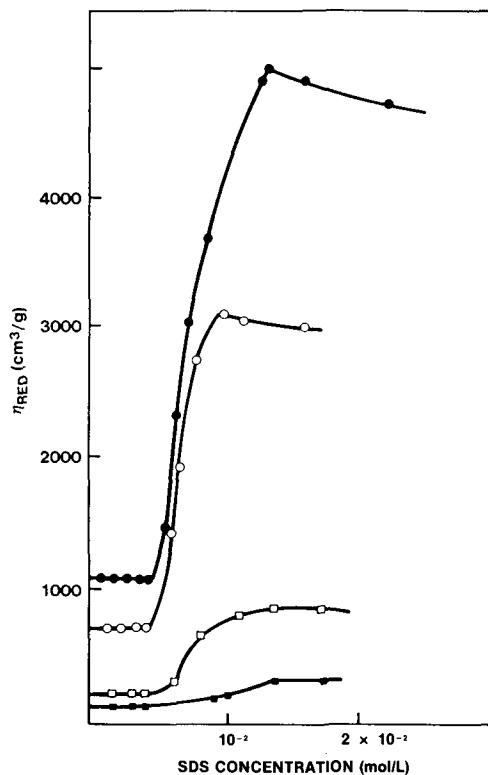
FIG. 11. Reduced viscosity of PEO as a function of SDS concentration (●), MW = 2 X 10⁶, conc. 6 X 10⁻¹ g/L; (○) MW = 10⁶, conc. 6 X 10⁻² g/L; (□) MW = 2 X 10⁵, conc. 5 X 10⁻¹ g/L (■) MW = 7 X 10⁴, conc. 5 X 10⁻¹ g/L. [Reproduced from Francois, J., et al., Eur. Polym. J, 21:165 (1985), with permission].

FIG. 12. Relative viscosity of 1% Polymer JR 400 as a function of added SDS concentration.

on its detailed structure (i.e., degree of substitution), it can possess a cloud point in the "ordinary" temperature range, i.e., ambient to about 40 or 50°C. Possession of a cloud point implies that the polymer becomes more hydrophobic with temperature, a clear indicator that it should become increasingly more reactive with ionic surfactants. Elegant confirmation of these ideas came from the extensive study of the EHEC/CTAB system by Carlsson et al. (53). As an illustration, these investigators found a tenfold increase in viscosity of a 1% EHEC/0.36% CTAB system on increasing the temperature from 28 to 45°C. Viscoelastic effects and gel formation were also encountered, and these will be referred to in the next section.

The molecular "stiffness" of the cellulose backbone is known to be a contributor to the high solution viscosity observed with cellulose ethers. The viscosity boosting effect, realizable by adding an interacting surfactant, can be expected to be further increased if the surfactant's interaction is reinforced by strong electrostatic forces. Figure 12 shows the viscosity of mixtures of the cationic cellulosic Polymer JR 400 and SDS. Viscosity increments of 200-fold are obtainable (54). A point of interest is that the highest development of viscosity through network formation occurs just prior to precipitation of the complex, i.e., when the network collapses.

Viscoelasticity and gel formation. The identification and investigation of polymer/surfactant systems that show gel-like characteristics have intensified in recent years. Implied in these manifestations is network forma-
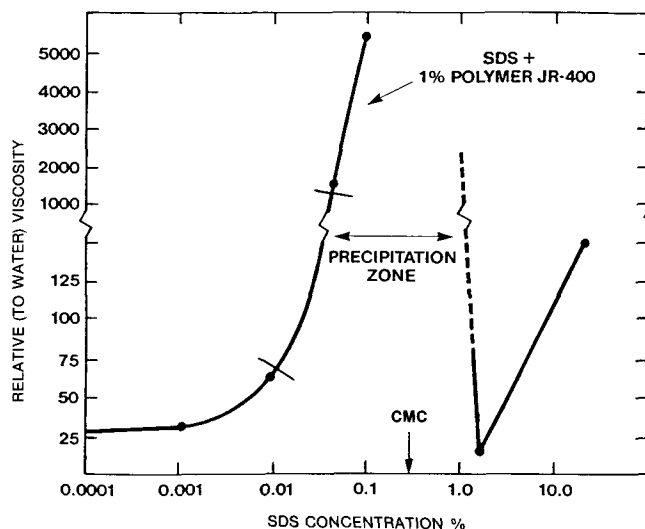
tion in the solution, presumably through interchain bonding, which may be caused by aggregation of surfactant molecules bound to different polymer chains. We digress here to discuss suitable rheological methods to characterize such systems.

Because gels are viscoelastic materials, i.e., they exhibit both liquid and solid characteristics, conventional rheological methods, such as viscosity determinations, are not the most useful or informative ways to study them. Anomalous behavior can be encountered, such as "climbing" of the specimen up the shaft of the rotor, in a typical rotational viscometric determination. To obtain more complete and reliable information, viscoelasticity is better studied by oscillatory measurements. Here, a sine wave strain, instead of a constant rotational strain, is applied to one of the elements in a typical measuring pair, e.g., concentric cylinders, and the stress and phase angle are measured on the second element. This allows the determination (as seen later) of both the storage (elastic) modulus and the loss modulus (representing viscous flow). For a viscoelastic material, the phase angle will be between 0 and 90°. For a purely elastic material, the generated stress is always in phase with the strain, i.e., δ = 0°. For a purely viscous material, there is a 90° phase difference between the two (Fig. 13).

The magnitude of δ establishes the relative contribution of the elastic and viscous components according to the following equations:

complex modulus: $G^* = \tau_0/\gamma_0 = G' + iG''$ [8]

elastic modulus: $G' = G^* \cos\delta$ [9]

loss modulus: $G'' = G^* \sin\delta$ [10]

dynamic viscosity: $\eta = G''/\omega$ [11]

where τ_0 and γ_0 are the stress and strain amplitudes, ω is the oscillation frequency in radians/s, and i is the imaginary constant, $\sqrt{-1}$. As would be expected, additional information can be obtained by determining the dependence of the above parameters on the oscillatory frequency (8).
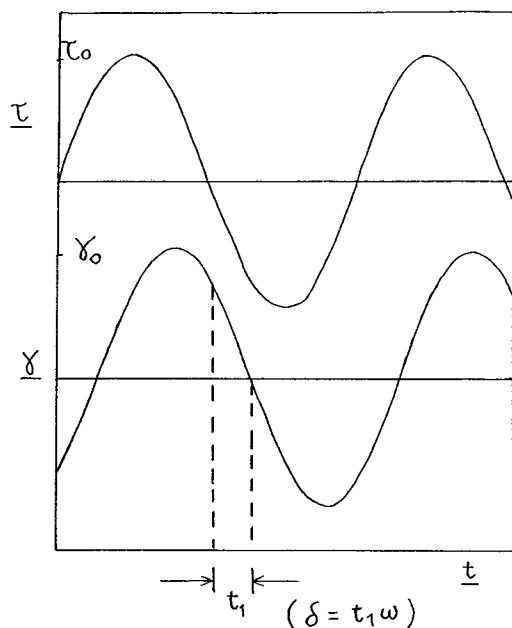
FIG. 13. Phase relationship of stress (τ) and strain (γ) for a viscoelastic material.

FIG. 14. Graphs of η'/η, G'/G, and G''/G vs. log (wt$_r$) based on the Maxwell model.

One can predict that as ω is increased it will become more and more difficult for the viscous element to respond to the applied strain, and that this element will present a progressively increasing mechanical impedance to flow. Thus, in a simple Maxwell model for a viscoelastic material, i.e., a spring and a dash-pot in series, typical behavior would be as follows: At low frequencies, G'' dominates over G', but at a critical frequency a crossover will occur. Ultimately, G'' will fall toward zero as G'' continues to rise, i.e., the model behaves progressively as a purely elastic element. The crossover point of G' and G'' defines the relaxation time, τ_r, of the body and is actually the reciprocal of the frequency value at crossover (Fig. 14).

By this method (oscillatory rheology), the system, examined by Carlsson et al. (53) (1% EHEC, 0.36% CTAB) and referred to in the last section, showed even more dramatic effects. The same 20°C rise in temperature resulted in a 100-fold increase in G', the elastic (or storage) modulus, reflecting the considerable increase in strength of the polymer/surfactant network over this temperature range (Fig. 15). Furthermore, Carlsson et al. (53) demonstrated that the formation of high-viscosity systems occurred under particular conditions ("windows") of temperature and added concentration of surfactants (usually CTAB) in the single-phase zone (Fig. 16). A rationalization of the behavior was as follows: As the temperature is increased, the polymer becomes less soluble, i.e., more hydrophobic, and more prone to interact with the surfactant, so that the tendency to crosslink via adsorbed alkyl chains increases and the viscosity rises progressively until gels are formed, at least in those systems evincing gel formation. A slow decrease of viscosity/gelling tendency on further increasing the temperature may reflect the tendency of the polymer itself to undergo thinning at higher temperatures. An optimum range of surfactant is required to initiate binding to the polymer and generate a sufficient number of mutually-interacting adsorbed
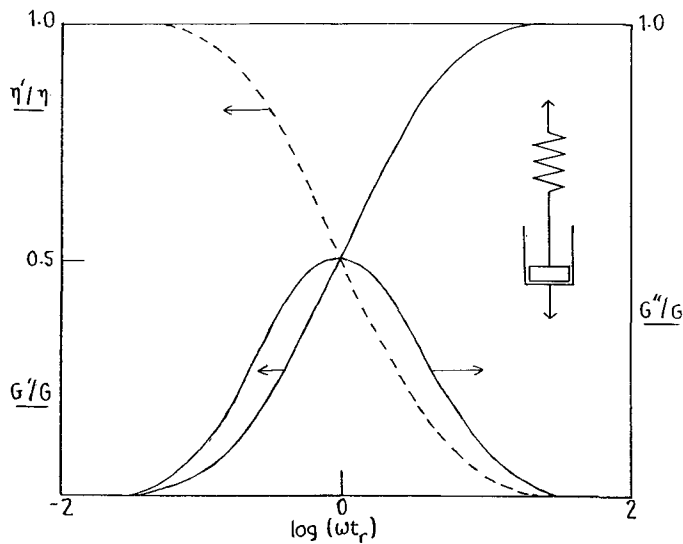
alkyl chains. When the polymer is saturated with surfactant, internal interactions (i.e., within one polymer molecule) are more likely; the clusters are probably more micelle-like and hydrophilic, and reduce the tendency for the chains to form crosslinks. Addition of excess surfactant constitutes a viable way to "de-gel" these systems.

In the previous section, we referred to the unusual rheological effects observed with a particular cationic cellulose/SDS combination. Even stronger effects would be expected in a combination of SDS and a higher-MW homolog of the same polymer with a greater tendency toward chain entanglement and network formation. Strong gels were indeed observed. For example, for a combination of 1% Polymer JR 30 M (MW $\approx$ 700,000 daltons) and 0.1% SDS, the value of the elastic modulus G', which dominates the complex modulus G^*, can exceed 500 Pascals, and the zero-frequency viscosity can exceed 10 kilopascal-seconds (Fig. 17). G' was found to increase up to 0.15% with SDS concentration, and then to decrease as the region of precipitation was approached. Similar trends were found with other types of anionic surfactant. These results, together with more details of the Polymer JR/SDS investigation, including a discussion of methods to liquify preformed gels, have been described previously (55,56).

An interesting case of "de-gelling" caused by polymer-surfactant interaction was reported by Brackman and Engberts (57). Polypropylene oxide was added to a gel formed by the combination of long-chain cetyltrimethyl-ammonium (CTA) cation and salicylate anion, a system well known to form viscoelastic solutions owing to the presence of long, rod-like micelles. Evidently, the competing interaction between the CTA$^+$ ions and polypropylene oxide is strong enough to disrupt the gel structure.

Solubilization and solubility enhancement. A traditional property of micellar surfactant solutions is their ability to dissolve or solubilize oil-soluble materials, such as hydrocarbons, esters, dyes, fluorescers and perfumes. Indeed, this property gave early support to the concept that micelles do exist in solutions of surfactants, and
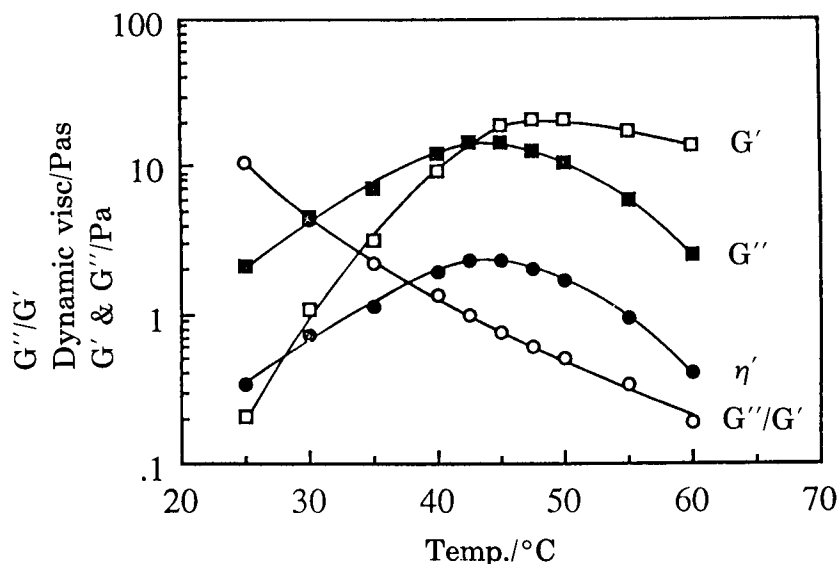
FIG. 15. Viscoelastic properties vs. temperature at constant frequency (1.0Hz) for 1% EHEC and 0.36% CTAB. [Reproduced from Carlsson, A., et al., Colloids Surfaces 147:47 (1990), with permission].
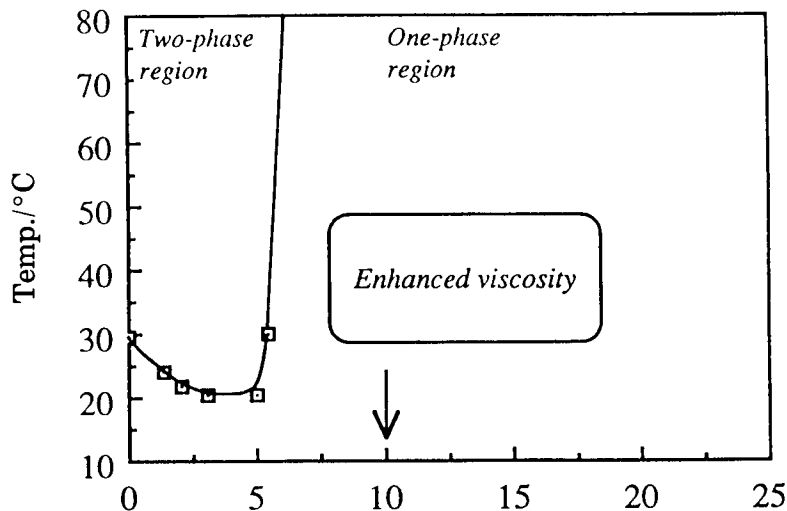

FIG. 16. Part of the phase diagram of 1% EHEC and CTAB in water. [Reproduced from Carlsson, A, et al., Colloids Surfaces 147:47 (1990), with permission].

solubilization was clearly recognized as being intimately involved in their mechanisms of detergency. In the same way, the solubilization method has been widely used to confirm and study the interaction between surfactants and polymers (58). In this respect, the most popular of such methods has been the dye technique. To the extent that complex formation with a nonionic polymer can be regarded as a depression of the aggregating concentration of the surfactant, (CAC < CMC), enhanced solubilization can be expected and has been confirmed in the mixed systems. Data by Lange (18) on PVP/alkylsulfate systems illustrate these phenomena well.

More pronounced effects have been found for certain polyelectrolyte/surfactant pairs (59). For the cationic cellulosic (Polymer JR 400)/SDS pair, a solubilization region for the dye Orange OT occurs at a low concentration of SDS, and the main solubilization zone is also widened (shifted to lower concentration as compared to simple SDS solutions) (Fig. 18). The solubilization occurring at a low concentration supports the existence of clustering, already indicated by the viscosity measurements on this system. In the main solubilization region (beyond the precipitation range), a string-of-beads structure (one polymer chain linked to, or wrapped around, several micelles) could account for this behavior (Fig. 19).

Dye solubilization for systems charged in the opposite sense (such as polyvinylsulfate/C_nTAB mixtures) has been studied in detail by Hayakawa et al. (60), who present a theoretical analysis of the observed behavior. A second example, the combination maleic anhydride/vinyl-
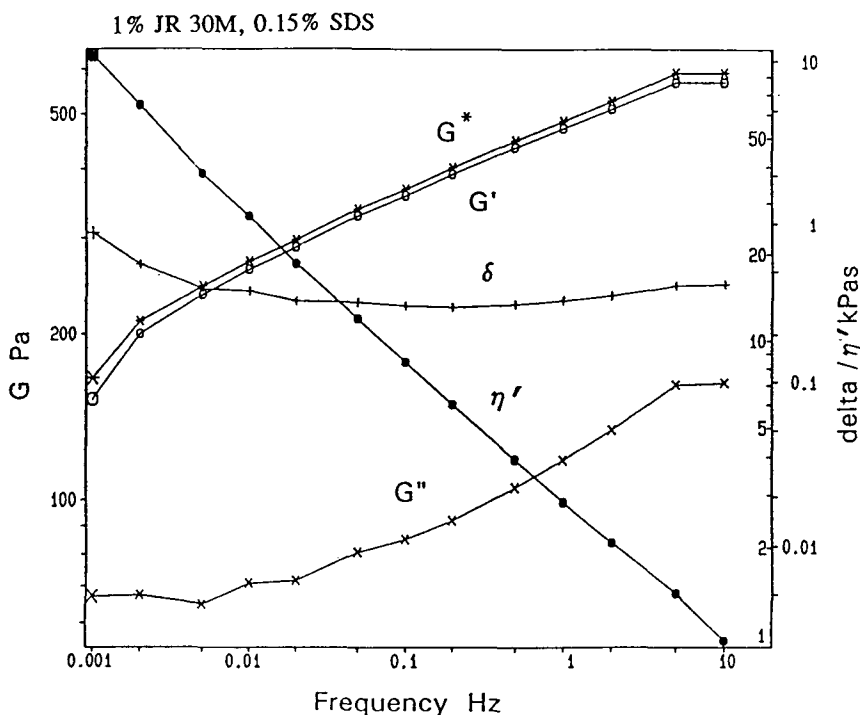
1% JR 30M, 0.15% SDS

FIG. 17. Elastic modulus, G', loss modulus, G'', phase angle, and dynamic viscosity, η', vs. oscillation frequency for 1% Polymer JR30M, 0.15% SDS mixture (55).
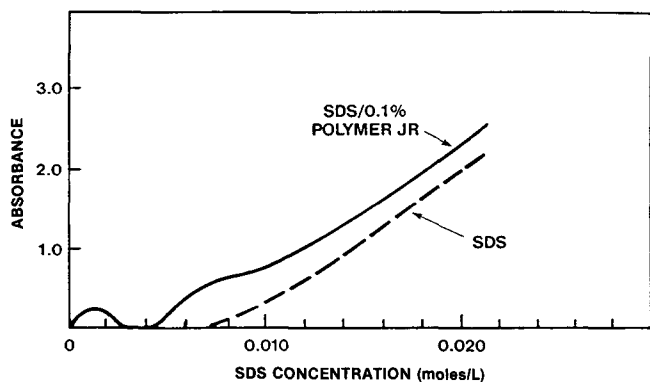
FIG. 18. Solubilization of Orange OT by SDS alone and in the presence of 0.1% Polymer JR 400 (59).

FIG. 19. Depiction of polycation/ionic surfactant micelle "string of beads" association structure.

methylether copolymer (Gantrez S-95, GAF Corp., Wayne, NJ) plus decylpyridinium chloride, efficiently solubilized chlorophenols, a finding of interest for those involved in the clean-up of contaminated water (61).

Because of the association of polymers and surfactants in solution, it would not be surprising if they could influence each other's solubility, as well as that of a third component. Indeed, it has been found that SDS, for example, can actually solubilize certain normally insoluble polymers, such as polyvinylacetate, as demonstrated by Isemura and Imanishi (62). Similar work had been carried out earlier by Sata and Saito (63). Solubilizing effects of this nature also have been demonstrated by Saito and Mizuta (64) for certain cationic surfactants.
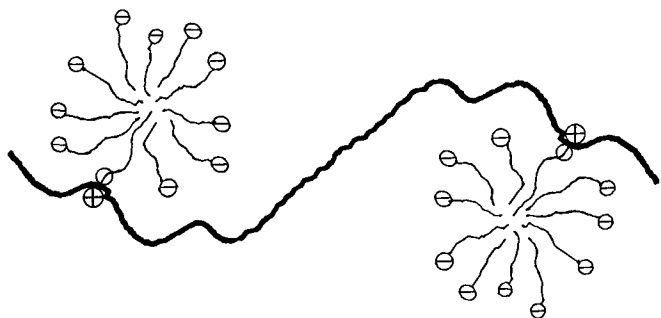
For an interacting nonionized polymer/ionic surfactant pair, it is logical to expect that increased solubility is manifested in the opposite sense, i.e., the polymer may increase the solubility of the surfactant because the monomer concentration required for aggregation of the surfactant is lowered in the presence of the polymer. Such an effect has, in fact, been reported by Schwuger and Lange (65), who showed that PVP can reduce the Krafft point of sodium hexadecyl sulfate by close to 10°C. A special case of enhancement of the solubility of a polymer by a charged surfactant, viz., elevation of cloudpoint, is treated in the next section.

[Note: It is well known that many conditioning polymers are polycationic, and we have pointed out that precipitation zones exist at certain ratios in combinations of such polyelectrolytes with anionic surfactants. In most

cases, however, such precipitates can be solubilized in the presence of excess surfactant or prevented by the co-presence of a nonionic surfactant (46,66,67).]

Cloud point elevation of polymers. Most uncharged polymers owe their solubility to the presence of polar groups, such as ether, hydroxyl, amide and carboxyl, which will hydrate in the presence of water. This hydration, especially of the ether group, can diminish progressively with temperature, and the critical balance governing solubility can be upset at a specific temperature (cloudpoint) at which the polymer comes out of solution. If the polymer can acquire charges, *e.g.*, by ionization of acidic or basic groups or by the adsorption of a charged species, such as a surfactant, enhanced solubility or elevation of the cloud point can be expected.

There is much evidence in the literature to illustrate these effects. Although PEO itself is not amenable to such studies (its cloud point exceeds 100°C), related polymers provide such information—PPO, by dint of possessing hydrophobic methyl groups, has much lower water solubility than PEO; PPOs of MW 1,025 and 2,000 have cloud points of about 40 and 20°C, respectively. Pletnev and Trapeznikov (68) showed that SDS and NaDDBS (sodium dodecylbenzene sulfonate) can raise these values to above 90°C. (In one sense, standard nonionic surfactants can be regarded as PEO polymers—that one can raise their cloud point by addition of ionic surfactants is a fact already known to formulators.) There are several references to increases of the cloud point of PVA polymers by addition of anionic surfactants, and similar elevation is well known for MeC. The behavior of the latter polymer has recently been examined in great detail by Carlsson *et al.* (69), and is somewhat complex. Cloud point alteration has usually been considered to reflect a monotonic increase with increase in ionic surfactant concentration, but recent work has shown that the first additions of ionic surfactant can sometimes lower the cloud point of cellulosic and other nonionic polymers, especially when salt is present (70–73). In fact, the phenomenon seems to be unusually sensitive to the presence of salt. Karlstrom *et al.* (70) have studied the phenomenon in detail and have presented phase relationships for a number of cellulosic polymers (especially EHEC/ionic surfactant pairs). The cloud point *vs.* surfactant concentration plot is affected by a number of factors, such as (i) the polymer itself; (ii) the surfactant (structure and chainlength); (iii) the presence of salt and its concentration; and (iv) the particular salt chosen. Specific ion effects, well known in salting out/in of polyether nonionic surfactants and polymers, are pronounced. In a qualitative way, it is proposed that the cloud point of the polymer is raised by association with an ionic surfactant because of electrical repulsion between the (now charged) polymer molecules. Evidently, this effect is sensitive to, and can be offset by, electrical screening on adding salt.

Reduction of monomer concentration. The fact that, in the presence of polymer, aggregates of surfactant can form at concentrations lower than the CMC means that the maximum monomer concentration of surfactant is reduced. For nonionized polymer/ionic surfactant combinations, the region involved would be in the T_1, T_2 concentration range. For polyelectrolyte/ionized surfactant pairs, this effect would be maximal in the preprecipitation binding zone. Because of the strong bonding forces involved

in the latter case, the reduction in monomer concentration would tend to be much higher.

Although the picture concerning the irritation to skin caused by exposure to surfactants, in particular anionic surfactants, is not completely clear, much evidence exists which suggests lowered monomer concentration of the surfactant can correspond to lowered irritation (58). Coupled with this, there is evidence (74–76) that addition of selected polymers to solutions of anionic surfactants can reduce the irritation caused by the latter. The implication is that formulations of lowered irritation potential could be more reliably created on this basis if a knowledge of the binding characteristics of the particular polymer/surfactant combination chosen were established. However, the possibility exists that any observed reduction of irritation occasioned by the presence of a polymer may involve more than one mechanism (77).

On the basis of extensive *in vivo* and *in vitro* testing, a hypothesis (77) was offered that cationic cellulosic polymers exert a protective influence on keratin substrates by adsorbing on the latter and, through a cross-linking mechanism, helping to keep the keratin polypeptide chain network intact.

We point out that extensive studies have been carried out on the influence of SDS on the adsorption of radiotagged Polymer JR on keratin substrates, which are negatively charged and water-swellable. Small additions of surfactant progressively reduced the adsorption of polymer owing to reduction of its positive charge density (78). However, at high levels of SDS (in the postprecipitation zone), adsorption of this polymer was fully restored (79).

Surface activity, adsorption and surface conditioning. The formation of highly surface-active complexes between polyelectrolytes and oppositely charged surfactants provides a synergistic enhancement of the surface activity of the two components. Consequences of this enhancement could include improved emulsifying ability, and especially foaming. On the other hand, nonionized polymer may reduce the surface activity (air/water interface) of ionic surfactants by binding the latter in the form of weakly surface-active complexes. Nonetheless, we concluded that some adsorption of the polymer at the air/water interface probably does occur under these conditions of incipient complex formation, and the stronger the tendency of the polymer to interact (*i.e.*, the more hydrophobic it is), the stronger its tendency to co-adsorb.

Several references can be found on the improvement of foamability and foam quality of ionic surfactants by the addition of unionized polymers, such as PVA, PEO, modified starches and cellulosics. Such implied alteration of surface properties can be understood if one considers the adsorbed layer of surfactant to resemble a surfactant micelle (in this case a "semi-infinite hemimicelle"), which is able to interact with the polymer in a way similar to that depicted in Figures 7 and 8. In other words, surfactant and polymer could influence each other's adsorption characteristics; hence, surface properties, including foaming, would be affected, even though the energy of association of the surfactant and the base monomer may be much weaker than when the polymer and surfactant are oppositely charged.

Because both polymer and surfactant can adsorb on solid surfaces, there has been much interest and

considerable work done to determine what effect each has on the extent of adsorption of the other. Most of the work done has involved mineral (or latex) solids (1,4) and will not be detailed here. Suffice it to say that positive and negative effects have been found for both adsorbing components, depending on the conditions, such as the actual components themselves, the addition sequence, the solid surface and the pH. As the adsorption energy per monomer unit of (especially) a nonionic polymer can be quite weak, it is not surprising that its overall adsorption can be affected by an added surfactant. The clear implication is that opportunities exist to modify the surface characteristics of chosen solids by appropriate choice of surfactants and polymers. Because the solid introduces a new phase (as in conditioning) and because other ingredients may also be present, determination of improved adsorption characteristics has to be done empirically in most cases.

Some recent examples of enhanced surface conditioning merit mention. For example, Kilau and Voltz (80) observed synergistic wetting of hydrophobic coal with a sulfonate surfactant (but not with a nonionic surfactant) in combination with a high-MW PEO. An approximate representation of the interfacial conditions in this case may be found in Figure 8 if the word COAL is substituted for the word AIR–in other words, the polymer is considered to interact with the adsorbed surfactant molecules in a hemimicellar array. For hydrophilic coal the surfactant molecules would adsorb with an opposite configuration, i.e., headgroups "away," and no synergistic effect was observed. Other evidence of an adsorbed surfactant (SDS) on a solid (alumina) promoting the adsorption of a polymer (PEO) has been given recently (81).

As an example of oppositely charged polymer-surfactant mixture conditioning, Somasundaran and Lee (82) have reported a strong synergistic effect of a small amount of a cationic polyacrylamide in combination with sodium dodecane/sulfonate (SDDS) in the flotation of quartz. The preadsorbed polymer acts primarily as a primer for the main collector, SDDS, which otherwise would show only feeble activity. When a charged polymer is present together with a large excess of oppositely charged surfactant, its charges are neutralized and the complex develops a net charge opposite in sign to its original one. This means that if the polyion adsorbs on an oppositely charged substrate (as with a conditioning polycation on keratin from an anionic surfactant solution), it must at least be transported to near the surface in the form of the complex. Because adsorption of a polymer under such conditions has actually been measured, a rearrangement of the complex has to be invoked to explain the adsorption mechanism under these conditions (83).

Hydrophobic water-soluble polymers. The favorable influence of some hydrophobic character in the water-soluble polymer, especially if uncharged, on its interaction with surfactants has already been mentioned. A simple indicator of reactivity is the lowering of the surface tension of water by the polymer itself. We have already given examples. Another example is that the relatively inert polymer, hydroxyethyl cellulose (HEC), is surface-inactive, whereas the much more reactive methylcellulose and hydroxypropyl cellulose (HPC) are known to have appreciable surface activity.

In the same way, highly surface-active polypropylene oxide is much more interactive than less surface-active PEO (84, 85). One penalty of higher surface activity of the polymer, however, is that the useful surface tension method of examining the interaction pattern with a surfactant becomes less informative and more difficult to interpret. Fortunately, as pointed out previously, there are a large number of alternative methods to study the interactions. As recent examples, cloud point determinations, phase mapping, rheology and NMR (for self-diffusion) in studies of a series of surface-active cellulose ethers (EHEC, MeC, HPC) and ionic surfactants have been employed by Lindman and Thalberg (8). Clear indication of pronounced interaction was obtained in all cases. An interesting variation on the theme of cellulose ether interaction with a surfactant was presented by Winnik (86), who studied the interaction of Pyrene-labelled HPC with the nonionic surfactants, n-octyl β-D-glucopyranoside and-(thio)glucopyranoside (OG and OTG). Evidence of clustering of the surfactant molecules around the pyrene chromophores was obtained. These results are reminiscent of the earlier work of Brackman *et al.* (84), who showed that if the water-soluble polymer is sufficiently hydrophobic (PPO; MW 1,000), association with a nonionic surfactant (the same OTG) does indeed occur. Other studies on the HPC/SDS system have been reported by Winnik and Winnik (87), who have deduced that the surfactant cluster size increases with SDS concentration above T_1, unlike the case of SDS clusters on PEO. Pyrene-labelling groups on a fairly hydrophilic polymer, *e.g.*, PEO, provide hydrophobic centers for interaction (88).

The next section is concerned with a special type of hydrophobic water-soluble polymer.

POLYMERIC SURFACTANTS

There is presently a great renewal of interest in "polymeric surfactants", as well as growing commercial recognition of their importance as so-called "associative thickeners" for use in latex and other formulated product systems. These materials are, in effect, conventional water-soluble polymers that have been modified by inclusion of hydrophobic moieties, particularly alkyl groups. They combine the properties of a surfactant/polymer mixture in one molecule and therefore display some of the properties of such mixtures. Then, when dissolved in water, they tend to self-associate, generating structures of high MW, and hence substantially increase the viscosity of their solution. Several recent papers on the subject of associative thickening polymers may be found (89). Other consequences of the associative tendency in molecules with this type of structure are the development of solubilizing properties for water-insoluble materials, including dyes, and also a strong tendency to produce foams of unusual stability. Goddard and Braun (90) showed that a hydrophobically-modified cationic cellulosic polymer, Quatrisoft LM (Union Carbide Corp.), could form the basis of an aerosol mousse.

The considerable revival of interest in water-soluble polymers with "well-defined" hydrophobic groups is a natural outgrowth of the work in the 1950s and 1960s on "polysoaps" or "polymeric surfactants," notably vinyl-alkylether/maleic anhydride copolymers and alkyl derivatives of poly-2-vinylpyridine (91). Analogies between polymeric surfactants and conventional surfactants have led

several authors to obtain evidence, chiefly by fluorescence methods, of self-association of the hydrophobic groups of such polymers in solution. Refer to Binana-Limbele and Zana (92) and Hsu and Strauss (93), and references contained therein, for studies of vinylalkylether/maleic anhydride copolymers; and by Chu and Thomas (94) and Shih *et al.* (95,96) for studies of α-olefin/maleic anhydride copolymers [in the latter case examined by Small Angle Neutron Scattering (SANS)]. The self-association of pyrene-labelled PEO (97,98) and HPC (99) provide further illustration of this effect, as does the self-association of a PEO polymer terminally tagged with alkyl groups (100). Viscosity studies on alkyl-substituted HEC ("HM-HEC") solutions have been carried out by Landoll (101), Gelman and Barth (102) and by Goodwin *et al.* (103), all of whom obtain evidence of polymer aggregation beyond a certain concentration. A recent compilation of contributions in this area has been published (104), extending an earlier one (89). Lastly, a model for the formation of "micelles" by these types of amphiphilic polymers has recently been developed by Hamad and Qutubuddin (105). Because the present article is concerned with polymers with added conventional surfactants, this important area is not pursued further here. What is important in the present context is that the presence of hydrophobic moieties in the polymer virtually ensures interaction with added surfactants (106).

D.R. Bassett (private communication) has prepared a qualitative depiction of possible structures involving association between hydrophobic polymeric species, including one in which micelles of added simple surfactant participate (Figs. 20 and 21). On defining polymeric surfactants as water-soluble polymers with alkyl group substituents of chainlength $\geq C_{10}$, one actually finds relatively few published papers on the subject of mixtures of these polymers with conventional surfactants. We refer briefly to a few such studies, all based on uncharged hydrophobically-modified cellulose ethers. Sau and Landoll (107) have reported substantial viscosity boosting effects on adding a nonionic surfactant to a dilute solution of HM-HEC. Viscosity peaks with added anionic surfactants were also found by these authors and by Dualeh and Steiner (108) and Carlsson and co-workers (53), with added
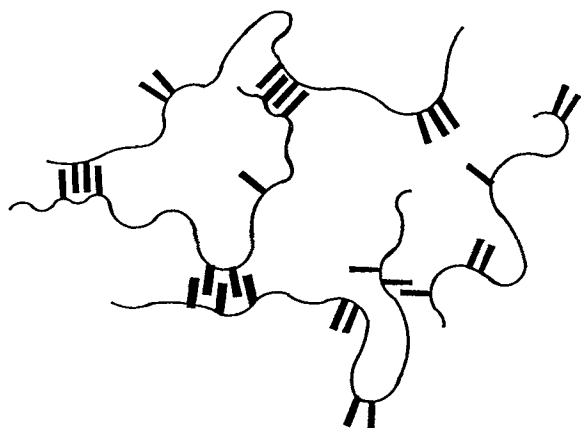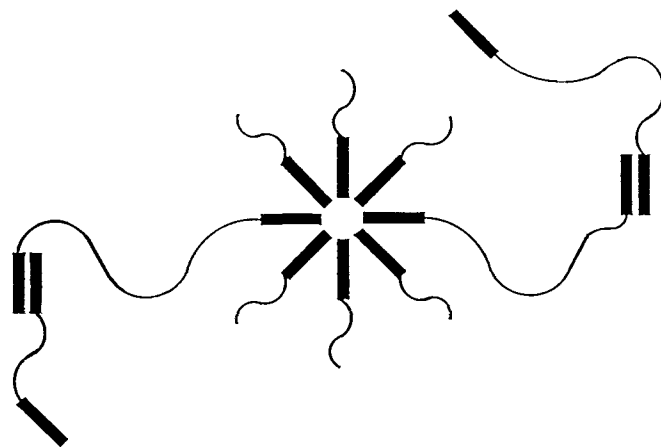

FIG. 21. Depiction of an end-substituted polymer associating *via* a micellar bridge (D.R. Bassett).

SDS yielding gels under certain conditions (109). Similar effects for such systems are evident in the work of Tanaka *et al.* (109) and of Sivadasan and Somasundaran (110), who also report pronounced interaction between HM-HEC and the nonionic surfactant $C_{12}EO_8$, as seen by fluorescence techniques. This method, as well as electrical conductivity, were used by Dualeh and Steiner (108) to verify the pronounced interaction of HM-HEC and SDS. Goddard has recently (111) cautioned that phase separation in such systems (*e.g.*, in HM-HEC, Tergitol NP-10 mixtures) is rather common in the region where the viscosity increases occur, and these results underscore the need for phase studies in such systems—a factor of potential importance to formulators. Clarification of these systems is to be expected at high concentrations of surfactants when micelles are sufficiently abundant.

Recently, Jenkins *et al.* (112) have shown that both PEO and polyacrylate-type water-soluble polymers, modified with undisclosed "novel" hydrophobic groups, show especially strong interaction with certain nonionic surfactants, as revealed by pronounced increases in viscosity of the mixed solutions. The interaction is sensitive to the number of EO groups in the surfactant, and the novel hydrophobic groups lead to much more pronounced interaction effects than do corresponding hexadecyl or nonylphenyl groups.

Turning to oppositely charged pairs, Ananthapadmanabhan *et al.* (113) showed by pyrene fluorescence methods that association of SDS and polymer occurs at a much lower surfactant concentration with a hydrophobically-substituted (C_{12}) cationic cellulosic polymer than it does with a conventional cationic cellulosic, Polymer JR, having a much higher degree of cationic substitution. This again shows the important effect on the association of the presence of hydrophobic groups in the polymer. Another interesting development has been the demonstration (114) that the above combination can provide gelling compositions in the post-precipitation, as well as in the preprecipitation, surfactant concentration range. This signifies that the basic molecular structure of the gels attainable in the two concentration ranges is different. Gels in the post-precipitation range are attainable with a

FIG. 20. Depiction of association structures of a hydrophobically modified polymer (D.R. Bassett).

variety of anionic surfactants, providing a wide latitude of formulation opportunities.

A question of some importance, which has recently been answered, is whether or not a hydrophobically-substituted charged polymer will interact with a surfactant of like charge. For example, will a polysoap interact with an anionic surfactant? McGlade et al. (115), working with poly (1-decene-co-maleic acid) and poly (1-octadecene-co-maleic acid) polyelectrolytes, found clear evidence by fluorescence and surface-tension measurements of interaction with SDS. In other words, interaction by hydrophobic association is able to offset the effect of the adverse electrical field gradient between the two species. A second example comes from the study of Iliopoulos et al. (116) on hydrophobically-modified poly(sodium acrylate). At certain ratios of added SDS (near its CMC), pronounced maxima, reflecting increments of three decades or more in viscosity, were encountered, again providing clear evidence of association.

A third example (114) involves the above-mentioned cationic polymer (113) in mixture with cationic surfactants. In a homologous series of alkyltrimethylammonium bromides, precipitation reactions ("salting out") were encountered with the two lower-chain-length homologues (C_{10} and C_{12}) but not with the higher homologues (C_{14} and C_{16}). Solubilization encountered at higher (>CMC) concentrations in the former case reveals the anticipated interaction between the polymer and the surfactants (in micellar form in this case). Such interaction should be well illustrated in phase diagrams of the type reported by Lindman and Thalberg (8).

From the foregoing, one can confidently say that the potential of polymeric surfactants is considerable, not only as thickeners but as specialty surfactants, specialty polymers and surface conditioners as well. In formulation flexibility is provided in the way that these polymers respond to the addition of different surfactants. In light of the current level of research on this category of materials, it is anticipated that many opportunities and applications will be forthcoming as new structures are developed and new uses defined.

REFERENCES

1. Goddard, E.D., Colloids Surfaces 19:255, 301 (1986).
2. Robb, I.D., in Anionic Surfactants in Physical Chemistry of Surfactant Action, edited by E.H. Lucassen-Reynders, Marcel Dekker, New York, 1981, p. 109.
3. Hayakawa, K., and J.C.T. Kwak, in Cationic Surfactants, edited by D.N. Rubingh, and P.M. Holland, Marcel Dekker, New York, 1991, p. 189.
4. Goddard, E.D., and K.P. Ananthapadmanabhan (eds.), Interactions of Surfactants with Polymers and Proteins, CRC Press, Boca Raton, 1992.
5. Shirahama, K., Colloid Polym. Sci. 252:978 (1974).
6. Sasaki, T., K. Kushima, K. Matsuda and H. Suzuki, Bull. Chem. Soc. Jpn. 53:1864 (1980).
7. Goddard, E.D., T.S. Phillips and R.B. Hannan, J. Soc. Cosmetic Chem. 26:461 (1975).
8. Lindman, B., and K. Thalberg, in Interactions of Surfactants with Polymers and Proteins, edited by E.D. Goddard, and K.P. Ananthapadmanabhan, CRC Press, Boca Raton, 1992, Chapter 5.
9. Birch, B.J., D.E. Clarke, R.S. Lee and J. Oakes, Anal. Chim. Acta 70:417 (1974).
10. Kresheck, G.C., and I. Constantinidis, Anal. Chem. 56:152(1984).
11. Gilanyi, T., and E. Wolfram, Colloids Surfaces 3:181 (1981).
12. Malovikova, A., K. Hayakawa and J.C.T. Kwak, in Structure/Performance Relationships in Surfactants, edited by M.J. Rosen, ACS Symposium Series No. 253, American Chemical Society, Washington, D.C., 1984, p. 225.
13. Hayakawa, K., and J.C.T. Kwak, J. Phys. Chem. 87:506 (1983).
14. Kiefer, J.J., P. Somasundaran and K.P. Ananthapadmanabhan, Langmuir 9:1187 (1993).
15. Cockbain, E.G., Trans. Faraday Soc. 49:104 (1953).
16. Jones, M.N., J. Colloid Interface Sci. 23:36 (1967).
17. Schwuger, M.J., Ibid. 43:491 (1973).
18. Lange, H., Kolloid Z.Z. Polym. 243:101 (1971).
19. Goddard, E.D., and R.B. Hannan, J. Colloid Interface Sci. 55:73 (1976).
20. Chari, K., and T.Z. Hossain, J. Phys. Chem. 95:3302 (1991).
21. Breuer, M.M., and I.D. Robb, Chem. Ind.:530 (1972).
22. Goddard, E.D., and P.S. Leung, Langmuir 8:1499 (1992).
23. Tirrell, M., in Interactions of Surfactants with Polymers and Proteins, edited by E.D. Goddard, and K.P. Ananthapadmanabhan, CRC Press, Boca Raton, 1992, Chapter 3.
24. Schild, H.G., and D.A. Tirrell, Langmuir 7:665 (1991).
25. Cabane, B., J. Phys. Chem. 81:1639 (1977).
26. Shirahama, K., K. Tsujii and T. Takagi, J. Biochem (Tokyo) 75:309 (1974).
27. Flory, P., Principles of Polymer Chemistry, Cornell University Press, Ithaca, 1974.
28. Winnik, F.M., M.A. Winnik and S. Tazuke, J. Phys. Chem. 91:594 (1987).
29. Saito, S., and T. Taniguchi, J. Colloid Interface Sci. 44:114 (1973).
30. Saito, S., Colloid Polymer Sci. 257:266 (1979).
31. Saito, S., and M. Yukawa, J. Colloid Interface Sci. 30:211 (1969).
32. Saito, S., and M. Yukawa, Kolloid Z. 234:1015 (1969).
33. Shirahama, K., Colloid Polym. Sci. 252:978 (1974).
34. Hill, A.V., J. Physiol. (London) 40:190 (1910).
35. Smith, M.L., and N. Muller, J. Colloid Interface Sci. 52:507 (1975).
36. Gilanyi, T., and E. Wolfram, Colloids Surfaces 3:181 (1981).
37. Nagarajan, R., Ibid. 13:1 (1985).
38. Ruckenstein, E., G. Huber and H. Hoffmann, Langmuir 3:382 (1987).
39. Nagarajan, R., J. Chem. Phys. 90:1980 (1989).
40. Evans, D.F., D.J. Mitchell and B.W. Ninham, J. Phys. Chem. 88:6344 (1984).
41. Brackman, J.C., The Interaction Between Water-Soluble Polymers and Surfactant Aggregates, Ph.D. Thesis, University of Gronigen, The Netherlands, 1990.
42. Balazs, A.C., and J.Y. Hu, Langmuir 5:1230 (1989).
43. Bloor, D.M., and E. Wyn-Jones, J. Chem. Soc. Faraday Trans. 2 78:657 (1982).
44. Bloor, D.M., W. Knoche and E. Wyn-Jones, NATO Adv. Study Inst. Ser., Ser. C (NASCDS), VC50, Techniques and Applications Fast Reactions in Solution, D. Reidel, Dordrecht, 1975, p. 265.
45. Zana, R., P. Lianos and J. Lang, J. Phys. Chem. 89:41 (1985).
46. Goddard, E.D., and R.B. Hannan, J. Am. Oil Chem. Soc. 54:561 (1977).
47. Satake, I., and J.T. Yang, Biopolymers 15:2263 (1976).
48. Shirahama, K., H. Yuasa and S. Sugimoto, Bull. Chem. Soc. Jpn. 54:375 (1981).
49. Shirahama, K., and M. Tashiro, Ibid. 57:377 (1984).
50. Delville, A., Chem. Phys. Lett. 118:617 (1985).
51. Francois, J., J. Dayantis and J. Sabbadin, Eur. Polym. J. 21:165 (1985).
52. Brackman, J.C., Langmuir 7:469 (1991).
53. Carlsson, A., G. Karlstrom and B. Lindman, Colloids Surfaces 47:147 (1990).
54. Leung, P.S., E.D. Goddard, C. Han and C.J. Glinka, Ibid. 13:47 (1985).
55. Leung, P.S., and E.D. Goddard, Langmuir 7:608 (1991).
56. Goddard, E.D., P.S. Leung and K.P. Ananthapadmanabhan, J. Soc. Cosmetic Chem. 42:19 (1991).
57. Brackman, J.C., and J.B.F.N. Engberts, J. Am. Chem. Soc. 112:872 (1990).
58. Saito, S., Kolloid Z. 154:19 (1957).

59. Goddard, E.D., and R.B. Hannan, in *Micellization, Solubilization and Microemulsions,* Vol. 2, edited by K.L. Mittal, Plenum, New York, 1977, p. 835.
60. Hayakawa, K., T. Fukutome and I. Sasake, *Langmuir 6:*1495 (1990).
61. Lee, B.H., S. D. Christian, E.E. Tucker and J.F. Scamehorn, *Ibid. 7:*1332 (1991).
62. Isemura, T., and A. Imanishi, *J. Polym. Sci. 33:*337 (1958).
63. Sata, N., and S. Saito, *Kolloid Z. 128:*154 (1952).
64. Saito, S., and Y. Mizuta, *J. Colloid Interface Sci. 23:*604 (1967).
65. Schwuger, M.J., and H. Lange, Proceedings of the 5th International Congress of Surface-Active Agents, Barcelona, 1968 Ediciones Unidas S.A., Barcelona, Vol. 2, 1969, p. 955.
66. Dubin, P.L., and D. Davis, *Colloids Surfaces 13:*113 (1985).
67. Dubin, P.L., M.E.Y. Vea, M.A. Fallon, S.S. The, D.R. Rigsbee and L.M. Gan, *Langmuir 6:*1422 (1990).
68. Pletnev, M. Yu, and A.A. Trapeznikov, *Kolloidn. Zh. 40:*948 (1978).
69. Carlsson, A., G. Karlstrom and B. Lindman, *Langmuir 2:*536 (1986).
70. Karlstrom, G., A. Carlsson and B. Lindman, *J. Phys. Chem. 94:*5005 (1990).
71. Carlsson, A., G. Karlstrom, B. Lindman and O. Stenberg, *Colloid Polym. Sci. 266:*1031 (1988).
72. Xie, F., C. Ma and T. Gu, *Colloids Surfaces 36:*39 (1989).
73. Drummond, C.J., S. Albers and D.N. Furlong, *Ibid. 62:*75 (1992).
74. Rhein, L.D., C.R. Robbins, K. Fernee and R. Cantore, *J. Soc. Cosmetic Chem. 37:*125 (1986).
75. Prescott, F.J., E. Hahnel and D. Day, *Drug and Cosmetic Industry 93:*443 (1963).
76. Ward, J.B., and G.J. Sperandio, *J. Soc. Cosmetic Chem. 15:*327 (1967).
77. Faucher, J.A., E.D. Goddard, R.B. Hannan and A. M. Kligman, *Cosmetics Toiletries 92:*39 (1977).
78. Faucher, J.A., and E.D. Goddard, *J. Soc. Cosmetic Chem. 27:*543 (1976).
79. Goddard, E.D., *Kem-Kemi 12:*375 (1985).
80. Kilau, H.W., and J.I. Voltz, *Colloids Surfaces 57:*17 (1991).
81. Ramachandran, R., and P. Somasundaran, in *Flocculation Dewatering, Proceedings Engineer Foundation Conference,* edited by B.M. Moudgil, and B.J. Scheiner, Engineering Foundation, New York, 1988, p. 631.
82. Somasundaran, P., and L.T. Lee, *Sep. Sci. Technol. 16:*1475 (1981).
83. Faucher, J.A., and E.D. Goddard, *J. Colloid Interface Sci. 55:*313 (1976).
84. Brackman, J.C., N.M. van Os and J.B.F.N. Engberts, *Langmuir 4:*1266 (1988).
85. Witte, F.M., and J.B.F.N. Engberts, *Colloids Surfaces 36:*47 (1989).
86. Winnik, F.M., *Langmuir 6:*522 (1990).
87. Winnik, F.M., and M.A. Winnik, *Polymer J. 22:*482 (1990).
88. Hu, Y-Z., C.L. Zhao, M.A. Winnik and P.R. Sundarajan, *Langmuir 6:*880 (1990).
89. Glass, J.E. (ed.) *Polymers in Aqueous Media,* Advances in Chemistry, No. 223, American Chemical Society, Washington, D.C., 1989.

90. Goddard, E.D., and D.B. Braun, *Cosmetics Toiletries 100:*41 (1985).
91. Goddard, E.D., and K.P. Amanthapadmanabhan (eds.), *Interactions of Surfactants with Polymers and Proteins,* CRC Press, Boca Raton, 1992, Chapter 6.
92. Binana-Limbele, W., and R. Zana, *Macromolecules 20:*1331 (1987).
93. Hsu, J-L., and U.P. Strauss, *J. Phys. Chem. 91:*6238 (1987).
94. Chu, D-Y., and J.K. Thomas, *Macromolecules 20:*2133 (1988).
95. Shih, L-B., D.H. Mauer, C.J. Verbrugge, C.F. Wu, S.L. Chang and S.H. Chen, *Ibid. 21:*3235 (1988).
96. Shih, L-B., E.Y. Shen, and S.H. Chen., *Ibid. 21:*1387 (1988).
97. Oyama, H.T., W.T. Tang and C.W. Frank, *Ibid. 20:*474 (1987).
98. Char, K., C.W. Frank, A.P. Gast and W.T. Tang, *Ibid. 20:*1833 (1987).
99. Yamazaki, I., F.M. Winnik, M.A. Winnik and S. Tazuke, *J. Phys. Chem. 91:*4213 (1987).
100. Wang, Y., and M.A. Winnik, *Langmuir 6:*1437 (1990).
101. Landoll, L.M., *J. Polym. Sci., Polymer Chem. Ed. 20:*443 (1982).
102. Gelman, R.A., and H.G. Barth, in *Water-Soluble Polymers,* edited by J.E. Glass, Advances in Chemistry, No. 213, American Chemical Society, 1986, p. 101.
103. Goodwin, J.W., R.W. Hughes, C.K. Lam, J.A. Miles and B.C.H. Warren, in *Polymers in Aqueous Media,* Advances in Chemistry No. 233, edited by J.E. Glass, Washington, D.C., 1989, p. 365.
104. Schultz, D.N., and J.E. Glass, *Polymers as Rheology Modifiers,* ACS Symposium Series No. 462, American Chemical Society, Washington, D.C., 1991.
105. Hamad, E., and S. Qutubuddin, *Macromolecules 23:*251 (1990).
106. Balazs, A.C., K. Huang and T. Pan, *Colloids Surfaces 75:*1 (1993).
107. Sau, A.C., and L.M. Landoll, in *Polymers in Aqueous Media,* edited by J.E. Glass, Advances in Chemistry, American Chemical Society, Washington, D.C., 1989, p. 343.
108. Dualeh, A.J., and C.A. Steiner, *Macromolecules 23:*251 (1990).
109. Tanaka, R., J. Meadows, P.A. Williams and G.O. Phillips, *Ibid. 25:*1304 (1992).
110. Sivadasan, K., and P. Somasundaran, *Colloids Surfaces 49:*229 (1990).
111. Goddard, E.D., *J. Colloid Interf. Sci. 152:*578 (1992).
112. Jenkins, R.D., B.R. Sinha and D.R. Bassett, *Polym. Mater. Sci. Eng. 6:*72 (1991).
113. Ananthapadmanabhan, K.P., P.S. Leung and E.D. Goddard, in *Polymer Association Structures,* edited by M.A. El-Nokaly, ACS Symposium Series No. 384, American Chemical Society, Washington, D.C., 1989, p. 297.
114. Goddard, E.D., and P.S. Leung, *Colloids Surfaces 65:*211 (1992).
115. McGlade, M.J., F.J. Randall and N. Tcheurekdjian, *Macromolecules 20:*1782 (1987).
116. Iliopoulos, I., T.K. Wang and R. Audubert, *Langmuir 7:*617 (1991).