

A Comparison of Block Copolymer Surfactant Gels¹

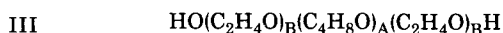
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The aqueous gel forming properties of three series of block copolymer surfactants, poloxamers, poloxamines, and Butronic[®] polyols, are briefly reviewed and compared. The differences in their gel formation properties are explained. Aqueous gel formation of these polymers is attributed to the aggregation of extended linear coil micelles in which the hydrophilic ends become entangled as the temperature rises, due to dehydration. The failure of the Butronic polyol gels to exhibit the same reverse thermal behavior shown by the other two polyol series is attributed to a more lipophilic hydrophobe and to the larger number of moles of water associated with the Butronic hydrophile. The reverse thermal characteristics of aqueous poloxamer and poloxamine solutions has led to the development of aerosol detergent systems which can form foamy gels, thereby expanding the usefulness of these surfactants.

KEY WORDS: Gels, micelles, poloxamers, reversible gelation, spray gels.

Three different series of block copolymer surfactants are known to form gels. These include the poloxamers, I, also known as the Pluronic[®] polyols (BASF Corp., Parsippany, NJ), the poloxamines, II, also known as the Tetronic[®] polyols (BASF Corp.), and the Butronic[®] polyols, III, (BASF Corp.) which are currently not commercially available.



All members of these surfactant series do not form gels in aqueous solution. This has been disclosed in detail for the poloxamers (1). Figure 1 indicates that only those poloxamers in which the molecular weight of the hydrophobe is 1750 or greater form gels. The Figure also indicates that, as the molecular weight of the hydrophobe increases, the minimum poloxamer concentration needed to form a gel decreases from 60% to 20%. The trend line, shown in Figure 2, shows the effect of increasing the molecular weight of the hydrophobe and increasing the ethylene oxide content of the polymer upon its ability to thicken water. The greater the ethylene oxide content, the greater the molecular weight of the hydrophobe, the greater the gelling property (or less polymer is needed to form a gel) will be.

Because only 20% of the poloxamer 407, also known as Pluronic polyol F-127, is needed to form a gel at 25°C, in studying and using poloxamer gels, the 407 grade has been primarily the only one utilized. It was pointed out that these gels exhibited the phenomenon of reversible behavior. That is, they liquified upon cooling below room temperature and gelled again upon rewarming. The gels were also reported to liquify at an elevated temperature.

The gel forming properties of the poloxamines also have been disclosed (2). Polymers in which the molecular weight of the hydrophobe was 4750, 5750, and 6750 were reported to form aqueous gels. The 1508 grade, based upon a hydrophobe molecular weight of 6750, also gels at only 20% at 25°C. Attempts to prepare aqueous gels at only a 15% concentration, with poloxamines having a hydrophobe with a molecular weight greater than 6750, were unsuccessful. The trend line (Fig. 2) could also be used for this series of surfactants. The poloxamer gels also exhibit a reversible thermal behavior.

The gel forming properties of the Butronic series of surfactants were first revealed in several U.S. Patents (3-5) and at an AOCS meeting (6). However, that report was never published, and all data were obtained from a 1984 U.S. Patent (7). It is claimed that a 3000 molecular weight polyoxybutylene hydrophobe was made by condensing 1,2 butylene oxide with 1,4 butanediol. Sufficient ethylene oxide was then added to comprise 80% of the total theoretical molecular weight of 15,000. This polymeric surfactant was reported to form an aqueous gel at only 16% concentration. The

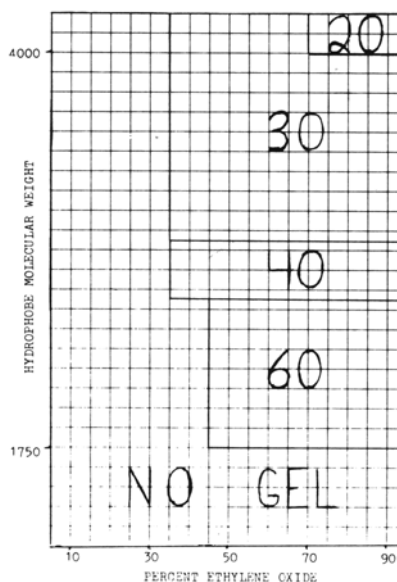


FIG. 1. Poloxamer gel grid.

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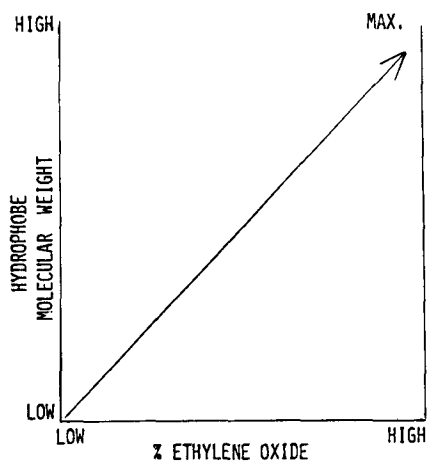


FIG. 2. Polymeric surfactant thickening trend.

patent also claimed that, as the molecular weight of the hydrophobe increased from 1200 to 3000, the highest value reported, the minimum weight of the polymeric surfactant needed to form a gel decreased from 25% to 16%.

How gels differ. What was more surprising was the report that, unlike the gels formed by the poloxamers and the poloxamines, these gels did not exhibit a reversible thermal behavior, but remained as gels, even at refrigerator and freezer temperatures. A comparison of the best gel formers among the three series of polymeric surfactants is shown in Table 1.

The many factors which influence the minimum surfactant concentration needed to form an aqueous gel have been previously reported (8). In addition to the molecular weight of the hydrophobe, these include other surfactants (which form mixed micelles with the block copolymers), solvents, such as ethyl or isopropyl alcohol, or polyoxyethylene glycols, all of which weaken the gel yield strength. On the other hand, the use of many water-insoluble organic compounds, or glycerine (but not propylene glycol or trimethylolpropane) will increase the gel yield strength.

In a comparison of aqueous gels prepared from poloxamers and poloxamines, two differences have been noted. Whereas it has been possible to prepare a stable gel of 3–6% hydrogen peroxide with poloxamer 407, the same gel made with poloxamine 1508 soon liquifies. This is believed to be due to the formation of an amine oxide from the reaction of the peroxide with the tertiary amine. It has also been noted that the poloxamine gel is more sensitive to acid than the poloxamer gel, due to the formation of an amine salt. This means that, in acid systems, more poloxamine 1508 is needed for gel formation than the poloxamer 407.

As previously noted, the main difference between the Butronic gel and the other gels lies in the fact that the Butronic gels do not exhibit the reversible thermal behavior below room temperature shown by the poloxamer and poloxamine gels, but remain as gels, even at refrigerator and freezer temperatures.

TABLE 1

A Comparison of the Best of Three Surfactant Series for Forming Aqueous Gels

Polyol	Hydrophobe mol. wt.	Final mol. wt.	Minimum % to form gel
Poloxamer 407	4000	12,500	20
Poloxamine 1508	6750	27,000	20
Butronic U-1	3000	15,000	16

Why gels form. When a poloxamer is added to water, the polymer dissolves due to the formation of hydrogen bonds between the many ether oxygen atoms and the protons of the water. It can be observed that hydrate formation has occurred when the temperature of the aqueous solution is raised. The solution becomes cloudy as the hydrogen bonds are broken and the polyol comes out of solution. The more hydrophilic surfactants, such as poloxamer 407 or poloxamine 1508, exhibit a cloud point above 100°C. Since the ether oxygen atoms are present in both the hydrophobe and the hydrophile, it is assumed that hydrogen bonding occurs in both areas.

Early studies on micelle formation of the poloxamers gave conflicting results, with some investigators claiming their absence (9–11), while others reported critical micelle concentration (CMC) values (12–18). Compounding the confusion were the widely differing CMC values that have been found, sometimes using the same measurement procedures. This has been reviewed previously (19).

In order to try to explain these discrepancies, it has been proposed (20) that these surfactants form two types of micelles. At a low concentration, a monomolecular micelle forms. As had been previously suggested (21), the polyoxyethylene chain may be rolled around the polyoxypropylene hydrophobe. Then, at a higher concentration, a more conventional poly-molecular micelle forms, in which several molecules come together to minimize their interaction with water.

The viscosity characteristics and gel regions of aqueous solutions of the poloxamers were first reported more than twenty years ago (1). The explanation given for the reverse thermal behavior was that micelles form when the poloxamer is dissolved in water and hydrate formation occurs, both in the hydrophile and in the hydrophobe. As the temperature rises, it was suggested that the polymer is partially dehydrated and micellar aggregation increases. The formation of larger aggregates would then entrap more water, leading in turn to more viscous solutions and gels as the temperature increased. Some free water, as well as water of hydration, may become entrapped in the process.

In the past few years, poloxamer gels were studied using the latest available instrumental techniques (22). Evidence was obtained from X-ray diffraction, thermal polarizing microscopy and differential scanning calorimetric techniques that these gels were micellar in nature and exhibited a cubic orientation. They were characterized as isotropic liquid crystals. More recently, dilute aqueous poloxamer 407 solutions were studied

(23) from 10 to 40°C, with ultrasonic velocity and light scattering techniques.

From light scattering data, below the CMC at 10°C, the presence of any mono-molecular micelles in significant concentration was precluded at this temperature, as had been previously suggested. Instead, the data indicated the presence of extended coils in solution. This is in contrast to previous light scattering measurements which had indicated that the micelles were spherical. The data, shown in Table 2, clearly indicates a micelle formation over the temperature range shown. The CMC decreases with the micelle enlargement, due to dehydration and the resulting enlargement. The aggregates were reported to be asymmetric at the lower temperature but, with the increase in temperature above 25°C, they increased in symmetry to become spheroidal. The micellar properties of dilute aqueous solutions of poloxamer 407 were studied (24) further, using both capillary and rotational viscometry. The data indicated mechanical entrapment of water by the extended polyoxyethylene chains in the form of a linear coil as the temperature rose. The dehydration of the micelle was attributed to a change in the conformation of the chains, which then resulted in the loss of mechanically bound water. Gels formed as a result of the interactions between polyoxyethylene chains of adjacent micelles. The entanglement becomes more effective in linking together micelles which form a gel when the chains become entangled at an elevated temperature.

A substantially similar conclusion was reported (25) from a study using ultrasonic relaxation and C^{13} NMR on poloxamer 407 dissolved in water as well as in deuterium oxide. It was concluded that the relaxation occurs primarily from conformational changes due to changes in the orientation of the methyl side chains in the polyoxypropylene hydrophobe. These changes are caused by the extrusion of hydrated water from the interior of the micelle as the temperature rises. This dehydration then causes further friction in the hydrophilic end groups, causing micellar entanglement and an increase in viscosity and gel formation in concentrated solution. Inasmuch as the behavior of aqueous solutions of the poloxamines is similar to that of the poloxamer aqueous solutions with respect to gel formation, it is suggested that conclusions drawn from the behavior of the poloxamers could also be attributed to the poloxamine surfactants.

Why differences exist. The same conclusion cannot be drawn about the Butronic series since, unlike the poloxamers and poloxamines, these concentrated aqueous solutions do not exhibit the same phenomenon. Two fundamental differences between the poloxamers and the Butronic series are offered as an explanation: i) Although no data have been reported to indicate that a Butronic surfactant does form micelles, it is believed that they do form in aqueous solution. It is obvious that the ethyl side chain on a Butronic polyol has a larger spatial requirement than the methyl side chain on a poloxamer molecule. This alone suggests that the Butronic micelle is a thicker coil than the poloxamer micelle, as also indicated by the fact that less Butronic is needed to form a gel than a poloxamer. It had been reported (26) that the addition of many water-insoluble organic chemicals to an aqueous

TABLE 2

Micellar Properties of Poloxamer 407^a

T, °C	MW × 10 ⁻⁴	Aggregation number	CMC % w/w	
			Light scattering	Ultrasonic velocity
10	8.8	6	1.75	—
17.5	—	—	—	>1.0
20	—	—	—	0.14
25	—	—	—	0.095
30	21.0	15	0.08	0.075
35	28.0	20	~0.01	—
40	61.8	44	~0.005	—

^aRassing *et al.* (23).

poloxamer 407 solution reduces the poloxamer concentration needed to form a gel. This could be due to expansion and thickening of the micellar coil. ii) The Butronic hydrophobe is known to be more lipophilic than the poloxamer hydrophobe, as shown by the lower molecular weight needed to form a hydrophobe, 500 vs 750 (27). Despite this, more water appears to be associated with a Butronic polyol gel than is associated with a poloxamer or poloxamine gel at the minimum polyol concentration needed to form an aqueous gel. These data, shown in Table 3, indicate an approximately one-third larger molar ratio of water to alkylene oxides for the Butronic polyol.

A greater percentage of this water would be expected to be associated with the Butronic hydrophile, compared to the poloxamer and poloxamine hydrophiles. This would result in easier entanglement or subsequent gel formation for this series of polyols, which is what experimental data have demonstrated. It is suggested that as the temperature of a Butronic gel is lowered, its hydrophilic ends are so entangled that no more ether oxygen atoms are available for additional hydrogen bonding in the hydrophile. This prevents the formation of additional water of hydration. In addition, the hydrophobe may be too hydrophobic to form any additional hydrogen bonds with water. Both factors could well contribute to prevent the reversible thermal behavior exhibited by the gels of the other two polymeric series.

New aerosol delivery technique. The unique physical property of an aqueous poloxamer or poloxamine solution, which is fluid at ambient temperature and increases in viscosity as the temperature is raised, has led to the concept that an aqueous poloxamer solution could be expelled from an aerosol container (28,29) by means of a volatile propellant to form a gel on a warmer surface. Alternatively, it is possible to prepare a formulation which is liquid at room temperature and which contains volatile components such that, upon loss of the volatiles, a gel forms at the same temperature. This is due to the increase in the poloxamer concentration. This aerosol system is amenable to many applications in the detergent and other industries.

The formulation for an acid gel cleaner, poloxamer, 25; phosphoric acid (85%), 10; water, 65; coloring, trace; total, 100; is best prepared with cold water or by the

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TABLE 3

A Molar Comparison of Three Aqueous Gels

Polyol	Weight water	Moles H ₂ O	Weight polyol	Moles E O	Moles P O	Total moles oxides	Moles water: oxides
P-407	80	4.44	20	0.318	0.104	0.442	10.5
P-1508	80	4.44	20	0.364	0.091	0.455	9.8
B U-1	84	4.67	16	0.291	0.044*	0.335	13.9

*Moles of B O.

use of refrigeration. If this product were diluted with the minimum amount of water or were a low boiling alcohol needed to liquify it, the contents could be put into an aerosol container and a propellant added. Then when it is sprayed upon a warmer surface, above 40°C, a foamy gel would form. The formation of a foamy gel, at ambient temperature, would require the addition of more surfactant to the formulation.

The same acid gel cleaner in an aerosol formulation, poloxamer 407, 15; phosphoric acid (85%), 6; water, 39; alcohol DME blend, 40; total, 100; is prepared by diluting 60 parts of the gel with 40 parts of a solvent-propellant blend. The ratio of alcohol and DME (dimethyl ether), or other propellant, can be varied, as well as the percent of the blend used. A ratio of one part of alcohol to three or four parts of propellant is suggested for initial experiments. After the loss of the volatile components in the acid gel cleaner in an aerosol formulation, the resulting composition approximates that of the formulation for an acid gel cleaner.

An alkaline gel cleaner, the formulation for which is poloxamer 407, 12.0; sodium hydroxide (50%), 1.2; water, 46.8; alcohol DME blend, 40.0; total, 100.0; is prepared by combining 40 parts of a solvent-propellant blend with 60 parts of an alkaline gel. These formulations illustrate the versatility of this surfactant gel system for detergent usage, in that it can encompass a broad pH range. The primary advantage of these gels delivered from aerosol containers would lie in their ease of application to a vertical solid surface, such as the walls of a vessel, where they would adhere due to their tackiness.

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