

# Polymer/Surfactant Interactions

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## ABSTRACT AND SUMMARY

Polyelectrolytes and oppositely charged surfactants form precipitation complexes which, in many cases, can be completely resolubilized by excess surfactant. In general, maximum precipitation appears to correspond to a single layer of surfactant adsorbed on the polymer, and the resolubilized form to a double layer of surfactant. Prior to formation of the latter, the complexes are highly surface active. An analysis of the solubility diagrams of a cationic hydroxyethyl cellulose derivative, and a homologous series of sodium alkyl sulfates, has provided a value of the adsorption energy,  $\Phi$ , of these surfactants into the first layer. The value of  $\Phi$ , viz., 1.1 kT per  $\text{CH}_2$  group, is somewhat higher than the corresponding value for micelle formation. Studies with a number of surfactants show that polymer/surfactant interaction is most favorable (a) the longer the hydrocarbon chain of the surfactant, (b) the straighter the chain, and (c) when the head group is terminal to the chain. Departures from these conditions reduce the extent of interaction and render difficult resolubilization of the complex. From results on a range of polymers, it is concluded that resolubilization of the precipitated complex is also difficult if the charge density of the polymer is too high.

## INTRODUCTION

Interactions in solution between surfactants and water soluble macromolecules have been under study for 30 years or more. Earliest work seems to have been carried out on protein, anionic surfactant systems (1-5); depending on whether the protein was below or above its isoelectric point, precipitation was observed, or was not observed, respectively. However, even above the isoelectric point, association took place and in both cases was related stoichiometrically to the number of positively charged sites on the protein.

More recently, interaction between surfactants and a number of nonionic polymers, such as polyethylene oxides (PEO) (6), polypropylene oxides (PPO) (7), polyvinylpyrrolidone (PVP) (8), polyvinylalcohol (PVA)

(9,10), polyvinylacetate (PVAc) (9,10), and methylcellulose (MC) (11), has been reported, and this field has been reviewed by Breuer and Robb (9). For reaction with ionic surfactants, the reaction sequence is reported (9) to be  $\text{PVA} < \text{PEO} < \text{MC} < \text{PVAc} \leq \text{PPO} \sim \text{PVP}$ ; and for (the weaker) reaction with cationic surfactants, it is reported to be  $\text{PVP} < \text{PEO} < \text{PVA} < \text{MC} < \text{PVAc} \sim \text{PPO}$ . Aside from the effect of residual charge, it is clear that interaction increases with increasing hydrophobicity of the polymer. In fact, it has been found possible to solubilize certain water insoluble polymers, e.g., PVAc (10) and polyvinylformal (12) by addition of anionic surfactant. In general, interaction between nonionic surfactants and uncharged polymers appears to be very weak.

In several recent publications we have reported on the strong association reactions which take place between a cationically charged derivative of hydroxyethyl cellulose (Polymer JR) and anionic surfactants, as studied by surface tension (13,14), solubility diagram (13,14), electrophoresis (14), and dye solubilization (15,16) methods. Perhaps the most cogent evidence of the strong association which can occur in such systems was the complete change in the characteristics of an alkyl sulfate monolayer accompanying the introduction of a minute (10 ppm) amount of the cationic polymer into the subsolution (14).

In the present paper we will examine in some detail the influence of structural features in the anionic surfactant on the interaction with the cationic polymer, and also enquire into the generality of the phenomena we have reported by examining the interaction patterns of a number of commercially available cationic polymers with the anionic surfactant, sodium dodecyl sulfate (SDS). Finally, a small amount of information is reported on the inverse system, viz., anionic polymer, cationic surfactant. The work is concerned largely with the construction of solubility diagrams of the polymer/surfactant mixtures and includes a small section on the surface tension behavior of selected systems.

## EXPERIMENTAL PROCEDURES

Solubility studies: Surfactant concentrate was added to

TABLE I  
List of Cationic Polymers

Name	Description	Side chain	pH of 0.1% solution
Gafquat 755	Quaternized vinyl pyrrolidone/aminoethyl methacrylate copolymer	Side chain	7.2
Carteretin F-4	Copolymer of adipic acid/dimethyl-aminohydroxy propyl diethylene triamine	Side chain Backbone	7.5
Merquat 100	Poly (N,N-dimethyl-3,5 methylene piperidinium chloride): DMDAC	Backbone	4.2
Merquat 550	Copolymer of DMDAC and acrylamide	Backbone	4.6
Calgon M502	Poly (N,N-dimethyl-3,5 methylene piperidinium chloride)	Backbone	7.2
Reten 220	Copolymer of acrylamide/ $\beta$ methacryloxy ethyl trimethyl ammonium chloride	Side chain	4.2
Jaguar C-13	Quaternized guar gum derivative	Side chain	7.1
PEI - 18	Polyethylene imine	Backbone	6.0
PHA	Experimental poly N(hydroxy-2 propyl) piperazine, 57% quaternized with trimethyl ammonium chloride	Backbone	7.4

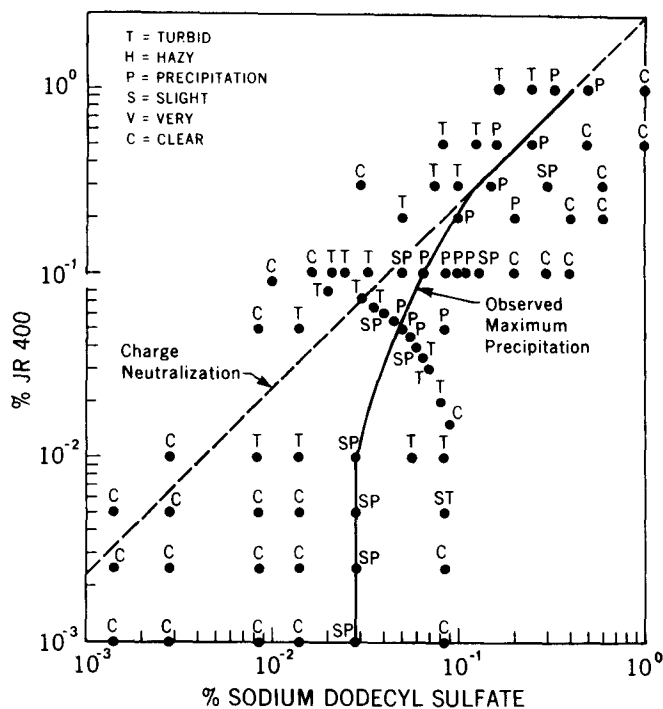


FIG. 1. Solubility diagram of the Polymer JR-400/sodium dodecyl sulfate system.

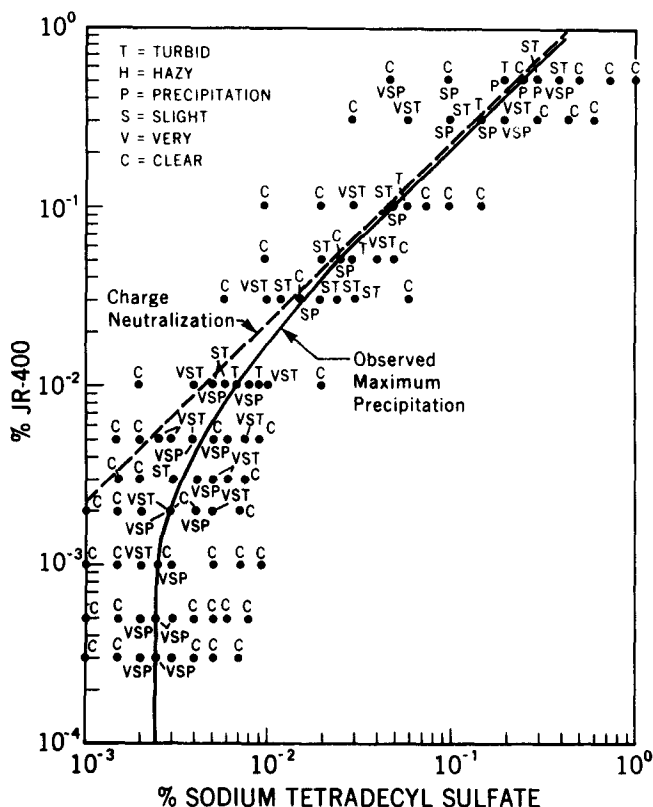


FIG. 2. Solubility diagram of the Polymer JR-400/sodium tetradecyl sulfate system.

polymer concentrate, to which the appropriate amount of water had been added, in small vials. These were shaken by hand and set aside for 1-3 days, and the appearance of the liquid and the precipitation ratings were adjudged by eye. The tests were conducted at room temperature ( $23 \pm 2$  C).

Surface tension: Surface tension was studied as a function of SDS concentration at a fixed concentration of

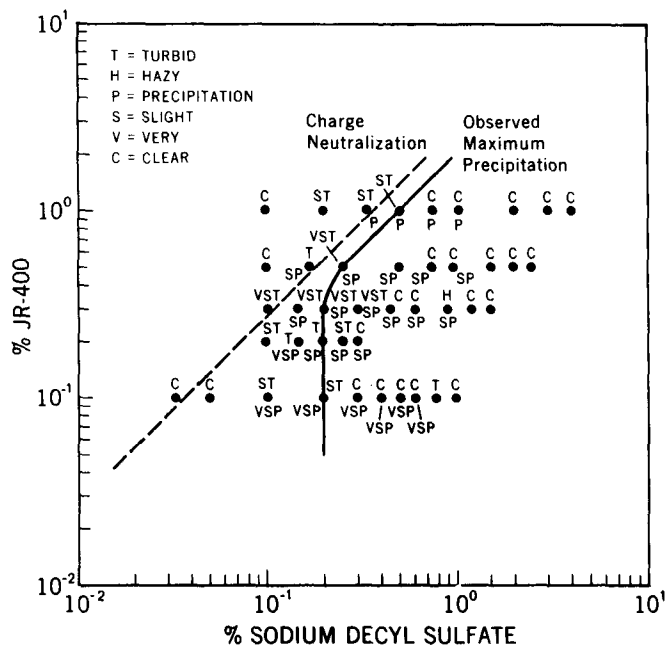


FIG. 3. Solubility diagram of the Polymer JR-400/sodium decyl sulfate system.

polymer. Solutions were prepared from a stock solution of polymer with a relatively high concentration of SDS which was then diluted serially with polymer solution of the same concentration. A Rosano Tensiometer was employed for the measurements. Because of surface ageing, values were taken 1 hr after generating a fresh liquid surface.

Materials: The SDS sample was a specimen from BDH, Poole, England. It was subsequently recrystallized three times from water and three times from ethanol. The tetradecyl, decyl, and octyl sodium sulfates were obtained from Eastman Kodak.

Tergitol Anionic 4 is a Union Carbide material; Tergitol 15-S materials referred to in the text were experimental products based on a straight chain, 11-15 C, random secondary alcohol. Aerosol MA and Sipon ES ethoxy sulfates, described in the text, were specimens from American Cyanamid and Alcolac, respectively.

Polymer JR-400 is a product of Union Carbide Corporation. It is quaternary nitrogen substituted cellulose ether of molecular weight around 400,000 (17). The other cationic polymers used were Gafquat 755 (GAF Corporation); Cartaretin F-4 (Sandoz); Merquats 100 and 550 (Merck); Reten 220 (Hercules); Calgon M-502 (Calgon); polyethyleneimine (PEI, Dow); Jaguar C-13 (Stein-Hall); and, poly-N (hydroxy-2 propyl) piperazine, partially quaternized (PHA, experimental). Further details concerning these polymers appear in Table I.

## RESULTS AND DISCUSSION

### Effect of Alkyl Sulfate Chain Length on the Polymer JR Interaction

Figures 1-4 represent the solubility diagrams of mixtures of Polymer JR and sodium dodecyl (SDS), tetradecyl, decyl, and octyl sulfates, respectively. Figure 1, for SDS, has previously been reported and analyzed. In brief, at higher concentrations of polymer ( $>0.2$  %) the line of maximum precipitation is straight, has a slope on the log-log plot of  $45^\circ$  corresponding to constant composition of the precipitated complex, and, furthermore, coincides with the stoichiometric charge

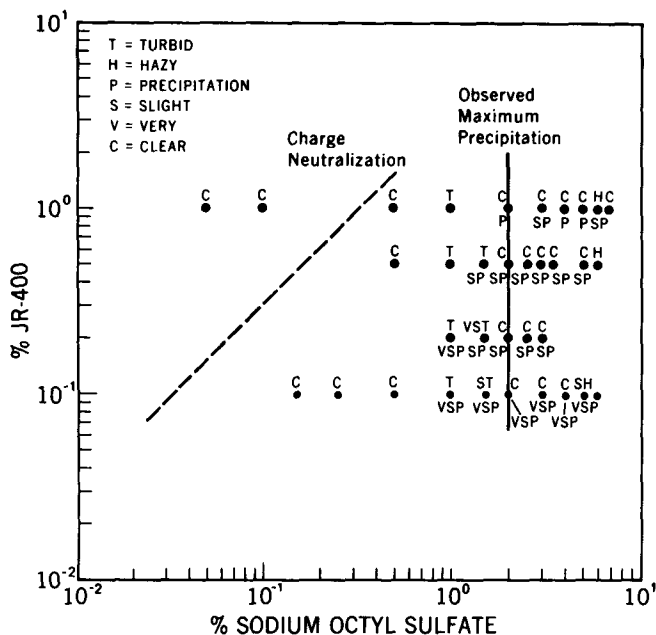


FIG. 4. Solubility diagram of the Polymer JR-400/sodium octyl sulfate system.

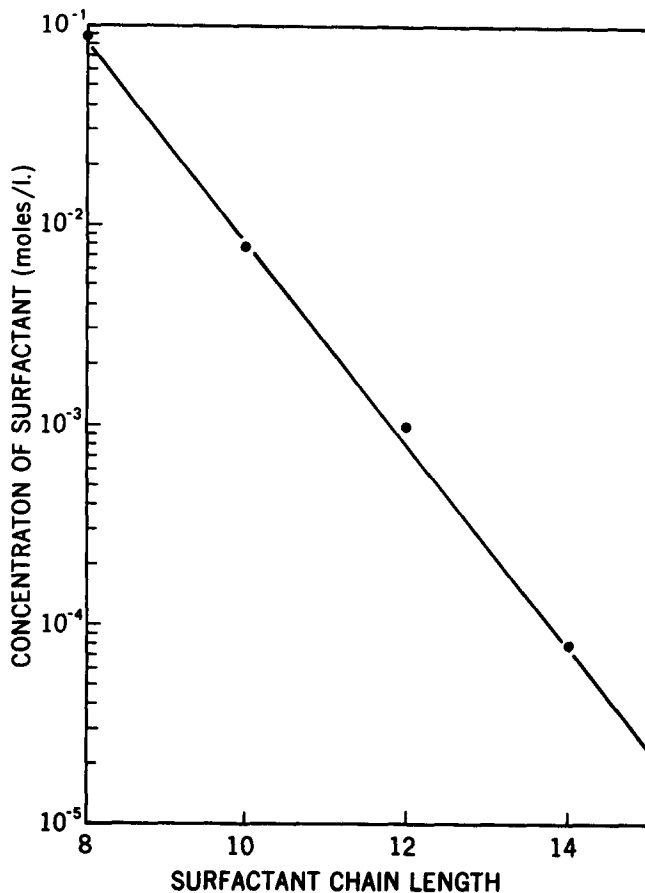


FIG. 5. Logarithm of the equilibrium concentration,  $C_e$ , of various sodium alkyl sulfates vs. their chain length,  $n$ . Conditions correspond to maximum insolubility of the Polymer JR/alkyl sulfate complexes.

neutralization line of the mixed polymer, surfactant system. In this condition we picture each positive charge of the polymer as having a negative surfactant molecule adsorbed onto it in head-to-head configuration. At lower concentrations of polymer, the slope of the maximum precipitation line increases, until at  $\leq 0.01\%$  polymer it becomes  $90^\circ$  and independent of polymer concentration. As the concentration of surfactant at a certain polymer concentration is increased beyond that required for maximum precipitation, resolubilization of the precipitate occurs and eventually the systems become completely soluble. We have postulated (13,14) that this process corresponds to the adsorption of a second layer of surfactant and the transformation of the polymer into a soluble polyanion. Turning to the tetradecyl sulfate system (Fig. 2), we see qualitatively similar behavior, except that the  $45^\circ$  linear region is more extended, and the transition to the higher slope regions occurs at lower polymer concentrations. In the case of the decyl sulfate shown in Figure 3, the  $45^\circ$  line of maximum precipitation is correspondingly displaced to higher surfactant concentration, and the transition concentrations are also higher. Finally, for the octyl sulfate system no  $45^\circ$  slope line is detectable in the concentration range examined, only a vertical segment is observed and this is displaced to an even higher surfactant concentration (see Figure 4).

Our previous analysis (14) led to the following equation describing the equilibrium in these system

$$(C_t - C_e) = k [P]$$

This equation refers to the condition of maximum insolubility;  $[P]$  is the polymer concentration,  $C_t$  is the total concentration of added surfactant, and  $C_e$  is the concentration of surfactant required to maintain equilibrium with the precipitated complex. The equation makes it clear that as  $[P]$  tends to zero, virtually all the added surfactant is required to maintain  $C_e$ , and, hence, why the precipitation line becomes vertical. It is qualitatively obvious, from inspection of Figures 1-4, that the affinity of the association reaction decreases strongly as the chain length of the surfactant decreases. This conclusion is emphasized by Figure 5 in which we plot the logarithm of the  $C_e$  values, i.e., the concentrations

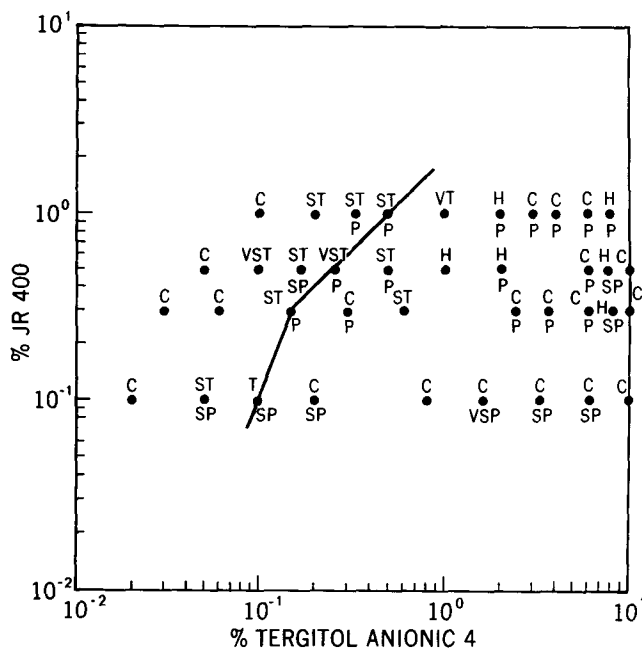


FIG. 6. Solubility diagram of the Polymer JR-400/Tergitol Anionic 4 system.

corresponding to the vertical lines in Figures 1-4, of the alkyl sulfates against their chain length; the plot is linear. The data allow a quantitative estimate of the interaction energy to be made.

The equilibrium governing the adsorption of anionic

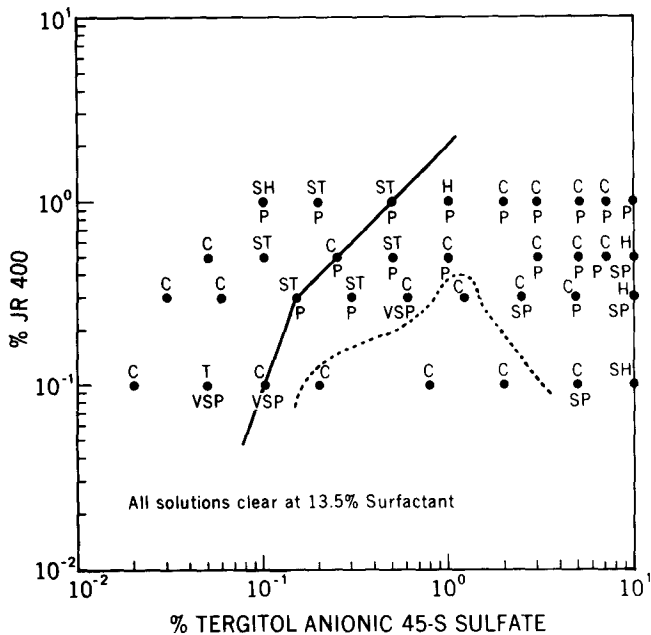


FIG. 7. Solubility diagram of the Polymer JR-400/Tergitol 45-S sulfate system.

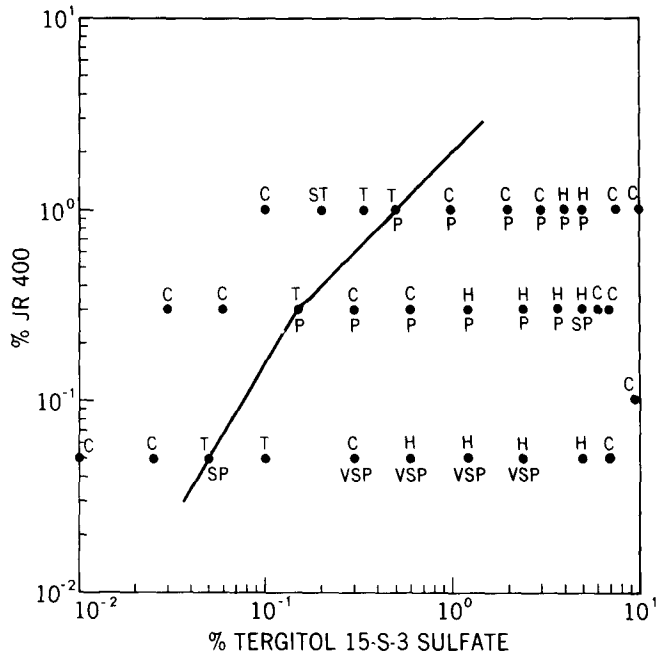


FIG. 9 Solubility diagram of the Polymer JR-400/Tergitol 15-S-3 EO sulfate system.

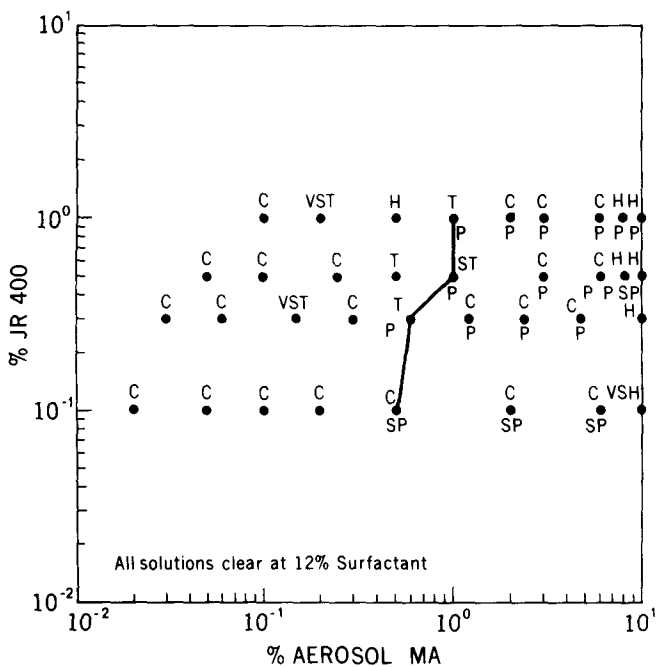


FIG. 8. Solubility diagram of the Polymer JR-400/Aerosol MA system.

value  $\Phi / 2.3 kT$ , and from Figure 5 we obtain a value of  $\Phi$  of 1.1 kT. This value is somewhat higher than the free energy of micelle formation of this kind of surfactant, viz., 0.8 kT/CH<sub>2</sub> group (18). The energy of cluster formation corresponds more closely to that of "hemimicelle" formation of ionic surfactants on oppositely charged mineral surfaces (19).

**Effect of Anionic Surfactant Structure on the Polymer JR Interaction**

The above results, and those reported by us previously, involved straight chain surfactants in which the alkyl chain was primary to the anionic head group. [For convenience, in this category we include a linear alkyl benzene sulfonate (13).] We will now examine departures from this structure. Tergitol Anionic 4 is a fourteen carbon secondary sulfate in which the anion is attached approximately midway along the main chain which itself possesses some branching. Figure 6 shows that the solubility diagram has become more complex, the salient feature being that with this surfactant it has become more difficult, i.e., more surfactant is required, to solubilize the complex. We note, however, the unusual clear zone around the 1% surfactant level at a polymer concentration of 0.1%.

Figure 7 presents corresponding, and similar, data for the Polymer JR/Tergitol Anionic 45-S sulfate system. The latter surfactant is based on a straight chain 14-15 carbon hydrocarbon in which the alcohol, and hence, sulfate groups are secondary and random along the chain. We note again the difficulty in solubilizing the complex at higher surfactant concentration, and also the appearance of an even larger, delineated "clear zone" at lower levels of the polymer. For both systems the 45° maximum precipitation line is evident at higher polymer concentration, and the slope increases at lower polymer levels. Results for the Polymer JR/Aerosol MA system (dimethylamylsulfosuccinate) are given in Figure 8. In this case not only are resolubilization difficulties encountered, but the maximum precipitation line, in the range investigated, is almost vertical.

Certain features concerning the affinity of the

surfactant onto a positively charged polymer can be expressed as

$$C_{ads} = C_b \exp \left\{ (e \psi_0 + n \Phi) / kT \right\}$$

where  $C_b$  is the equilibrium concentration of surfactant in solution,  $C_{ads}$  is the concentration of adsorbed surfactant in undefined units,  $\psi_0$  is the electrostatic potential around the polymer,  $n$  is the number of CH<sub>2</sub> groups in the surfactant chain,  $\Phi$  is the adsorption energy per CH<sub>2</sub> group, and  $k$  and  $T$  are the Boltzmann constant and absolute temperature, respectively. If we consider conditions corresponding to maximum precipitation and charge neutralization, the equation simplifies to

$$C_{ads} = C_e \exp (n \Phi / kT) = a \text{ constant.}$$

Hence, the slope of the log<sub>10</sub>  $C_e$  vs.  $n$  plot has the

polymer/surfactant interaction, as judged by the formation of the maximum precipitation line (first surfactant layer) and resolubilization of the complex (second surfactant layer), now start to emerge. Interaction is most favorable (a) the longer the hydrocarbon chain of the surfactant, (b) the straighter its chain, (c) when the anionic head group is terminal to the chain. Conditions are least favorable in a surfactant molecule like Aerosol-MA where the alkyl groups are short and branched and the head group is centrally positioned in the molecule. The reason for the "clear zones" in solubility diagrams of Polymer JR and Tergitol Anionics 4 and 45-S sulfate is not apparent: it may be connected with a salting-out phenomenon as the surfactant concentration is increased.

Ethoxy sulfates comprise the last group of anionic surfactants examined. Solubility diagrams for Polymer JR/Tergitol 15-S-3 EO sulfate and Tergitol 15-S-7 EO sulfate are presented in Figures 9 and 10. We see the features of 45° precipitation lines at high concentration and the need for high solubilizing concentrations of these surfactants, but no anomalous clear zones. In other experiments it was established that the presence of ethoxy groups, per se, does not adversely affect the interaction, so confirming previous results (20); both a twelve carbon monoethoxy sulfate and a triethoxy sulfate (Sipon ESY and ES) displayed strong interaction features, viz., a 45° precipitation line in the range of polymer concentration tested (0.1 to 1%) and also relatively low values of resolubilization concentrations.

#### Polymer JR/Non-Anionic Surfactants and Other Systems

We have reported previously (13) that nonionic surfactants, such as Tergitol 15-S-9, and betaine surfactants, such as N tetradecyl, N,N dimethylglycine, give no indication of reaction with Polymer JR as judged by both surface tension and solubility criteria. Cationic surfactants fit into this category as well. In the same way it has been found that no interaction occurs between tetradecyl sulfate and the negatively charged carboxymethyl cellulose (21).

#### Influence of Added Salt on Polymer JR/SDS Interaction

Solubility diagram experiments demonstrated that inorganic salts such as NaCl, Na<sub>2</sub>SO<sub>4</sub>, etc., have little effect on the polymer/surfactant precipitation even at the relatively high added level of 0.1%. Only when there was an influence on the solubility of one or other of the interacting components, e.g., formation of magnesium dodecyl sulfate on adding MgCl<sub>2</sub>, was some effect seen. These results show that the driving force for the interaction is associated with the cationic polymer and the surfactant anion itself, and not other parameters such as ionic strength.

#### Interaction of Other Polycations with SDS

The generality of polycation/anionic surfactant interactions is demonstrated in Figure 11 which presents partial solubility diagrams of mixtures of various polycations with SDS. Here, only the lines corresponding to maximum precipitation are depicted for each system; the remainder of each diagram will be described qualitatively. These polycations were with one exception commercial samples and are described in Table I. The degree of cationic functionality of several of them would vary with pH, but they were used as supplied without adjustment of pH, since our purpose was to establish the general nature of the interactions rather than specific aspects. A com-

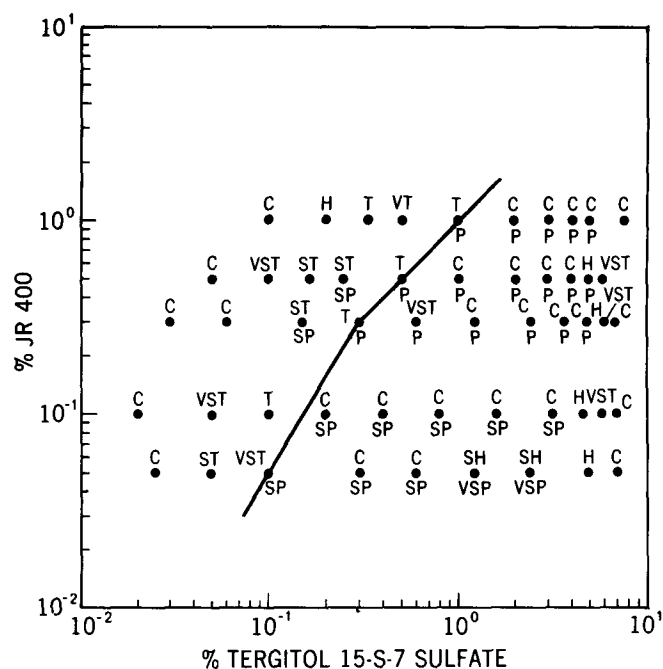


FIG. 10. Solubility diagram of the Polymer JR-400/Tergitol 15-S-7 EO sulfate system.

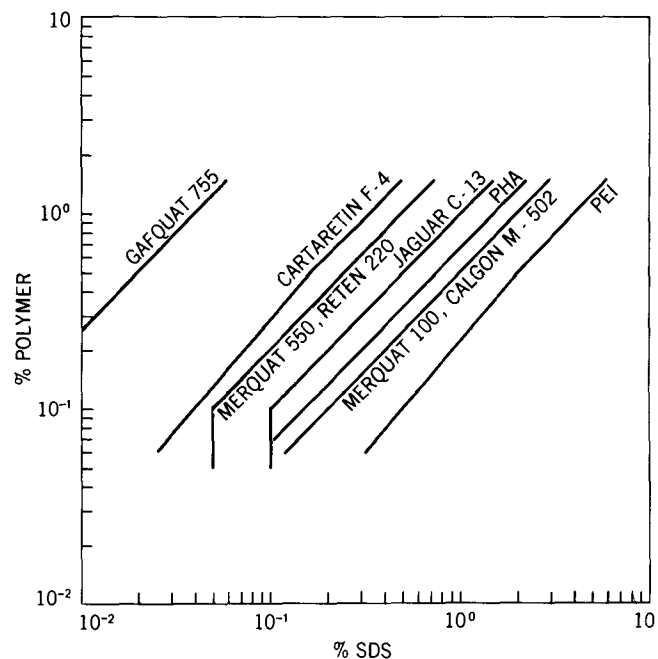


FIG. 11. Partial solubility diagrams of a series of polycation/sodium dodecyl sulfate systems. The lines drawn correspond to conditions of maximum precipitation.

mon feature in each solubility scheme is the slope of 45° of the lines of maximum precipitation at higher polymer concentrations (>0.1%). Presumably, these lines correspond to charge neutralization through adsorption of a surfactant ion at each cationic site along the polymer chain although the stoichiometry is not readily verifiable as many of the polycations have an incompletely identified structure and/or contain an amino functionality for which the ionization state was not determined. An exception to this was the fully quarternized homopolymer Merquat 100 (and also Calgon M502) for which the observed polymer/SDS ratio of 1:2 at maximum precipitation closely corresponds to a calculated molecular weight residue, per cationic charge, of 162. Two of the polymers,

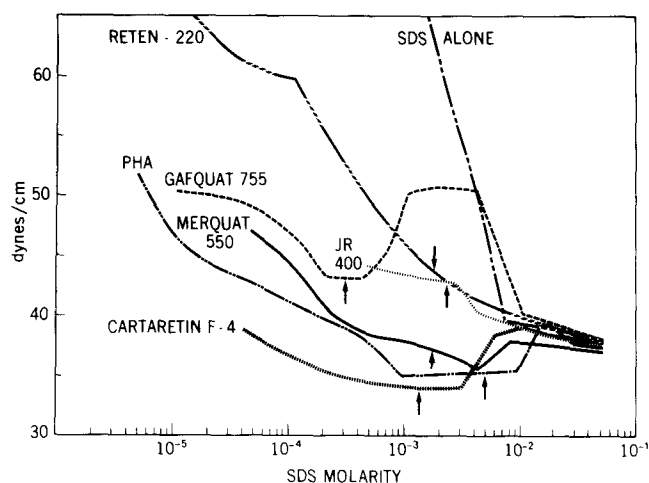


FIG. 12. Surface tension results for a series of polycation/sodium dodecyl sulfate systems at 25 C. Polycation concentration is 0.1%. Arrows indicate points of maximum insolubility.

viz., Reten 220 and Jaguar C-13, were investigated at concentrations low enough to verify the change in slope towards the vertical.

A qualitative description of the unshown portions of the solubility diagrams is of interest regarding the ease with which each precipitated system can be resolubilized by added surfactant. All of the polymers displaying maximum precipitation at a polymer/SDS ratio less than or equal to unity, i.e., Jaguar C-13, PHA, Merquat 100, Calgon M-502, and PEI, proved difficult to resolubilize, requiring large excesses of surfactant. The remaining polymers were readily resolubilized in the manner of Polymer JR. It appears that a critical charge density exists above which adsorption of the second, resolubilizing surfactant layer becomes unfavorable owing to mutual repulsion of the ionic head groups.

Surface tension (S.T.) measurements were conducted on several systems at a constant polymer concentration of 0.1%, and the results together with those previously reported for Polymer JR/SDS (14) appear in Figure 12 plotted against the logarithm of the surfactant concentration. Points corresponding to maximum precipitation are indicated by arrows. In all cases it is seen that the presence of the polymer, itself only weakly surface active, produces a sharp depression of the S.T. at SDS concentrations below its critical micelle concentration. Similar depressions, but smaller, have been reported for nonionic polymers in the presence of SDS (6,7). This lowering of the surface tension can be ascribed to adsorption of surfactant anions onto the polymer backbone, markedly decreasing its solubility and rendering it highly surface active at the air/water interface. Subsequent resolubilization of the complex through further addition of surfactant may or may not produce a minimum in the S.T. plot, depending on the relative surface activity of the partially resolubilized complex. Eventual coincidence of the S.T. value with that of micellar SDS indicates that adsorption onto the polymer is completed, the concentration of single surfactant ions remains sensibly constant, and further addition of surfactant results in the formation of micelles. Further evidence of this effect was obtained by dye solubilization experiments on the Polymer JR/SDS system (15,16).

It is of interest that the extent of S.T. depression obtainable by a polycation in the presence of SDS appears dependent upon the position of the cationic functionality in the polymer structure. Polymers for

which the cation is incorporated directly into the backbone, viz., Merquat 550, PHA, and Carteretin F-4, give rise to a greater S.T. lowering than the remaining polymers studied, for which the cationic groups are located on side chains.

In closing this section, mention should be made of other work recently carried out on polycation/SDS systems. Thus, van den Berg and Staverman (22) investigated the binding of SDS onto PEI by a study of the ensuing pH shifts. Likewise, this technique was employed to examine complex formation in PEI/SDS and PHA/SDS systems by Vanlerberghe (23) et al. These authors also studied the interaction by use of surface tension, wetting, conductance, and electrophoresis techniques.

#### Interaction of Anionic Polymers with Cationic Surfactants

All the work we have described so far has concerned polycation/anionic surfactant systems. Considerably less work has been devoted to polymer/surfactant systems in which the charges are reversed although Saito has reported the interaction of polyacrylic acid with cationic surfactants (24). We have studied the solubility diagram of sodium carboxymethyl cellulose (Hercules L-7) and an experimental hydroxyethyl carboxymethyl cellulose with cationic alkyl trimethyl ammonium chlorides. In these systems the polymer/surfactant ratio at maximum precipitation agreed well with that calculated for charge neutralization, and the difficulty we observed in resolubilization of the polymer/surfactant complexes is consistent with the relatively high charge density (degree of substitution equal to 0.7) of these polyelectrolytes.

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