Viscosity Characteristics of Aqueous Solutions of Block Copolymers of Propylene and Ethylene Oxides

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Abstract

Brookfield viscosity measurements were made on aqueous solutions of surface-active agents composed of block copolymers of propylene and ethylene oxides in which the molecular weights of the polymers varied from 1100 to over 15,000. The hydrophobic bases were polyoxypropylene glycols varying in molecular weight from 940 to 4000. To these were added varying amounts of ethylene oxide so that the polyoxyethylene hydrophil comprised from 15 to 80% of the surfactant total weight.

This work has materially expanded previous viscosity studies of aqueous solutions of nonionic surfactants by using a unique type of hydrophobe, two ethylene oxide chains, and far higher molecular weights of hydrophobe and of hydrophil, up to 280 moles of ethylene oxide.

The surface-active agents with hydrophobe base molecular weights from 940 to 1100, and in which the polyoxyethylene sections comprised from 15 to 80% of the total weight, did not form gels in aqueous solution. Some surfactants with a hydrophobe base molecular weight of 1750 to 2750, to which varying amounts of polyoxyethylene were added, formed gels in water at a surfactant concentration range of 40% to 80%. With a hydrophobe molecular weight of 3250, gels formed at from 30% to 90% surfactant concentration, while with one nonionic derived from a 4000 molecular weight hydrophobe, a gel formed at only 20% polyol concentration.

Two viscosity maxima were found in some cases, as reported occasionally for other systems. An increase in temperature from 0C to 50C generally reduced the viscosity of systems based on hydrophobes of 1175 and lower molecular weights, and increased it in systems based on hydrophobes of 1750 and higher molecular weights.

The behavior of these surfactants in forming gels is explained on the basis of hydrogen bonding, micellar aggregation and water entrapment. The moles of water per ethylene oxide group in the adduct varied with the hydrophobe base weight and with the polyoxyethylene hydrophil, and within systems showing maximum viscosities, ranged from 0.3 to 17.1, at 25C, which is much higher than observed in other nonionics.

Introduction

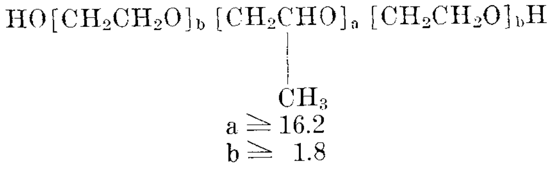
The viscosity characteristics of aqueous solutions of nonionic surface-active agents have been described in several publications. Thus, Boedeker reported on anomalies in the viscosities of aqueous solutions of ethylene oxide adducts of alkyl phenols (1). Schönfeldt, at the Third International Congress of Surface Activity, discussed (2) oxyethylated commercial lauryl and oleyl alcohols, and coco and oleyl fatty amines, in which the moles of ethylene oxide added to the hydrophobe ranged from 5.3 to 30.0. Other investigation (3) has shown that the polyoxyethylene glycols themselves do not exhibit unusual viscosity increases or form gels.

Other studies of a similar nature have been reported (4). Rösch, in discussing (5) the hydration of aqueous solutions of surface-active oxyethylated alcohols, argued for the existence of 1:1, 1:2 and 1:4 hydrates of the ether linkages. Most recently, Elworthy and Macfarlane have intensively studied (6) solutions of oxyethylated cetyl alcohol, with particular efforts to apply concepts of micellar structure to their findings.

However, the viscosity and gelation characteristics of one class of commercially available nonionic compounds were not mentioned, nor have they been described elsewhere in the literature. These are the block copolymers of ethylene and propylene oxides, which are sold commercially as Pluronic and Tetronic surfactants (Wyandotte Chemicals trademarks). The nonionic surfactants, which are the subject of this investigation, were made by the addition of ethylene oxide to a polyoxypropylene glycol hydrophobe. They are identified here by the molecular weight (mol wt) of the hydrophobe and by the moles of ethylene oxide added. The active agent contents of all are essentially 100%. Their structural formula, shown in Fig. 1, reveals that the hydrophil consists of two substantially equal chains, separated by the hydrophobe.

Experimental

Polyol solutions were prepared at intervals of 10%, by weight, from 10% to 90%. All solutions were prepared in and measured in 8-oz French square wide-mouth bottles. Viscosities were measured in a constant temperature water bath at 0C, 25C and 50C with the use of a model LVF Brookfield Synchrolectric Viscometer. Viscosity measurements were also made on the polyols themselves, where possible. The use of an ice bath was adequate to maintain the temperature at 0C–2C. The water bath temperatures for the 25C and 50C measurements were maintained within ±1C. Visual observations were made on all systems. Several developed two liquid phases on standing and no viscosity data were recorded. Mixtures that were viscous usually required alternate chilling and shaking at room temperature on a laboratory shaker to accelerate solution. A few mixtures remained cloudy and some, which were rather viscous, retained trapped air bubbles despite all efforts to remove them. Viscosity measurements of non-Newtonian fluids were made at two or more spindle speeds and the data averaged.



$$HO[CH_2CH_2O]_b\,[\underset{\displaystyle CH_3}{CH_2CHO}]_a\,[CH_2CH_2O]_bH$$

$$a \geqq 16.2$$
$$b \geqq 1.8$$

FIG. 1. Structural formula of block copolymers of propylene and ethylene oxides.

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[1] Presented at the AOCS Meeting, Cincinnati, October 1965.

Results

Fixed Hydrophobes, Variable Hydrophil

The first group of surfactants studied were adducts of a polyoxypropylene glycol of 940 mol wt, in which the ethylene oxide added varied from 3.6 to 92.8 moles. At 25C, no gel regions or viscosity irregularities were found. The viscosities of the several adducts generally reached maxima, up to 500 centipoises, at 90% polyol concentrations.

The second group of surfactants comprised derivatives of a polyoxypropylene glycol of 1175 mol wt, in which the ethylene oxide content added ranged from 10.4 to 39.7 moles. Apparently Newtonian liquid behavior was observed, as found with the previous series. A representative viscosity concentration curve is shown by the solid line in Fig. 2. All the surfactants of the first two groups had similar viscosity concentration curves, with a viscosity maximum at 90% polyol concentration.

A typical viscosity concentration curve for an adduct of a polyoxypropylene glycol hydrophobe of 1750 mol wt, represented by the broken line in Fig. 2, revealed a different picture. The data for this group of surfactants, given in Table I, generally show increased viscosity values, from 50%–90% polyol concentration, over the corresponding surfactants in the previous groups. Ethylene oxide content here ranged from 5.7 to 139.5 moles. A gel region and a viscosity peak were observed with the 25.6 mole ethylene oxide adduct. Gel regions, but no second viscosity maximum, were also observed with the higher mole ethylene oxide adducts. The moles of water per mole of ethylene oxide for this series of compounds ranged from 0.4 to 4.4.

When the mol wt of the polyoxypropylene glycol hydrophobe was increased to 2250, the same anomalous behavior was noted. The data are also shown in Table I. Gel formation was found, embracing the 53.5 mole ethylene oxide adduct on through the 193.2 mole adduct. The nonionic containing 11.4 moles of ethylene oxide exhibited two viscosity maxima despite the absence of gel formation. The ratio of moles of water per ethylene oxide group ranged from 0.3 to 7.2, a substantially widened range, even without attention to the 13.4 ratio applying at the second viscosity maximum. A typical viscosity concentration curve for this group of surfactants is shown by the solid line in Fig. 3, which also depicts the gel region.

TABLE I

Viscosities of Ethylene Oxide Adducts of Polyoxypropylene Glycol Bases of the Indicated Molecular Weights

EO Moles	Max visc., cp	Conc, wt %	Molar ratio H_2O/EO	Second max Visc, cp	Second max Conc, wt %	Second max Molar ratio H_2O/EO
Mol wt 1750						
5.7	380	90	2.2			
17.1	15,000[a]	70	3.5			
25.6	34,000[a]	80	1.6	Gel	60	4.2
37.7	Gel	90–60	0.6–3.4			
49.2	Gel	90–50	0.5–4.4			
139.5	Gel	90–50	0.4–3.1			
Mol wt 2250						
11.4	1,530	80	3.3	6,050	50	13.4
53.5	Gel	80–40	1.2–7.2			
119.2	Gel	90–40	0.4–5.2			
193.2	Gel	90–40	0.3–4.6			
Mol wt 2750						
16.6	Gel	80–70	2.9–5.0	6,000	50	11.7
49.1	Gel	80–40	1.4–8.3			
84.1	Gel	90–30	0.5–10.0			
244.2	Gel	90–30	0.3–7.2			
Mol wt 3250						
12.3	Gel	80–70	4.3–7.3	15,760	50	17.1
37.7	Gel	90–30	0.8–16.9			
63.6	Gel	90–30	0.6–12.3			
75	Gel	90–30	0.5–11.3			
279.6	Gel	90–30	0.3–7.0			
Mol wt 4000						
16.1	Gel	80–50	4.1–16.3			
30.5	Gel	90–80	1.1–2.4	Gel	50	9.7
48.9	Gel	90–30	0.8–16.3			
273	Gel	90–20	0.4–13.0			

[a] Measured in non-Newtonian flow region.

An increase in the mol wt of the polyoxypropylene glycol hydrophobe to 2750 showed progressive results, as listed in Table I. Adducts ranged from 16.6 to 244.2 moles of ethylene oxide. The 16.6 mole adduct showed gel, and a viscosity maximum, at different concentration ranges. Gel formation occurred over the entire range of ethylene oxide adducts. A typical viscosity concentration curve for this group of surfactants is similar to the solid line shown in Fig. 3.

With an increase in hydrophobe mol wt to 3250, the same phenomena were repeated, as listed in Table I. A viscosity maximum and gel region are shown by the 12.3 mole ethylene oxide adduct, and gel regions are shown by all the nonionics, ranging from 12.3 to 279.6 moles of ethylene oxide added. Accompanying the increasing mol wt of this series of nonionic

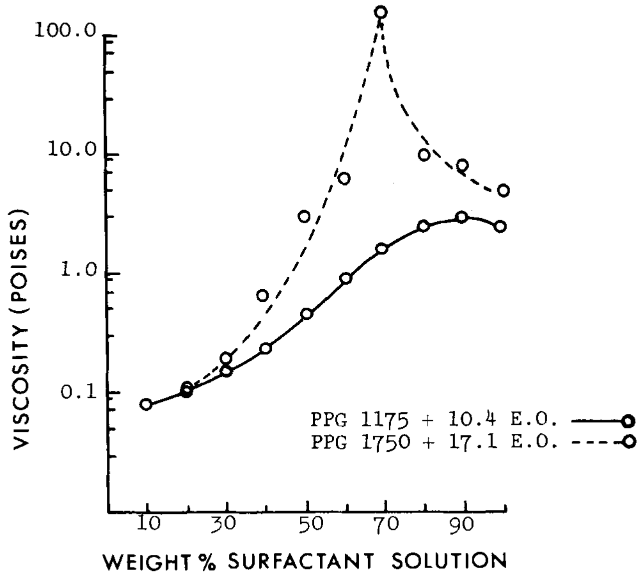

FIG. 2. Viscosity-concentration curves of propylene and ethylene oxide block copolymers, 25C.

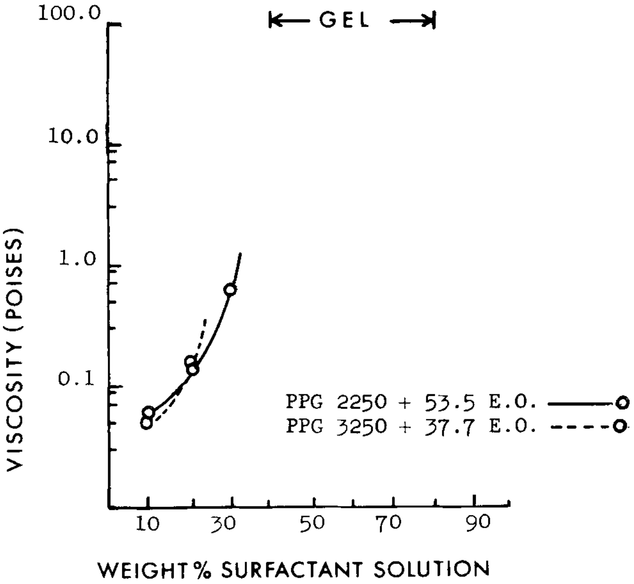

FIG. 3. Viscosity-concentration curves of propylene and ethylene oxide block copolymers, 25C.

surfactants, the moles of water per ethylene oxide unit exhibit a much wider range than before, varying here from 0.3 to 17.1. A typical curve for this group of surfactants is shown by the broken line in Fig. 3.

The highest mol wt hydrophobe studied was polyoxypropylene glycol 4000. The data are listed in Table I. The ethylene oxide content ranged from 16.1 to 273 moles, and all nonionics yielded gels over the very wide concentration ranges or two separated ranges. The 30.5 mole ethylene oxide adduct showed the latter and both gels were beyond the capacity of the instrument. Very broad molecular ratios of water to ethylene oxide prevail throughout this series. The typical viscosity concentration curve for this group of surfactants resembles very closely the broken line shown in Fig. 3.

Fixed Hydrophil, Variable Hydrophobe

It is instructive to compare the effect of hydrophobe mol wt on consistency, for systems having polyoxyethylene chains of substantially equal length. This may be done by the aid of Fig. 4, wherein these chains vary only within the range of 15.6 to 16.5 moles of ethylene oxide.

With the hydrophobe of 1175 mol wt, a Newtonian gel-free fluid, shown by the solid line in Fig. 4, is obtained. Maximum viscosity of 2280 cps is reached at 90 wt % polyol. With a hydrophobe of almost double the weight, 2050, viscosities increase rapidly to a maximum of 8000 centiposis at a 70 wt % polyol concentration, as shown by the small-dash line. A further doubling of the hydrophobe mol wt to 4000 results in a gel region between 50 and 80 wt % polyol and in a two-phase system at lower concentrations. This polyol is represented by the large-dash line in Fig. 4.

Effect of Temperature

More interesting information can be obtained by a comparison of the viscosity properties as a function of temperature, at the lower concentration ranges. An examination of data at 0C, 25C and 50C for surfactants derived from polyoxypropylene glycol hydrophobes of 940 and 1175 mol wt, reveals that the viscosity tends to decrease with a rise in temperature. Typical curves, shown in Fig. 5, are for a polyoxypropylene glycol of 1175 mol wt, to which 39.7 moles of ethylene oxide are added.

The decrease in viscosity at 50C is more marked at the higher polyol concentrations. However, with those surfactants having a polyoxypropylene glycol mol wt of 1750, the reverse behavior is noted; namely, the viscosity rises with an increase in temperature. This same phenomenon is also true of nonionics derived from the higher molecular weight polyoxypropylene glycols. This is illustrated in Fig. 6 where typical curves are shown for a polyoxypropylene glycol of 1750 mol wt, to which 17.1 moles of ethylene oxide are added.

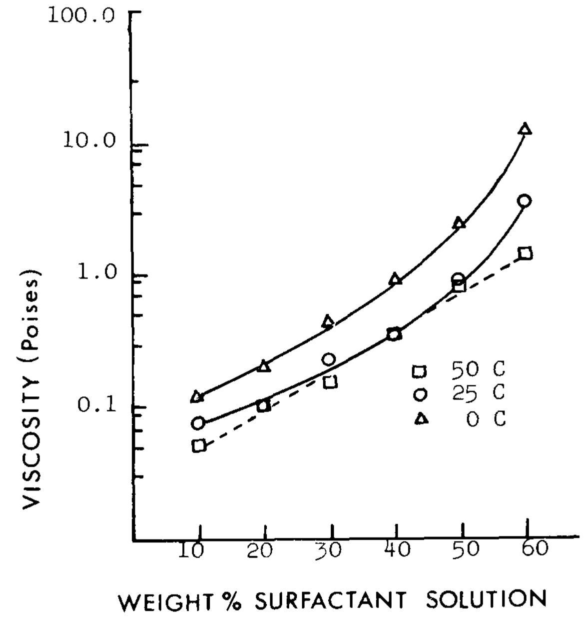

Fig. 5. Viscosity-concentration curves as a function of temperature, polyoxypropylene glycol 1175 plus 39.7 moles ethylene oxide.

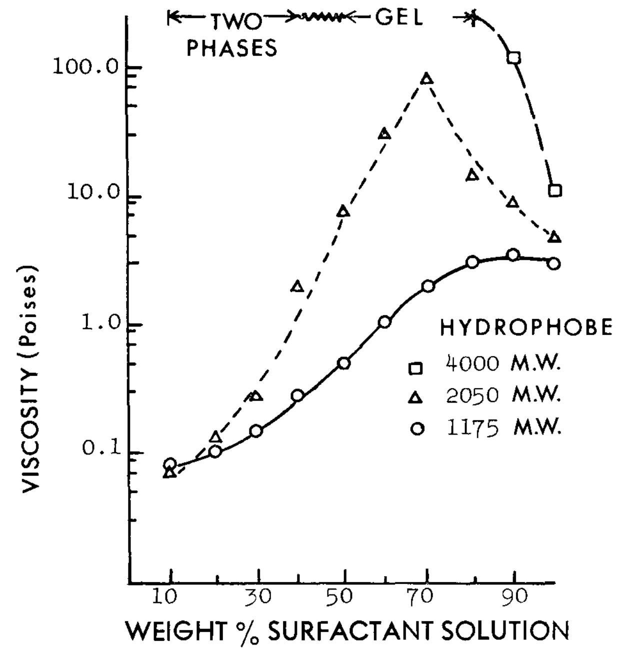

Fig. 4. Viscosity-concentration curves of surfactants of constant hydrophile (16 moles EO) with increasing polyoxypropylene glycol hydrophobe molecular weight at 25C.

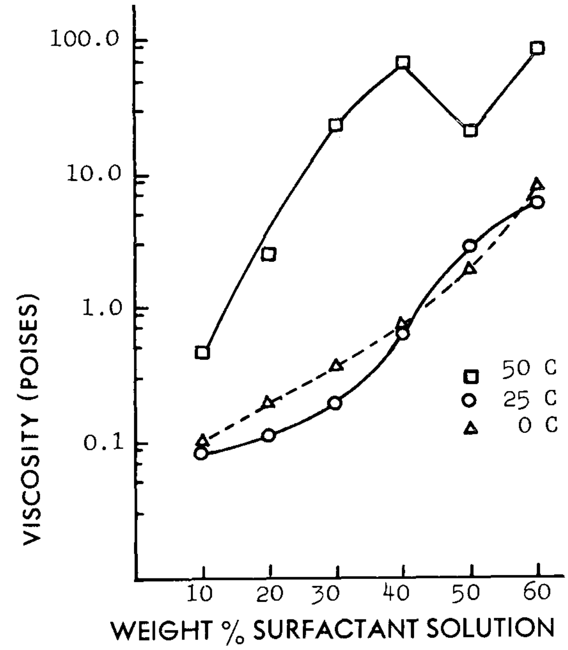

Fig. 6. Viscosity-concentration curves as a function of temperature, polyoxypropylene glycol 1750 plus 17.1 moles ethylene oxide.

The difference in viscosity between the 50C and the lower temperatures is readily apparent. One can also note two viscosity maxima at 50C.

The difference in viscosity behavior as a function of temperature between the two groups of polyols is also apparent from Table II. This lists the viscosities, in centipoises, of the solutions of two polyols each of which contains approximately 25 wt % ethylene oxide. Viscosities of aqueous solutions of the polyol with the hydrophobe mol wt of 1175 decrease as the temperature increases, while the opposite effect is noted with solutions of the polyol having a hydrophobe of 2050 mol wt.

A comparison is also made in Table II between two other polyols which are also similar in ethylene oxide content. These surfactants are more hydrophilic than the previous pair, in that they each contain approximately 50 wt % of ethylene oxide. The same marked difference in behavior is noted. Solutions of the polyols derived from a polyoxypropylene glycol of 940 mol wt decrease in viscosity as the temperature rises, while with the polyols derived from the polyoxypropylene glycol 1750, just the opposite effect is clearly apparent.

Discussion

In the areas of maximum viscosity shown by aqueous solutions of polyoxypropylene-polyoxyethylene block copolymers, the ratios of moles of water per ethylene oxide group exhibit a much wider range, 0.3–17.1, and are generally higher than those shown by oxyethylated surfactants studied by others. This wide range must relate, in part, to the unusual character of the polyoxypropylene glycol hydrophobe which, first, is much higher in molecular weight than the hydrophobe of other types of nonionics and, secondly, may in its own right immobilize water, independently of the oxyethylene chain, by hydrogen bonding.

It is noteworthy that gel formation occurs at 25C even where the surfactant contains more than 200 moles of ethylene oxide, or over 100 moles per block. With oxyethylated nonyl phenol, on the other hand, gel formation is reported (4) to stop short of a 40 mole ethylene oxide adduct. The former is due, it is thought, to an inability to form micelles as closely packed as in other oxyethylated nonionics. The structural formula of this type of nonionic surfactant, as shown in Fig. 1, exhibits a hydrophobe lying between two equal hydrophils, whereas nonionics commonly encountered, such as the oxyethylated fatty alcohols and alkyl phenols, have only one hydrophilic chain. This difference in structure suggests that a loose micellar structure is obtained with this class of nonionics, and that gel formation would more readily involve entrapment of water in addition to water due to hydrogen bonding. The physical entrapment of free water has been previously suggested by Greenwald and Brown (3) in a study on the viscosity of aqueous solutions of oxyethylated alkyl aryl nonionics.

TABLE II

Variation of Viscosities[a] of Surfactant Solutions with Temperature

Nonionic block copolymer	Wt. % Polyol	0C	25C	50C
Polyoxypropylene glycol, 1175 mol wt + 10.4 E.O. (25% E.O.)	10	8	8	[b]
	20	15	10	[b]
	30	28	15	[b]
	40	63	23	[b]
	50	150	45	50
	60	320	88	55
Polyoxypropylene glycol, 2050 mol wt + 16.5 E.O. (25% E.O.)	10	14	7	[b]
	20	16	13	[b]
	30	39	28	[b]
	40	90	202	550
	50	254	765	1030
	60	1270	3140	5450
Polyoxypropylene glycol, 940 mol wt + 21.6 E.O. (50% E.O.)	10	10	8[c]	5
	20	23	9[c]	8
	30	30	14[c]	13
	40	70	25	18
	50	163	45	25
	60	390	95	45
Polyoxypropylene glycol, 1750 mol wt + 37.7 E.O. (50% E.O.)	10	11	5	4
	20	23	9	15
	30	45	22	37
	40	104	141	560
	50	382	2062	[d]
	60	[d]	[d]	[d]

[a] All values in centipoises.
[b] Two-phase system.
[c] Cloudy.
[d] Gel.

It is interesting to note that two viscosity maxima were obtained in each group of surfactants, starting with the 1750 mol wt polyoxypropylene glycol hydrophobe, through the maximum of 4000 mol wt. Similar viscosity anomalies with other nonionics have been reported by other workers. We are unable to account for this phenomenon.

As the temperature of the nonionic solution rises, it is believed that the hydrophil is partially dehydrated and micellar aggregation increases. These observed changes in the viscosity property of the surfactant of 1750 and higher mol wt hydrophobe strongly suggest increased micellar aggregation. It has been previously reported that the critical micelle concentration of a polyoxypropylene-polyoxyethylene block copolymer derived from a 1750 mol wt hydrophobe increases as the temperature increases, below its cloud point (7). The formation of larger aggregates by the higher mol wt hydrophobes which would then entrap additional water, leading in turn to more viscous solutions and gels as the temperature increases, is suggested. However, it is not understood why this same phenomenon does not occur with the lower molecular weight homologs.

There is a need to describe more thoroughly the transitional phenomena and different states observed between Newtonian liquid and "unmeasurable" gel behavior. A detailed study (8) of parts of systems based on the 1750 mol wt hydrophobe has established many sharply defined phase boundaries in a true solubility sense, and new phenomena were observed. Mapping of the thermodynamically correct phase relationships obviously provides a far stronger base from which to undertake to formulate concepts of molecular constitution. Future efforts will be directed to the investigation of systems in this manner. There have been only a few publications of this type, one being that of Weston (9).

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