Foam Inhibition in an Aqueous Sodium Dodecylbenzene Sulfonate Solution by Poly(dimethylaminoethyl Methacrylate)

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Synopsis

The mechanism of foam inhibition in an aqueous sodium dodecylbenzene sulfonate (DBSNa) solution by temperature-sensitive, water-soluble poly(dimethylaminoethyl methacrylate) (PDM) was investigated. The solution's foam collapsing rate, % transmittance, surface tension, pH, temperature, and degree of hydrophobicity of PDM showed that aging a PDM–DBS solution 125 to 280 hr produced a turbid solution and effectively inhibited foaming. Likewise, controlling the pH at $4 \leq pH \leq 7$ and increasing the hydrophobicity of PDM enhanced the foam-inhibiting action of the polymer. The reaction between DBSNa and PDM was temperature dependent and the temperature effect was almost reversible. When compared with other available commercial antifoaming agents, PDM was found most effective in suppressing foam formation in aqueous DBSNa solution.

INTRODUCTION

Saito et al.[1] have reported on the ability of inorganic salts, viz., Na, Mg, Al, and ethylene diisothiuronium hydrobromide[2] or hydrochloride to suppress foaming in dilute aqueous solutions of sodium alkylbenzene sulfonate.

In pursuit of a more effective and versatile antifoaming agent and to throw some light on the mechanism of foamation and defoamation, we investigated the action of poly(dimethylaminoethyl methacrylate) (PDM), a temperature-sensitive water-soluble macromolecule on the aqueous solution of dodecylbenzene sulfonate. We reported[3,4] that PDM was an effective flocculant for HEDORO where an irredispersible macrofloc was obtained induced by an electrostatic force of attraction and by the tackiness of the emulsion particles.

In this paper, the efficacy of PDM as a foam-inhibiting agent in aqueous DBS solution is explained by the formation of a surfactant–polymer complex attributed to both an interionic reaction and hydrophobic bonding.

EXPERIMENTAL

Materials

The sodium dodecylbenzene sulfonate (DBSNa) used was extrapure reagent grade, with 95% active solutes, obtained from Nakarai Chemicals. This was dried under vacuum to constant weight at 40°C after which a stock solution with a concentration of 1×10^{-2} mole/l. (ca. 3484 ppm) was prepared using deionized distilled water.

Poly(dimethylaminoethyl methacrylate) (PDM) was synthesized from a 30 vol-% dimethylaminoethyl methacrylate (DM) monomer in a benzene solvent using α,α'-azobisisobutyronitrile (AIBN) as initiator which was 0.2 wt-% of the monomer content. Polymerization proceeded in a nitrogen atmosphere at 70°C for 24 hr and at 90°C for another 24 hr. The product was then precipitated in petroleum ether and dried at room temperature overnight. This was redried for 24 hr under vacuum at 50°C. The intrinsic viscosity (η) of the resulting polymer in benzene solution at 30°C using the Ubbelohde dilution-type viscometer was 0.414. A stock solution of concentration of 1.273×10^{-3} monomer mole/l. (ca. 200 ppm) was prepared from deionized distilled water.

The copolymerization of DM with three different monomers, viz., styrene, butyl acrylate, and acrylonitrile was conducted under the same conditions as described above. The overall 30 vol-% monomer in the polymerization recipe was made up of ca. 10 vol-% of the comonomer and ca. 90 vol-% DM. The DM contents in the copolymers, as verified by conductometric titration with HCl, were as follows: 90.34 monomer wt-% in poly(DM–St), 90.10 monomer wt-% in poly (DM–BA) and 90.97 monomer wt-% in poly(DM–AN).

The commercial antifoaming agents used were E-20 and SAG-10. E-20 is a neutral antifoamant from Matsumoto Chemicals, which is soluble in kerosene. SAG-10 is a food-grade antifoamant with 10% dimethylpolysiloxane used in most aqueous systems, supplied by Union Carbide. All the additive concentrations in their respective solutions were uniform at 200 ppm, and they were added with stirring to the DBS solution.

Foam Collapsing Rate

The methods of determining foaminess of liquids commonly employed are the dynamic and static methods[5–8]; in the former observations are made during foam formation, while in the latter the foam is formed first and observation follows. By these methods we either produce wet foam, from a foaming liquid not thoroughly gassed, as by a bubbler-type foam meter, or stirred, employing mechanical stirrers; or we produce dry foam, where an excess of gas is introduced.

We used the static foaming method (Fig. 1). The foam was generated by bubbling nitrogen gas at a controlled rate through the liquid. Thermostating water circulated through the glass jacket enclosing the vertical foam cylinder and terminated in a temperature-regulated water bath.

Twenty milliliters of the aged surfactant–polymer solution, which was continually stirred in a flask kept in a bath thermostated at the desired temperature, was pipetted carefully into the foaming column in close proximity to the glass bubbler to avoid any incipient foaming. Nitrogen was supplied to the bottom of the glass bubbler (porosity from supplier's specifications is 1-G-4) at a rate of 400 ± 25 cc/min. This gas flow rate was observed to be within the limits where a suitable amount of homogeneous foam was generated and was reproducible. Some experience was required to keep the gas flow rate within the desired range.

The foam generated then rose up the column and, depending on the capacity of the solution to foam, was given a certain height to reach, and the gas was quickly cut off. The time it took the foam to rupture and collapse from its
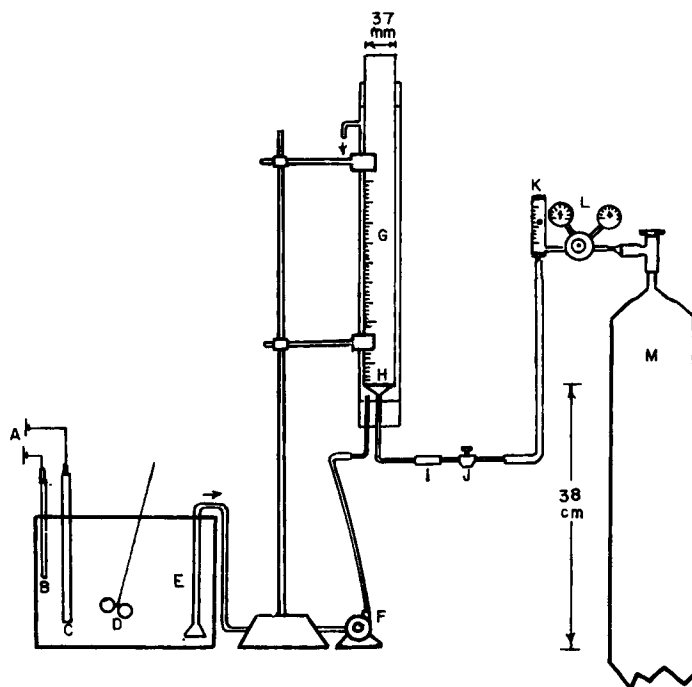
Fig. 1. Schematic diagram of static foam meter: (A) electronic relay; (B) thermoregulator; (C) heating element; (D) motor-driven stirrer; (E) delivery hose; (F) pump; (G) foaming column meter with heating jacket; (H) glass bubbler (1-G-4); (I) convenient rubber duct; (J) stop cock; (K) gasometer; (L) pressure gauge; (M) nitrogen tank.

original foam height to a predetermined final height (depending on the stability of the foam) was recorded and the foam collapsing rate (FCR) was calculated as follows:

$$FCR = \frac{\text{original foam height} - \text{final foam height}}{\text{time}}$$

Turbidity

This was observed by the use of a Hitachi digital spectrophotometer Model 191 E equipped with a constant temperature cell within 0.1°C accuracy level. All readings were directly read as % transmittance under a wavelength of 600 nm and a 3-cm light path length.
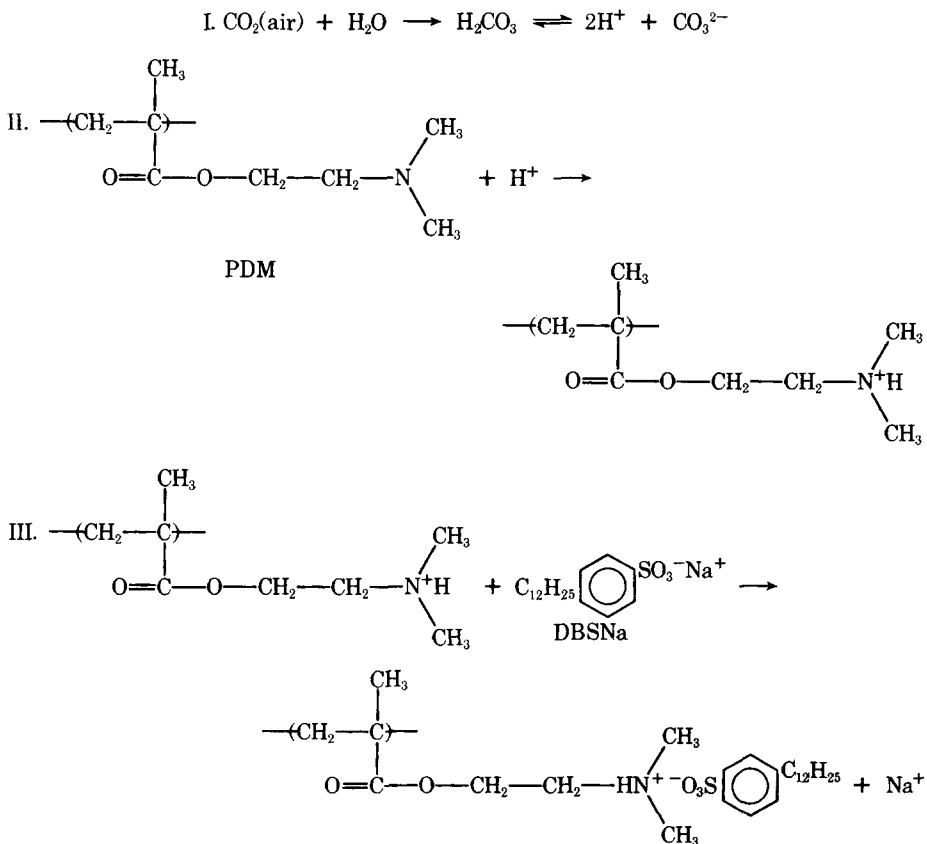
Surface Tension

Surface tension was measured as a function of surfactant concentration using a Shimadzu Du Noüy tensiometer at 30 ± 0.5°C. The ring was immersed in the test solutions for about 5 min prior to measurement, and the apparent values were corrected accordingly.[9]

RESULTS AND DISCUSSION

Foam Decay Upon Aging

Figure 2 shows the foam stability decay rate curves (foam collapsing rate in ml/sec vs aging time in hr) for DBS at 20°C and at a fixed concentration of 500 ppm with PDM at various concentration after a period of aging. It is evident from the curve that PDM is ineffective as a foam deppressant for the aqueous DBS solution during the early stage of aging. However, after some 125 hr of aging, PDM exhibits foam-inhibiting properties and gradually reaches a maximum at ca. 280 hr, beyond which a constant value is obtained. A very interesting factor behind the phenomenon is the gradual change of the pH of the solution from alkaline to neutral as aging progressed.

From these results, we believe that on prolonged standing PDM underwent hydrolysis whereby its tertiary nitrogen was protonated to a polycation. The protonated PDM then reacted with the anionic DBS ions forming a surfactant–polymer complex. The reaction may be illustrated as follows:

I. $CO_2(air) + H_2O \longrightarrow H_2CO_3 \rightleftharpoons 2H^+ + CO_3^{2-}$

II.

$$-(CH_2-\underset{\underset{C=O}{|}}{\overset{\overset{CH_3}{|}}{C}})- \quad O=C-O-CH_2-CH_2-N(CH_3)_2 \quad + \; H^+ \longrightarrow$$

PDM

$$-(CH_2-\overset{\overset{CH_3}{|}}{C})- \quad O=C-O-CH_2-CH_2-N^+H(CH_3)_2$$

III.

$$-(CH_2-\overset{\overset{CH_3}{|}}{C})- \quad O=C-O-CH_2-CH_2-N^+H(CH_3)_2 \quad + \; C_{12}H_{25}-\underset{DBSNa}{C_6H_4}-SO_3^-Na^+ \longrightarrow$$

$$-(CH_2-\overset{\overset{CH_3}{|}}{C})- \quad O=C-O-CH_2-CH_2-HN^+(CH_3)_2 \; {}^-O_3S-C_6H_4-C_{12}H_{25} \quad + \; Na^+$$

The leveling-off of the curve after more than 280 hr of aging indicated the saturation of the available sites of adsorption of the polymer in solution. The aging process was, however, too slow since the system was dependent on the supply and on the content of the acidifying constituents of air, e.g., CO_2.
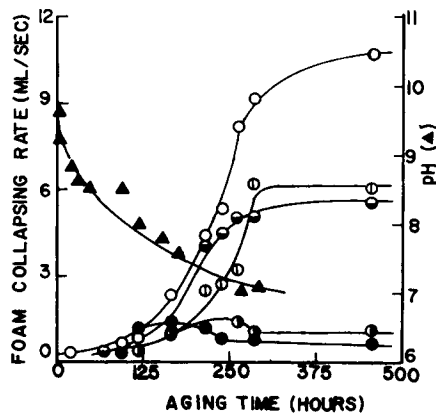
Fig. 2. Foam decay curves for DBS-PDM solutions at various concentrations, and pH change of a 500 ppm DBS–110 ppm PDM solution with respect to time. Solution composition: (●) 500 ppm DBS/70 ppm PDM; (◑) 500 ppm DBS/90 ppm PDM; (◒) 500 ppm DBS/110 ppm PDM; (◐) 500 ppm DBS/120 ppm PDM; (○) 500 ppm DBS/130 ppm PDM. Operating temperature = 20°C.

Turbidity of Solution

The polymer–surfactant complex formation was accompanied by a reduction in the per cent transmittance (Fig. 3). The turbidity caused by particles in a very fine degree of dispersion, which could not be precipitated by an ultracentrifuge, followed a curve pattern characteristic of Figure 3; the solutions, particularly those of high PDM concentration, slightly darkened after some 125 hr of aging and reached a maximum after a period of ca. 280 hr, beyond which turbidity remained constant.

pH Effect

To determine the effect of pH, we treated a series of fresh solutions of 110 ppm PDM and 500 ppm DBS with either 0.2M NaOH or 0.2M HCl and observed their foaming character and appearance at 30°C. Figure 4 shows that at pH above
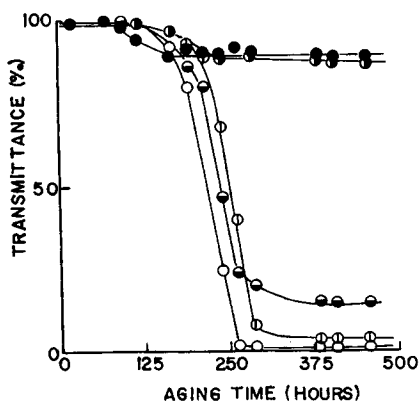

Fig. 3. Transparency degradation curves for DBS–PDM solutions at various concentrations with respect to time. Solution composition: (●) 500 ppm DBS/70 ppm PDM; (◑) 500 ppm DBS/90 ppm PDM; (◒) 500 ppm DBS/110 ppm PDM; (◐) 500 ppm DBS/120 ppm PDM; (○) 500 ppm DBS/130 ppm PDM. Operating temperature = 20°C.
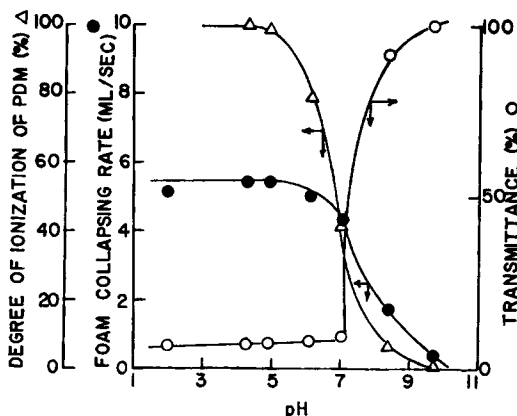
Fig. 4. Effect of pH on % transmittance and on foam inhibition ability of a 110 ppm PDM on 500 ppm DBS solution, and relationship between degree of the ionization of PDM and pH of the solution. Operating temperature = 30°C.

7.0, the foam tends to be stable and shows no great change in its appearance. At pH below 7.0, however, the foam stability is destroyed rendering a fast foam collapsing rate. Likewise, the solution at this region is markedly turbid, confirming our earlier observations.

The degree of ionization of PDM, which was calculated from its pK_a value[10] of 6.8 and from the Ph of the solution, was plotted versus pH in Figure 4.

Interestingly, all three curves, the foam collapsing rate, the % transmittance, and the degree of ionization, intersect at pH 7.0 and level off at about pH 5.0, at which point PDM is 100% ionized, suggesting the occurrence of a complete reaction.

Temperature Effect

Three sets of solutions of the same concentration (110 ppm PDM in 500 ppm DBS solution) were aged at different temperatures, viz., 20°, 30°, and 40°C, to determine the effect of temperature on the foam collapsing rate of the solution. The foam collapsing rate with respect to time was markedly increased when the temperature was increased from 20° to 30°C (Fig. 5). At 40°C, however, PDM was ineffective as a foam-inhibiting agent. The enhancement of foam inhibition from 20° to 30°C may be attributed to the hydrophobic force of attraction to the overall interaction between PDM and DBS. The role of the degree of hydrophobicity in surfactant–macromolecule interaction is well documented[11,12] to be sensitive to temperature change. On the other hand, the behavior of the curve at 40°C is in accord with our earlier work where we have noted that PDM assumed a "compact" and flocculated configuration at 34°C and above.[10] At 40°C, it was then difficult for the DBS ions to penetrate the PDM matrix, which consequently promoted the accumulation of "free" DBS ions accounting for the stabilization of the foaming system.

The % transmittance curved downward (above 125 hr of aging) while the foam collapsing rate moved upward. The curves confirm our hypothesis that the suppression of foaming in surfactant solution is characterized by the generation of complex insoluble particles that have rendered the solution turbid.

The inset in Figure 5 shows the foam collapsing rate-versus-temperature curve
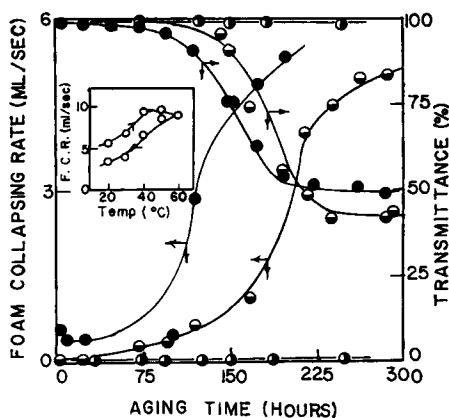
Fig. 5. Temperature dependence of the defoaming character and transparency of a 500 ppm DBS–110 ppm PDM solution with respect to time: (◒) 20°C; (●) 30°C; (◐) = 40°C. Inset: Temperature dependence and degree of reversibility of the foaming and defoaming character of a 500 ppm DBS–110 ppm PDM solution evaluated after 280 hr of aging.

of a 110 ppm PDM–500 ppm DBS solution aged for 280 hr at 20°C. Temperature gradually increased from 20° to 60°C then changed reversibly to 20°C. The graph indicates that defoaming was enhanced for 20°C to 30°C, which is believed to be caused by the temperature dependence of the contributive hydrophobic bonding forces in the reaction. Its contradictory behavior at 40°C, however, is more likely caused by the difference in the experimental procedure employed.

Increasing the temperature to 50°C effected no appreciable change and, further, up to 60°C adversely promoted foaming, which is attributed to the dispersive kinetic thermal motion on the configuration of PDM and on the bonded ions as well. Although hysteresis was evident, the inset curve appears to indicate an almost reversible effect. The slight hysteresis may be attributed to the inability of the interacting solutes and solvent to immediately restore their original conformation in so short a period of test evaluation time. We alloted approximately 1 hr for each temperature change for thermal equilibrium attainment.

Effect of the Degree of Hydrophobicity of Polymer

To verify our earlier postulation that the interaction between PDM and DBS is partly ionic and partly hydrophobic, the interaction between PDM and DBS was investigated as a function of the hydrophobic character of the polymer, using comonomers of increasing degree of hydrophobicity, viz., acrylonitrile < butyl acrylate < styrene. The foam-inhibiting action of poly(DM–AN) is below par compared with that of poly(DM–BA) and poly(DM–St) (Fig. 6). The curves followed the order of the hydrophobicity of the copolymers, attesting to the contributive role of the hydrophobic character of the polymer in its adsorption mechanism with detergents.

In terms of % transmittance, the results are contradictory because the % transmittance of poly(DM–St) is higher than that of poly(DM–BA) and PDM (Fig. 7). The position of the curve of poly(DM–AN) is corroborative. We believe that this behavior is caused by the difference in the diameters of the aggregates formed.
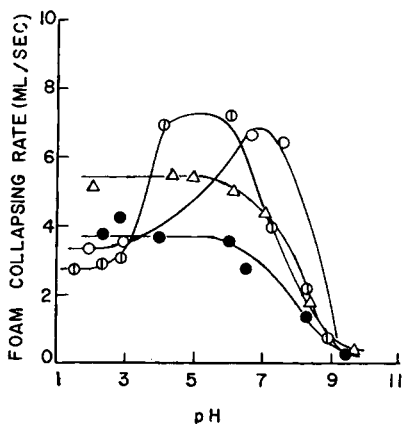
Fig. 6. Effect of degree of hydrophobicity of a copolymerized PDM on its foam inhibiting action on a 500 ppm DBSNa solution at variable pH. Defoamant concn. = 110 ppm, operating temperature = 30°C: (Φ) poly (DM–St); (O) poly (DM–BA); (●) poly(DM–AN); (△) poly(DM).
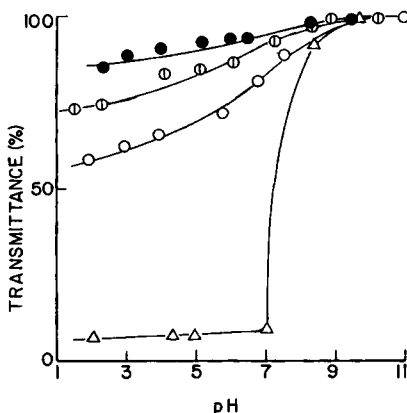

Fig. 7. Transparency of a DBS solution upon the addition of foam-inhibiting copolymers with differing degrees of hydrophibicity measured at variable pH. DBSNa concn. = 500 ppm, defoamant concn. = 110 ppm, operating temperature = 30°C: (Φ) poly(DM–St); (O) poly(DM–BA); (●) poly(DM–AN); (△) poly(DM).

Stoichiometric Ratio of Reactants

In an attempt to determine how much of the complex formed is due to an interionic reaction and how much is due to hydrophobic bonding, various concentrations of fresh DBS solution were mixed with a fresh solution of PDM maintaining the final concentration of PDM at 110 ppm. The pH of the resulting solution was fixed at 4.5 ± 0.5, which was earlier observed to be the most effective pH range against the foaming property of DBS. There appear to be four distinct phases in all three parameters (the foam collapsing rate, % transmittance, and the surface tension) which were all evaluated against the variable DBS concentration at 30° ± 1°C (Fig. 8). The same unique curve was produced on another set of solutions (designed as a confirmatory test) of the same concentration makeup which were left to stand for a period of 13 days at 18°C, instead of controlling the pH.

The curves of the three parameters in Figure 8 are each made up of four phases: phase I, the induction phase; phase II, the reaction phase; phase III, the saturation phase; and phase IV, the micellization phase.
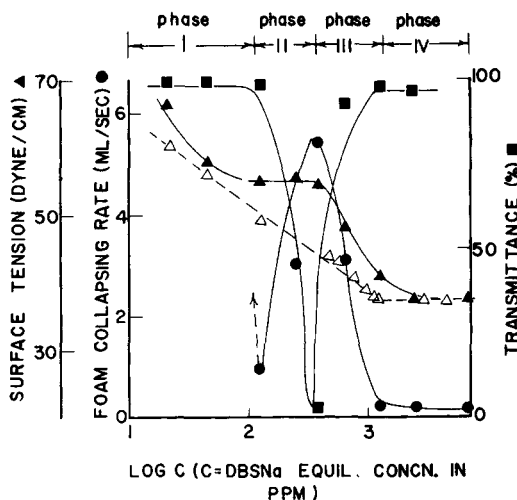
Fig. 8. Interrelationship of surface tension, foam collapsing rate, and % transmittance of DBS solution at variable concentration treated with 110 ppm PDM. (Open triangles in dotted lines represent surface tension curve of a pure DBSNa solution.) Operating temperature = 30°C, solutions pH = 4.5 ± 0.5.

Phase I (Induction Phase)

The degree of foamation in this region was found negligible, and the foam collapsing rate was rather difficult to measure. This region is reflected in Figure 8 by the dotted lines. In this phase, PDM is thought to have assumed an "expanded" configuration in solution as a result of the repulsive forces existing between its positive charges coupled with its polar attraction with water. In most probability, very few DBS ions could exist as "free" ions here because they would be "readily devoured" by PDM. As we gradually increased the concentration of DBS, the surface tension slightly decreased, implying that the present number of "free" DBS ions was enough to effect a surface change phenomenon but not enough to support foaming. To stress the difference, we have also presented the surface tension curve of pure DBS solution (Fig. 8) by open triangles in the dotted lines. We wish to emphasize here that a pure DBS solution at this concentration foams and the foam is too stable at appreciably high concentrations to be conveniently measured by the static foam meter.

Using the expression

$$FCR = 1/[D]_f \tag{1}$$

we could expect a very fast collapsing rate (FCR) if the solution contained very few "free" DBS ions, $[D]_f$, and vice versa. If we represent the number of complexed DBS ions as $[D]_c$, the total DBS ions added to the solution, $[D]_t$, would be

$$[D]_t = [D]_f + [D]_c \tag{2}$$

where $[D]_f < [D]_c$ in phases I and II. At the point of terminating phase I, the number of "free" DBS ions that had accumulated as the DBS concentration was increased was already more than enough to support foamation.

Phase II (Reaction Phase)

In the region of phase II, the foam collapsing rate curve tapered to a maximum while the % transmittance curve sloped downward to a minimum at the same DBS concentration of ca. 383 ppm.

Using our earlier model of an "expanded" polymer configuration, we presume that PDM has assumed the most conducive arrangement in solution so that the "immediate" point of contact between the polymer and the surfactant would be between the polar head groups. This would then leave the nonpolar segment of the polymer protruding into the surrounding medium inviting the attachment of other DBS ions through the secondary hydrophobic force of attraction.

As we increase the DBS concentration, the number of positive charges in the polymer is drastically reduced rendering it more hydrophobic because the hydrocarbon segment of the DBS molecules have now "sprouted out" from the polymer chain. This process of charge neutralization in addition to the repulsive forces which now exist between the complex and the polar solvent would now compel the PDM–DBS complexes to aggregate and assume a "compact" configuration rendering the solution turbid.

It is interesting to note that while the foam collapsing rate and % transmittance curves abruptly changed within this region, the surface tension curve remained constant. This implies that although the amount of $[D]_t$ in eq. (2) was increased, the amount of $[D]_f$ did not correspondingly increase because most of the added DBS solutes were presumed to have been incorporated into the hydrophobic complex formed.

From the curve of the foam collapsing rate in Figure 8, the concentration of DBS at the point terminating phase II is 383 ppm (ca. 1.1×10^{-3} mole/l.), which is more than the stoichiometric requirement of a 110 ppm PDM (ca. 0.7×10^{-3} monomer mole/l.) following the significance of reaction eq. III. In light of the above explanation, if we infer that the interionic reaction of the overall reaction obeys a 1:1 stoichiometric ratio, we would attribute the "excess" DBS solutes (1.1×10^{-3}–0.7×10^{-3} mole/l.) as the amount of DBS that has been incorporated into the PDM matrix by the secondary force of attraction. By this token, the hydrophobic force of attraction would be approximately 36% while the coulombic force of attraction, which is considered the primary bonding force in this system, would be 64% of the overall reaction output.

Phase III (Saturation Phase)

From the DBS concentration of 383 ppm, the foam collapsing rate curve immediately sloped downward until it reached a surfactant concentration of 1394 ppm (ca. 4.0×10^{-3} mole/l.), at which point it began to level off. In this region it is presumed that after all available sites of adsorption have been saturated, the surfactant solutes added to the system would now exist as "free" DBS ions, greatly depressing the surface tension of the system while at the same time promoting foamation. And as we continually add DBS, the "compact" hydrophobic complex tends to contact with the nonpolar segment of the "free" DBS ions by the hydrophobic force of attraction, and as a result of this process, the chemical character of the complex reverses to a hydrophilic entity, redispersing itself in solution. This would then lead to a high % transmittance (Fig. 8).
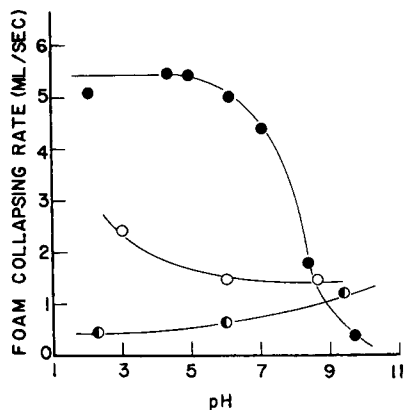
Fig. 9. Comparative foam-inhibiting capabilities of PDM and commercially available antifoaming agents. Operating temperature = 30°C: (●) PDM; (◐) E-20; (○) SAG-10.

Phase IV (Micellization Phase)

In this region all the parameters level off to a constant value, indicating the presence of micelles. In this phase two species are likely to coexist, namely, the DBS micelles and the polymer–surfactant complex.

Commercial Antifoaming Agents

The conditions set forth in the experiment were those employed in the earlier experiments (which are favorable for the reaction between PDM and DBS), and it is possible that the above commercial antifoaming agents may not be found effective per se. Nevertheless, the efficacy of PDM as a feasible antifoaming agent is shown in Figure 9.

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