

Mechanism of Antifoam Behavior of Solutions of Nonionic Surfactants Above the Cloud Point

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ABSTRACT: Aqueous solutions of nonionic surfactants exhibit low foaming above their cloud point, a temperature above which the homogeneous solution separates into two phases: a dilute phase containing a low surfactant concentration and a coacervate phase containing a very high surfactant concentration (e.g., 20 wt% surfactant). In this work, foam formation was measured for the dilute phase, the coacervate, and the mixed solution using the Ross–Miles method for nonylphenol polyethoxylates with 8, 9, or 10 ethylene oxide moieties per molecule. The dilute phase showed no antifoam effect above the cloud point if the coacervate phase was not present, and the coacervate phase foamed little in the absence of the dilute phase. The coacervate phase acts as an oil droplet antifoam to the dilute phase. From surface and interfacial tension data, entering, spreading, and bridging coefficients for this system make it appear probable that the coacervate phase is forming bridges across the film lamellae of the dilute-phase foam and acting to suppress foam formation through the bridging mechanism.

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KEY WORDS: Antifoam, cloud point, coacervate, foams, nonionic surfactants.

Foam control in many industrial products and processes is an important task because foaming can limit the rate of these processes and the usability of the products, e.g., laundry detergents and dishwashing liquids (1). As the temperature of an aqueous solution of nonionic surfactants is increased, a temperature is reached at which the solution appears cloudy, defined as the cloud point (2). At and above the cloud point, the solution consists of two phases: a “dilute” phase in which the surfactant concentration is from about 2 to 100 times the critical micelle concentration (CMC), and a “coacervate” phase in which the surfactant is highly concentrated (sometimes exceeding 50 wt%). At the cloud point, the coacervate forms emulsion droplets in the continuous dilute phase; it is this emulsion that appears cloudy or milky (3). As shown in Scheme 1, if the solution is held quiescent at a temperature at or above the cloud point,

the solution will separate into bulk phases with the coacervate more dense than the dilute phase. The foamability of a nonionic surfactant is drastically reduced above the cloud point (4–10). This property is used in the design of the so-called cloud point antifoams, which now are commercially available (11,12). The presence of the coacervate phase is the key factor in foam reduction above the cloud point (7,8,10), as clearly demonstrated by Koretskaya (7), who showed that removal of the cloud phase droplets by filtration restores the foamability despite the reduction in overall surfactant concentration.

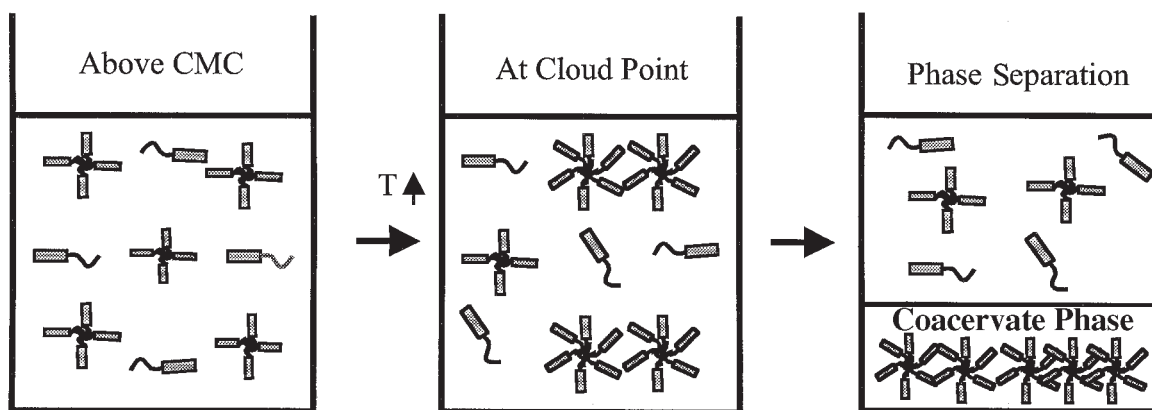
Garrett (13) observed that antifoams are often largely composed of oils that are present as undissolved droplets in foaming solution. Several mechanisms have been proposed for their antifoam action. Two of the most widely mentioned are the spreading and bridging mechanisms (reviewed in References 13–20).

As shown in Scheme 2, in the spreading mechanism, the oil drop is believed to enter the air–liquid interface initially. It then spreads as a duplex film on the film surface, causing foam rupture (i) by replacing the stabilizing surface by a spread film of antifoam, which is unstable (16,21); (ii) by inducing a Marangoni-driven flow in the liquid underneath the oil film, resulting in local film thinning and rupture (13); and (iii) by creating a chemical or mechanical shock to the surface by the simple act of spreading (22,23). Robinson and Woods (24) used the entering coefficient and spreading coefficients as defined by Harkins (25) as criteria for the entering and spreading of the antifoam liquid on the film surface. If they are positive, the processes are thermodynamically favorable. They found better correlation of the antifoam activity with the entering coefficient than the spreading coefficient. Several workers have made similar studies and found many materials that spread without antifoaming action and vice versa (17,26–29). This has led Garrett (13) and later Denkov *et al.* (15) to conclude that spreading is not a necessary condition for antifoaming, although it may operate in some types of antifoams.

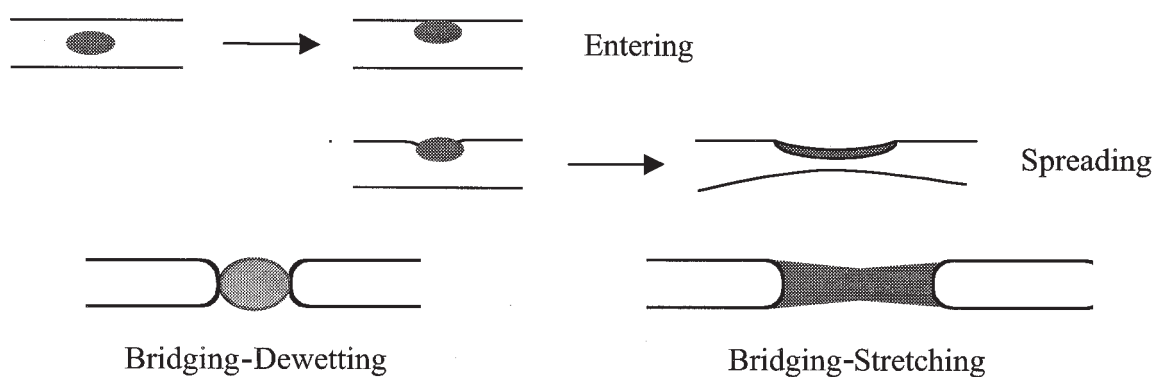
As shown in Scheme 2, in the bridging mechanism, the oil drop first penetrates the film surface. When the film thins down to the size of the oil drop through drainage, an oil bridge is formed in the foam film. Foam rupture may then occur *via* two different routes. According to the bridging–dewetting mechanism proposed by Frye and Berg (30),

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Abbreviations: CMC, critical micelle concentration; EO, ethylene oxide.



SCHEME 1. Schematic of phase separation.



SCHEME 2. Schematic of entering, spreading, and bridging mechanisms in antifoaming [adapted from Fig. 14.9 in Kralchevsky and Nakayama (17)].

the hydrophobic surface of the oil induces a dewetting of the bridge, causing foam rupture. However, Denkov *et al.* (15) proposed another mechanism whereby the oil bridge stretches due to noncompensated capillary pressure at the oil/water and air/water interfaces with the eventual foam film rupture at the center of the bridge. They termed this the bridging–stretching mechanism. Garrett (31) introduced a bridging coefficient as the criterion for the bridging mechanism. A positive value of the coefficient indicates the formation of an unstable bridge, which will lead to eventual foam rupture.

Several authors have used these two mechanisms to describe the antifoam action of the coacervate phase at the cloud point. Ross and Nishioka (32) suggested that the antifoam action at the cloud point is due to the spreading action of the surfactant-rich phase at the surface of the foam films, while others (7,33,34) have suggested formation of oil lenses by coacervate phase droplets. Bonfillon-Collin and Langevin (8) used the bridging coefficient to support the bridging mechanism induced by the coacervate phase. Similar results were obtained by Chaisalee (10) for a series of nonyl phenol ethoxylates. Nemeth *et al.* (12) also deduced that the cloud-point antifoams used in their work function by the bridging mechanism. In addition to spreading and bridging, other mechanisms also have been proposed. For example, Dupré *et al.* (35) attributed this phe-

nomenon to a rate effect. At the cloud point, the dehydrated micelles combine into larger aggregates. Diffusion of surfactant molecules from these large aggregates to the newly created interface involved in film formation is much slower than from the smaller hydrated micelles, thus decreasing the stabilization of the foam lamellae.

In this study, the foamability of three nonylphenol polyethoxylate surfactants with different ethoxylated chain lengths was studied to obtain a better understanding of the role of the coacervate phase in reducing foamability of nonionic surfactants above the cloud point. Insight into the mechanism of antifoam behavior is gained from unique foaming experiments performed here with the dilute phase alone and the coacervate phase alone, in addition to the foaming of the mixed phases as has been reported before.

EXPERIMENTAL PROCEDURES

Materials. Three nonyl phenoxy poly(ethyleneoxy)ethanols with an average of 8 mol [NP(EO)₈: Igepal CO-610], 9 mol [NP(EO)₉: Igepal CO-630], and 10 mol [NP(EO)₁₀: Igepal CO-660] of ethylene oxide (EO) per mole of nonyl phenol from Rhodia (Cranbury, NJ) were used as received in this study. These surfactants are polydisperse and are a mixture of components with different degrees of polymerization. The structure of the three surfactants and their average

degree of polymerization can be represented as C_9H_{19} -phenyl- $(CH_2CH_2O)_nOH$, where $n = 8, 9,$ or 10 .

Methods. The determination of the cloud point temperature was carried out in accordance with ASTM method D 2024-65 (36). A 0.02-M surfactant solution was prepared at a temperature below 30°C. The solution was agitated until the surfactant was completely dissolved, and 50 ± 5 mL of the solution was transferred to a 25×200 mm test tube. The solution was then heated in a water bath with occasional stirring until the solution became cloudy. The solution was then removed from the heat and cooled at a rate of 1°C/min with occasional stirring until the solution was again clear. The temperature at which the solution became clear was recorded to the nearest 1°C and taken as the cloud point of the solution.

Foamability and foam stability of the test solutions were measured by using the Ross–Miles foam test method (ASTM D 1173-53) (36). In this method, 200 mL of the test solution in a pipette was allowed to flow into a receiving column containing 50 mL of the same solution. The foam height was read off the scale as soon as the solution was run out from the pipette, and the foam height was taken again after 5 min to measure foam stability.

Surface tension and interfacial tension were measured by DuNoüy ring tensiometry using a Krüss Model K10T Digital Tensiometer. In surface tension measurements, the test solution was loaded into the vessel and the platinum ring was dipped into sample. After zeroing, the value of the surface tension was read off the instrument. Each experiment was repeated five times with the same sample. The interfacial tension was measured by following the surface tension method with zeroing made at the interface of the coacervate phase. The dilute phase was then poured slowly onto the coacervate phase and the interfacial tension between dilute and coacervate phases was read.

Phase separation was carried out in a 5000-mL beaker containing 0.02 M surfactant. The beaker was placed in an isothermal water bath until equilibrium was reached, generally after about 3 d, depending on the type of surfactant. The dilute phase was sampled every 12 h until a constant surfactant concentration was reached. After the phase separation was complete, the fractional volume and the concentration of each phase were measured using a CE 2000 series UV spectrometer at 223 nm (3).

RESULTS AND DISCUSSION

Cloud points and phase behavior. The cloud points (°C) of the three surfactants at a concentration of 0.02 M were NP(EO)₈, 23; NP(EO)₉, 54; and NP(EO)₁₀, 66. Cloud points are relatively insensitive to concentration and are often measured at 1 wt% (36), but there is no universally accepted concentration for this measurement. For consistency, we measured the cloud points at the same constant molar concentration used for the foaming experiments.

At equilibrium above the cloud point (as shown in Scheme 1), the fractional phase volumes of and surfactant concentrations in dilute and coacervate phases are shown in Table 1 at several temperatures for the three surfactants studied. As is normally observed (37,38), the fractional volume occupied by the coacervate phase decreases and the coacervate surfactant concentration increases as temperature increases above the cloud point. At a constant temperature, by comparison (with some extrapolation) of data from Table 1, the coacervate phase volume is greater and the coacervate surfactant concentration less as the EO number of the surfactant increases. Since it is how far above the cloud point the temperature is that drives the coacervate to be more concentrated in surfactant, this is expected. To appreciate how concentrated the coacervate phase can be, the concentrations given in Table 1 correspond to between 6 and 30 wt% surfactant. The coacervate can be extremely viscous, as one can tell by empirical observation.

The dilute phase surfactant concentration decreases with increasing temperature, as expected (37,38). Note that the dilute-phase surfactant concentration is substantially above the CMC (38). Although we did not obtain exact values of the CMC of the surfactants at the temperatures used here, since this information was not important, the CMC of the nonylphenol polyethoxylates below the cloud point was on the order of 0.1 mM. The dilute-phase surfactant concentration is from 16 to 125 times this value (Table 1). While the coacervate is about two orders of magnitude higher in surfactant concentration than the dilute phase, the dilute phase is over an order of magnitude above the CMC.

When the solution is above the cloud point and is agitated or shaken, or has just been heated above the cloud point, the coacervate phase is emulsified in the dilute phase. Even though the coacervate is quite viscous, this

TABLE 1
Fractional Volume and Surfactant Concentration in Dilute and Coacervate Phases

Surfactants ^a	Temperature (°C)	Fractional volume		Concentration (M)	
		Coacervate	Dilute phase	Coacervate	Dilute phase
NP(EO) ₈	25	0.0822	0.9178	0.1075	0.0125
	35	0.0762	0.9238	0.2447	0.0020
	45	0.0520	0.9480	0.3432	0.0016
NP(EO) ₉	55	0.0800	0.9200	0.1638	0.0075
	70	0.0310	0.9690	0.4943	0.0045
NP(EO) ₁₀	70	0.0520	0.9480	0.3105	0.0040

^aNP(EO)_n, nonyl phenoxy poly(ethylene oxide) ethanol, where $n = 8, 9,$ or 10 .

emulsion appears to have the approximate viscosity of water. It is this emulsion that is referred to as the "original solution" when comparing foaming to that of the dilute phase or the coacervate obtained after equilibration and phase separation.

Foaming of surfactant solutions. Foaming of the 0.02-M solutions of the three surfactants is shown in Figure 1 as a function of temperature below and above the cloud points. Both the initial foam heights and the heights after 5 min in the Ross–Miles foam test are shown. The initial foam height is fairly independent of temperature below the cloud point and declines substantially above the cloud point, an effect that is well known (4–10). The decline is quite dramatic for NP(EO)₉ and NP(EO)₁₀, probably because the foam height is greater below the cloud point compared to NP(EO)₈. In the case of NP(EO)₉ and NP(EO)₁₀, the foam height after 5 min falls off with increasing temperature well before the cloud point is approached; also, there is a narrow temperature range in the immediate vicinity of the cloud point where foam formation increases before the dramatic decline as the temperature increases further. There can actually be a foam stabilization effect from insoluble oils as their concentration approaches the solubility limit in surfactant solutions, above which concentration they form droplets of the separate oil phase, and these droplets act as an antifoam (17,39–41). Since the coacervate phase can be thought of as approaching its solubility limit in the dilute phase as the

cloud point is approached, this approach to a solubility limit is probably the explanation for the foam stabilization over this narrow temperature range observed here. Since we are primarily concerned with antifoaming effects here, we do not address this foam enhancement anomaly further. Also, since we are primarily concerned with the antifoaming effect above the cloud point, we do not pursue the more ambiguous property of foam stability (foam height after 5 min) further here but report only initial foam height.

Foaming of dilute and of coacervate phases. Our purpose is to elucidate the mechanism of reduced foam formation above the cloud point. The coacervate phase is thought to act as an antifoam to the dilute phase, similar to the effect of droplets of oil in foam destabilization in aqueous solutions (13–17,21–23,39–41). This research considers the effect of forming a coacervate phase on foam formation apart from the effect of temperature. That is, since the coacervate phase forms once the cloud point is exceeded, is the coacervate phase responsible for foam formation reduction, or is there a temperature effect on some other property of surfactant, or water, or surfactant–water interaction that is responsible for the antifoam effect? If the phase separation is indeed responsible for foam suppression, is the coacervate acting as an antifoam in the dilute phase or is the dilute phase acting as an antifoam in the coacervate? Finally, if the coacervate is acting in analogy to an oil antifoam, which of the possible mechanisms (entering, spreading, or bridging) by which these antifoams work is responsible in this case?

Scheme 3 shows the effect of temperature on dilute phase and coacervate surfactant concentrations as demonstrated for our surfactants in Table 1. At the cloud point, the dilute phase is in equilibrium with the coacervate. If the total solution concentration is below the dilute-phase concentration that would be present for the equilibrated system at this temperature (C_A at temperature T_A in Scheme 3), the dilute phase could not be in equilibrium with a coacervate, and no coacervate phase or clouding of the solution would occur at the reported cloud point of that surfactant. Remember that the cloud point in the present system is measured at 0.02 M, well above the dilute phase

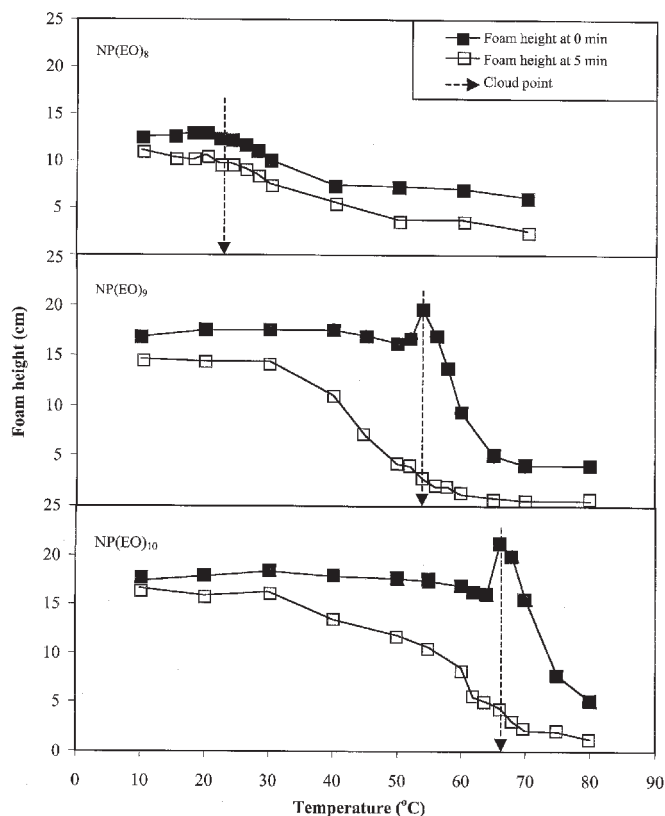
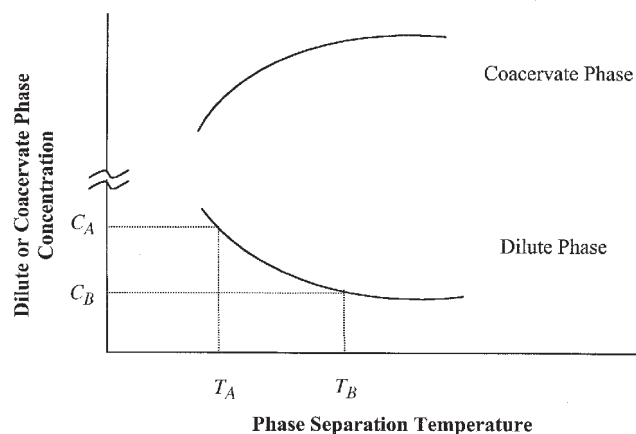
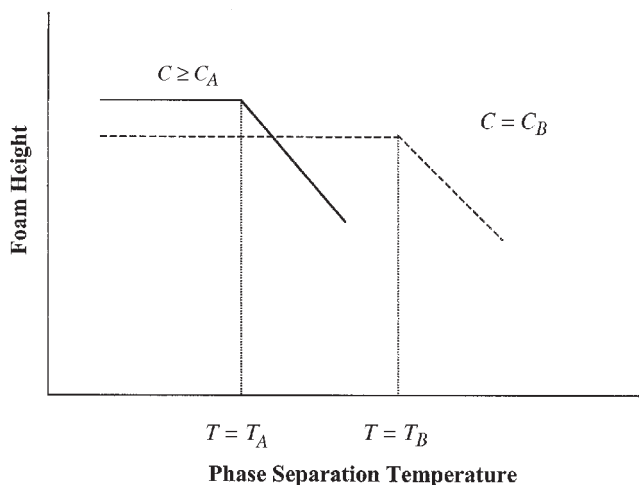


FIG. 1. Foaming of NP(EO)_n, nonyl phenoxypoly(ethylene oxide)-ethanol, where $n = 8, 9,$ or 10 , as determined in the Ross–Miles foam test.



SCHEME 3. Schematic of dilute and coacervate phase surfactant concentrations as a function of temperature.



SCHEME 4. Schematic of foaming at different surfactant concentrations as a function of temperature. See Scheme 3 for the relationship of C_A and C_B to dilute-phase surfactant concentrations.

concentrations shown in Table 1. Let us assume that the 0.02-M solution was allowed to equilibrate at T_B , the dilute phase removed, and the solution temperature cooled to T_A . The solution would not form a coacervate phase at T_A since the dilute phase surfactant concentration is too dilute to be in equilibrium with the coacervate phase. The solution at concentration C_B would not form a coacervate until temperature T_B was reached, as illustrated in Scheme 4. Even if the ostensible cloud point of the surfactant were T_A , if the equilibrium dilute phase obtained at T_B were formed, the antifoam effect should not be observed until temperature T_B were reached if the coacervate phase were responsible for the antifoam effect. This concentration/temperature effect on foam height is illustrated in Scheme 4. Experiments of this kind can separate temperature from phase separation effects.

Figures 2 and 3 show the initial foam height for original (0.02-M surfactant concentration) solutions and for dilute phases equilibrated at different temperatures for NP(EO)₈ and NP(EO)₉, respectively. The dilute phases do not exhibit the antifoam effect until a temperature is reached that is at or a little above that at which the dilute phase was equilibrated. This demonstrates that the formation of the coacervate phase is necessary for the antifoam effect to be seen and it is not due to other temperature-related effects. Owing to the high cloud point, these experiments could not

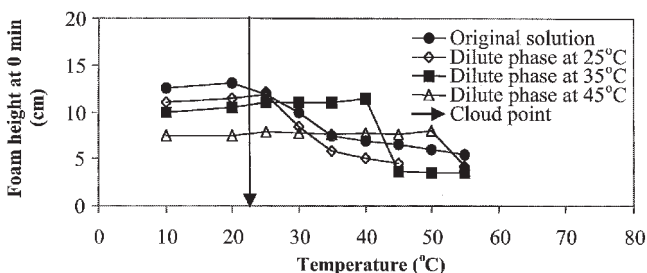


FIG. 2. Foaming of feed and dilute phases for NP(EO)₈. For abbreviation see Figure 1.

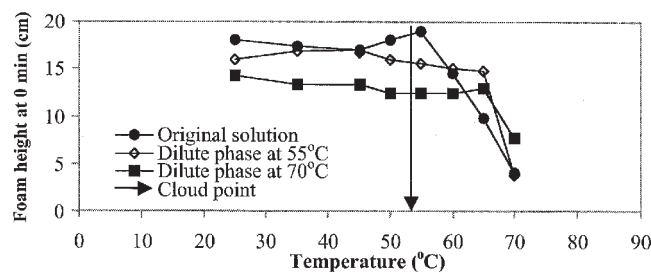


FIG. 3. Foaming of feed and dilute phases for NP(EO)₉. For abbreviation see Figure 1.

be performed for NP(EO)₁₀ because of excessive evaporation rates; the NP(EO)₉ data are less precise than that for NP(EO)₈.

Figures 4 and 5 show the initial foam height for original solutions and for coacervates equilibrated at different temperatures for NP(EO)₈ and NP(EO)₉, respectively. As illustrated in Scheme 3 and shown quantitatively in Table 1, as temperature increases, the coacervate becomes more concentrated. So a coacervate equilibrated at a certain temperature will separate into a more concentrated coacervate and a dilute phase if heated, but will remain as a single phase if cooled down. As shown in Figures 4 and 5, the coacervate phase never approaches the foam height of the original solution below the cloud point. Therefore, the dilute phase is not acting as an antifoam to the coacervate phase. This is true whether the foam experiment is run at a temperature where the coacervate remains a single phase or the phase separates. Since viscosity effects can be important to foam stability and since a coacervate generally has a high viscosity, interpreting fine points from Figures 4 and 5 is risky and the hypothesis being tested (that the coacervate is not an effective foaming phase by itself) is the only interpretation we will attempt based on this coacervate foaming data.

Mechanism of foam suppression above the cloud point. Having proved that the coacervate phase acts as an antifoam to the dilute phase above the cloud point, the three general phenomena by which oil droplets suppress foam formation in aqueous solution can be considered with the coacervate functioning as an oil. As illustrated in Scheme 2 (adapted from Ref. 17), entering (where the oil droplet enters the surface of the foam lamellae), spreading (where the entered oil droplet spreads over the surface of the film and introduces surface tension gradients that thin the film to rupture), and bridging (either dewetting or stretching, where

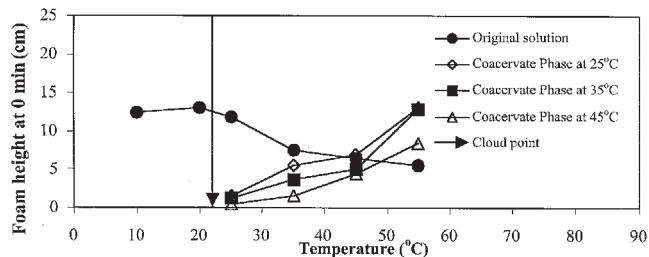


FIG. 4. Foaming of feed and coacervate phases for NP(EO)₈. For abbreviation see Figure 1.

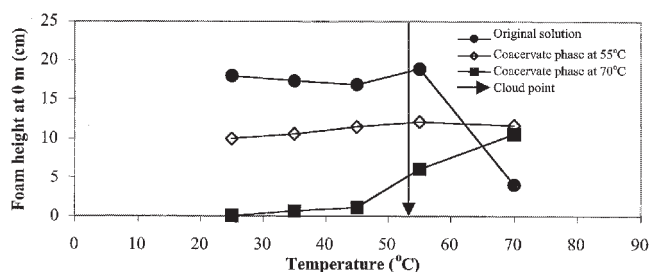


FIG. 5. Foaming of feed and coacervate phases for NP(EO)₉. For abbreviation see Figure 1.

the oil droplet completely bridges the film) are the three phenomena primarily responsible for antifoaming behavior. The tendency of a system to exhibit these phenomena can be quantified by the entering (E), spreading (S), and bridging (B) coefficients (17):

$$E = \sigma_{AW} + \sigma_{OW} - \sigma_{OA} \quad [1]$$

$$S = \sigma_{AW} - \sigma_{OW} - \sigma_{OA} \quad [2]$$

$$B = \sigma_{AW}^2 + \sigma_{OW}^2 - \sigma_{OA}^2 \quad [3]$$

where σ_{AW} is the surface tension at the air–water interface, σ_{OW} is the interfacial tension at the oil–water interface, and σ_{OA} is the surface tension at the oil–air interface. In our case, water is the dilute phase and oil is the coacervate in Equations 1–3. The measured value of the two surface tensions and the interfacial tension and the calculated coefficients from Equations 1–3 are shown in Table 2. The more positive the coefficient, the more important the phenomena to foam suppression (17). The spreading coefficient is small for all the systems and even slightly negative for one system; the entering coefficient is small but consistently positive; and the bridging coefficient is highly positive. Apparently, bridging of the coacervate phase across the dilute phase foam lamellae is responsible for the antifoam effect above the cloud point of these systems.

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TABLE 2
Spreading, Bridging, and Entering Coefficients^a

	NP(EO) ₈			NP(EO) ₉		NP(EP) ₁₀
	25°C	35°C	45°C	55°C	70°C	70°C
Dilute phase surface tension (mN/m)	30.5	30.1	30.0	30.3	29.4	29.9
Coacervate phase surface tension (mN/m)	29.9	29.6	29.3	30.1	28.9	29.9
Interfacial tension between coacervate and dilute phases (mN/m)	0.3	0.2	0.3	0.35	0.1	0.1
Spreading coefficient (mN/m)	0.3	0.3	0.4	-0.1	0.4	0.0
Bridging coefficient (mN/m) ²	36.3	30.8	42.5	13.4	25.8	4.0
Entering coefficient (mN/m)	0.9	0.7	1.7	0.6	0.6	0.2

^aFor abbreviations see Table 1.

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