Surfactants & Detergents

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♣ Nonionic Surfactants Containing Propylene Oxide[1]

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Physical and surface active properties of ethoxylates are altered by the inclusion of propylene oxide (PO) groups. The location of PO within the ethoxylate (EO) chain can be as important a factor as the relative amounts of PO and EO. The optimum position of the PO was shown to be a single discrete block of PO located in approximately the middle of the ethoxylate chain.

The influence of PO on surfactant properties was assessed for several alcohol ethoxylates and nonylphenol ethoxylates. Pour points and gelling tendencies were lowered at the expense of detergency, foaming and wetting power.

Conventional nonionic surfactants are most commonly ethoxylates of fatty alcohols or alkylphenols. Including propylene oxide with the ethylene oxide can change the physical and surface active properties of nonionic surfactants in profound ways. This effect has been exploited for years by many surfactant manufacturers.

Propylene oxide is more hydrophobic than ethylene oxide; in fact, if the oxypropylene chain is long enough (about 15 or more PO groups), it becomes a surfactant hydrophobe. One well-known example is the Pluronic® family of products of BASF Wyandotte (1) in which polypropylene glycol is the hydrophobe.

Union Carbide's Tergitol® X nonionics, monofunctional ethoxylates of propoxylated lower alcohols (2,3) (Table 1, Structure A), are another example. The polyoxypropylene chains contain some oxyethylene groups.

Much smaller amounts of PO are required to build a surfactant hydrophobe from middle range alcohols such as octanol (4,5). Olin's Poly-tergent® SL surfactant family uses this approach (Fig. 1, Structure A).

Capping conventional ethoxylates with propylene oxide renders them hydrophobic on both ends. Such materials are widely used as low-foaming surfactants (Table 1, Structure B). There are many manufacturers of this type of product.

The third way of incorporating propylene oxide into a nonionic surfactant is direct placement into the

TABLE 1

Positions of PO in Ethoxylates

Structure	Mode of PO Addition
A. $RO(PO)_n(EO)_nH$	PO block
B. $RO(EO)_n(PO)_pH$	PO block
C. $RO[nEO, pPO]H$	PO block or EO,PO mix
D. $RO(EO)_m(PO)_p(EO)_nH$	PO block

polyoxyethylene hydrophile (6-12). This may be achieved by premixing EO and PO, adding alternating blocks of EO and PO, or a combination of both (Table 1, Structure C). The quantity and distribution of the PO within the EO chain may be varied widely. This paper will explore the effect of PO on the physical and surface active properties of such surfactants.

Texaco Chemical's product, Surfonic® JL-80X (formerly J-4), is of this type (13,14), as are BASF Wyandotte's Plurafac® B and D nonionics. According to the disclosures of Milligan (13,14) the PO is contained in a single block in roughly the middle of the EO chain (Table 1, Structure D). The reasons for choosing this particular structure will be discussed.

EXPERIMENTAL

Synthetic methods. Most of the EO-PO adducts were

prepared in a 3-gal. steam-jacketed stirred reactor equipped with nitrogen and oxide inlet lines at the bottom of the vessel.

A typical procedure for a coconut alcohol adduct was as follows: A one-kg charge of coconut alcohol (5.1 mol) (CO-1214, Procter & Gamble Industrial Chemicals) and 4 g flaked potassium hydroxide were purged under vacuum at 100 C for 30 min. Ethylene oxide (900 g = 4.0 equiv.) was added incrementally at 120 C at a rate which maintained a pressure of 60 psi in the reactor. After the EO addition was complete, the pressure was allowed to drop to a constant value. In the same manner, 0.6 kg propylene oxide (2.0 equiv.) was added and digested to constant pressure. The second portion of ethylene oxide (850 g = 3.8 equiv.) followed. Cloud point (1% aqueous) of the adduct after digestion and neutralization was 58.6 C. Hydroxyl number was 90.2 mg KOH/g, corresponding to a molecular weight of 622.

Analytical techniques. Analytical methods for characterizing PO-containing adducts relied on nuclear magnetic resonance spectroscopy (NMR). The EO/PO molar ratio was determined by proton NMR. ^{13}C NMR proved useful for characterizing qualitatively the EO/PO distribution along the polyether chain and measuring quantitatively the relative amounts of primary and secondary hydroxyl (15) at the end of the polyether chain.

The NMR spectrum of Figure 1 illustrates the separate chemical shifts of the two types of carbon attached to hydroxyl

$$\overset{*}{-CH_2OH} \quad \text{and} \quad \overset{\displaystyle CH_3}{\underset{}{\overset{*|}{-CH-OH}}}$$
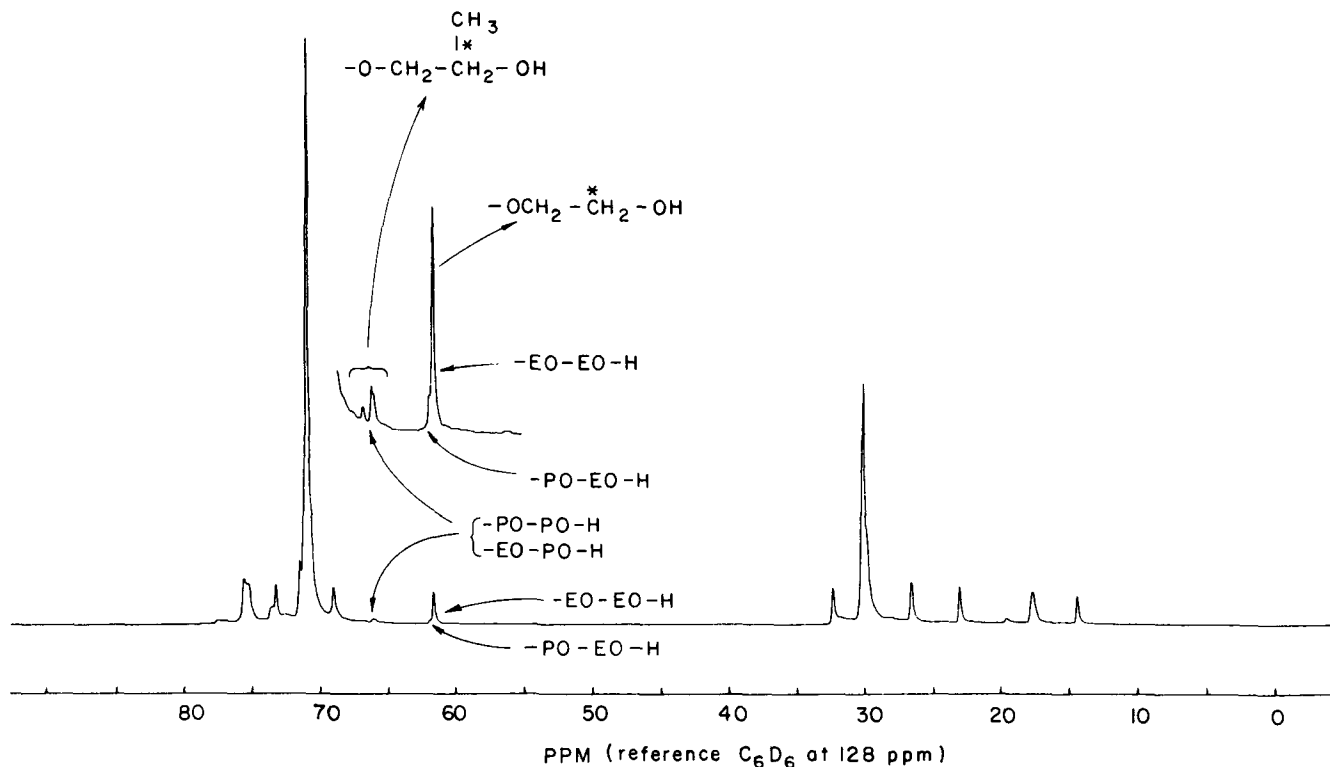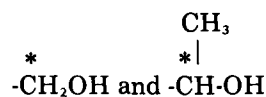
FIG. 1. ^{13}C NMR spectrum of alcohol-EO-PO-EO adduct.

at 62 ppm and 66 ppm, respectively. The two absorption bands were integrated to obtain the relative amounts of primary and secondary hydroxyl in the samples. In the example the primary hydroxyl was calculated to be 80%.

The two peaks comprising the hydroxypropyl group indicate a mixture of -PO-PO-H and -EO-PO-H terminal groupings, both in significant amounts. The sizable -PO-PO-H component is evidence for a PO block.

RESULTS AND DISCUSSION

Effect of PO block position on primary hydroxyl. Because PO is less reactive than EO, and secondary OH is less reactive than primary OH toward epoxides, even a small amount of PO added early in the polyether growth reaction has a measurable impact on the primary OH content of the finished polyether. The adduct whose

spectrum is shown in Figure 1 has a PO block near the center of the EO chain. The relationships of the amount of PO added and its manner of addition to the primary hydroxyl are dependent on such variables as temperature, catalyst level and type, reaction time between oxide blocks and reactor operating pressure. While it may be difficult to quantify, there is a clear qualitative correlation.

A series of five adducts of $C_{10\ 12}$ alcohol (3:1 C_{10}:C_{12} blend), all with cloud points of 60 C, were prepared. They each contained a total of about 7.5 oxyethylene and 1.5 oxypropylene groups. The PO block position within the structure
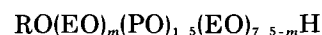
$$RO(EO)_m(PO)_{1\ 5}(EO)_{7\ 5-m}H$$

varied from m = 0 to m = 7.5 with intermediate values
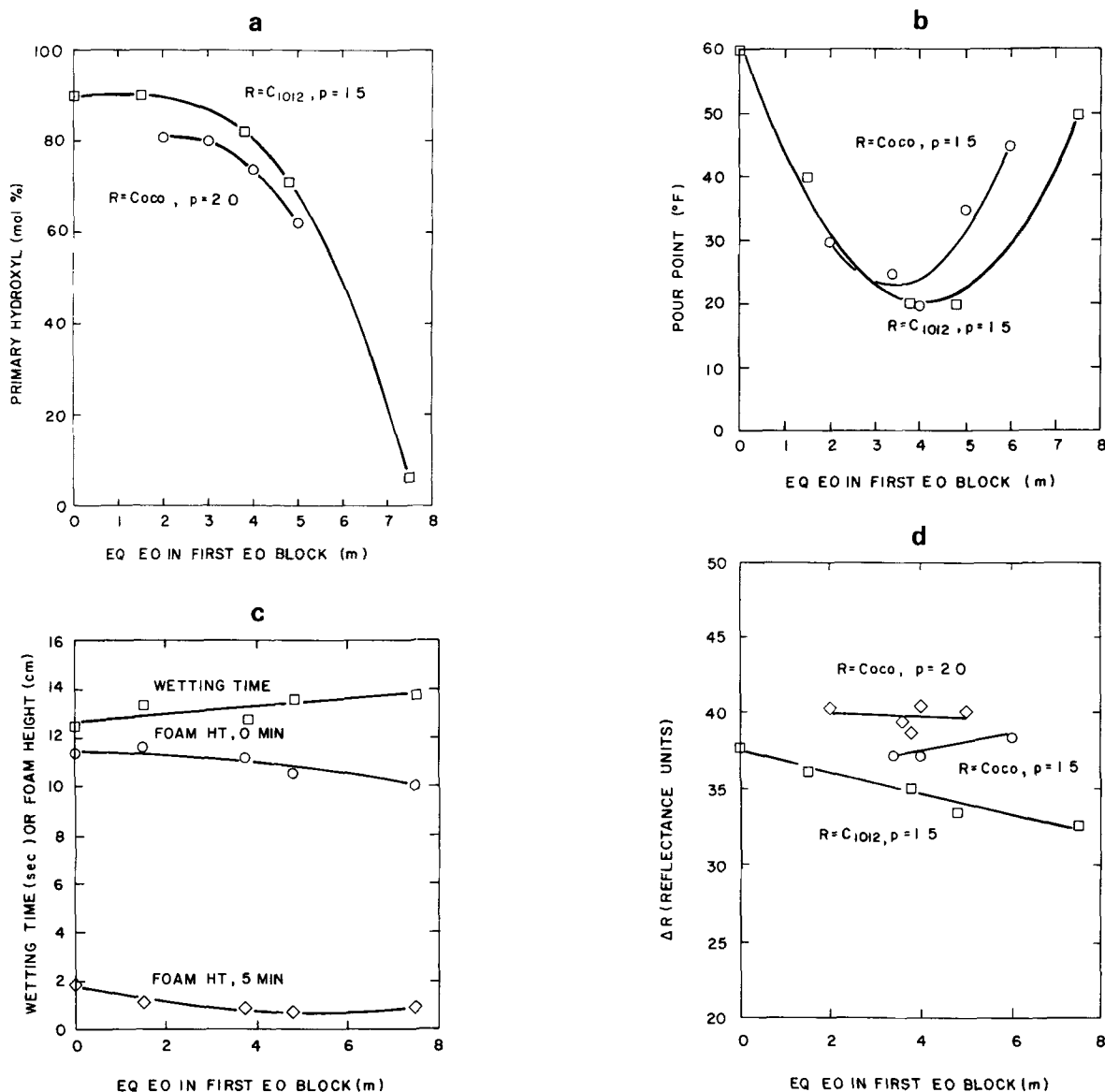
FIG. 2. Effect of PO block position in $RO(EO)_m(PO)_p(EO)_{7\ 5-m}H$ on a, primary hydroxyl value; b, pour point; c, wetting and foaming (p = 1.5), and d, detergency.

of m = 1.5, 3.8 and 4.8.

The dependence of the primary hydroxyl content on the position of the propylene oxide block within the polyoxyethylene chain is illustrated by Figure 2a. The plot follows the decrease of primary hydroxyl as the propylene oxide block moves toward the hydroxyl end of the polyether chain. It begins at ~90% primary hydroxyl when the propylene oxide is added first to the hydrophobe prior to the ethylene oxide (m=0) and declines in a smooth manner down to about 70% when m=4.8. When all the ethylene oxide is added first (m=7.5) and capped with propylene oxide, the measured primary hydroxyl is only 6%.

This curve is smooth perhaps fortuitously, because in practice the primary hydroxyl value is dependent on, in addition to the amount of ethylene oxide added after the propylene oxide (7.5 m), the completeness of propylene oxide reaction prior to the addition of the final block of ethylene oxide and the operating condition of the NMR spectrometer.

The second curve shows the same correlation for a series of four coconut ($C_{12\ 14}$) alcohol adducts, each having 60 C cloud point and containing a 2.0 equiv. PO block: a downward trend of primary hydroxyl with increasing m.

Effect of PO block position on pour point. Pour point lowering is the most striking effect observable from placing a PO block into the middle of the polyoxyethylene chain. Ethoxylates which are slushes or solids at room temperature become clear liquids when a PO block containing at least one equivalent of PO is inserted. This effect can be attributed to the PO disrupting the normal oligomer distribution of ethoxylates and linearity of the ethoxylate chain.

Figure 2b plots *pour point versus position* of PO block within the polyoxyethylene chain for the two series of adducts described above. The total ethylene oxide chain length was 7.5 to 8 equivalents of EO in each case. (Pour point is measured in °F and has an uncertainty of about ±5 F.) For the series of $C_{10\ 12}$ alcohol adducts in which the PO block was composed of 1.5 equivalents of PO, there was a very deep minimum for the pour point when the propylene oxide block was in the middle of the ethylene oxide chain. When the propylene oxide block was added directly to the alcohol and then capped with ethylene oxide (m=0), the pour point was ~60 F. When it was on the end of the EO chain (m=7.5), the pour point was about 50 F, but the intermediate pour points were as low as 20 F.

Coconut alcohol adducts in which the propylene oxide block consisted of 2.0 equivalents of PO followed the same pattern.

Effect of PO block position on surfactant properties. Minimum pour points are achieved over a range of PO block positions near the middle of the EO chain (Fig. 2b), roughly 1/3 to 2/3 of the distance along the EO chain. Surfactant properties were examined for 60 F cloud point adducts in which the position of the 1.5 equivalent PO block was varied and contained a total of 7.5 equivalents EO.

Figure 2c shows wetting times and foam heights as functions of the PO block position. The wetting times were influenced little if any over the useful pour point range, staying virtually constant. (Total wetting time was the sum of 3 g and 1.5 g hook sink times in the Draves test.)

Initial Ross-Miles foam heights declined slightly over this range, while the 5-min foam heights remained about the same.

Detergency of adducts based on $C_{10\ 12}$ alcohol declined (Fig. 2d) as the PO block (1.5 equiv. PO) moved along the EO chain from the alkyl end to the hydroxyl end. However, the same trend is not observed with the two coconut alcohol adduct series. They displayed no trend dependent on PO block position. The detergencies were measured at 80 F on three soiled polyester-cotton fabrics: dust-sebum soil, Testfabrics Inc. soil, and U.S. Testing Company soil, and are expressed as total reflectance units gained. (Confidence limits were about ±1 unit within each of the three series). The three curves of Figure 2d cannot be compared quantitatively because the detergency measurements were made at different times (Fig. 3d).

Thus, there is no advantage to moving the PO block from the middle of the ethoxylate chain in either direction, except for not allowing it past the middle toward the hydroxyl end in $C_{10\ 12}$ alcohol adducts.

Effect of PO block size on surfactant properties. Both coconut alcohol $C_{10\ 12}$ alcohol adducts with 1.0 equivalent of PO in the middle of the EO chain had pour points near 40 F and, with 1.5 equivalents of PO, pour points below 30 F (Fig. 3a). Tallow alcohol adducts showed only modest pour point reduction (all adducts had 60 C cloud points).

Figure 3b shows the effect of the PO block size on wetting time, surface and interfacial tension of coconut alcohol adducts with 60 C cloud points. As the centrally located PO block increased in size from 0 equivalents up to 3, the surface tension increased steadily from just under 30 dynes/cm for 0.10% solutions up to almost 33 dynes/cm. Interfacial tension stayed the same, about 5 dynes. Wetting power declined (i.e., wetting time increased) as the PO block increased in size.

A similar trend in wetting power is seen for $C_{10\ 12}$ alcohol adducts going from no PO up to 1.5 equivalents of PO (Fig. 3c). Also shown are the Ross-Miles foam heights for the same series of adducts. Foaming decreased as the PO block size increased. The 5-min foam height values stayed the same.

Three series of alcohol adducts were tested for detergency. Figure 3d shows declining detergency for all three series as the size of the PO block at the center of the EO chain increases. The three alcohols were $C_{10\ 12}$, coconut range ($C_{12\ 14}$) and tallow range ($C_{16\ 18}$). (Confidence limits for reflectance values were about ±1 unit.)

These data establish that there is a small but real adverse effect due to the propylene oxide within the EO chain of nonionic surfactants on the important surfactant properties of wetting, detergency, foaming and surface tension lowering. This inhibitory effect suggests that the size of the PO block be made only large enough to achieve the pour point desired. A block of about 1.5 equivalents of propylene oxide is sufficient to attain the minimum pour point but does not seriously affect any of the surfactant properties.

*Effect of PO distribution on physical and surfactant properties.*The adducts described so far were prepared by adding discrete oxide blocks, i.e. digesting each block completely before adding the next oxide block; the
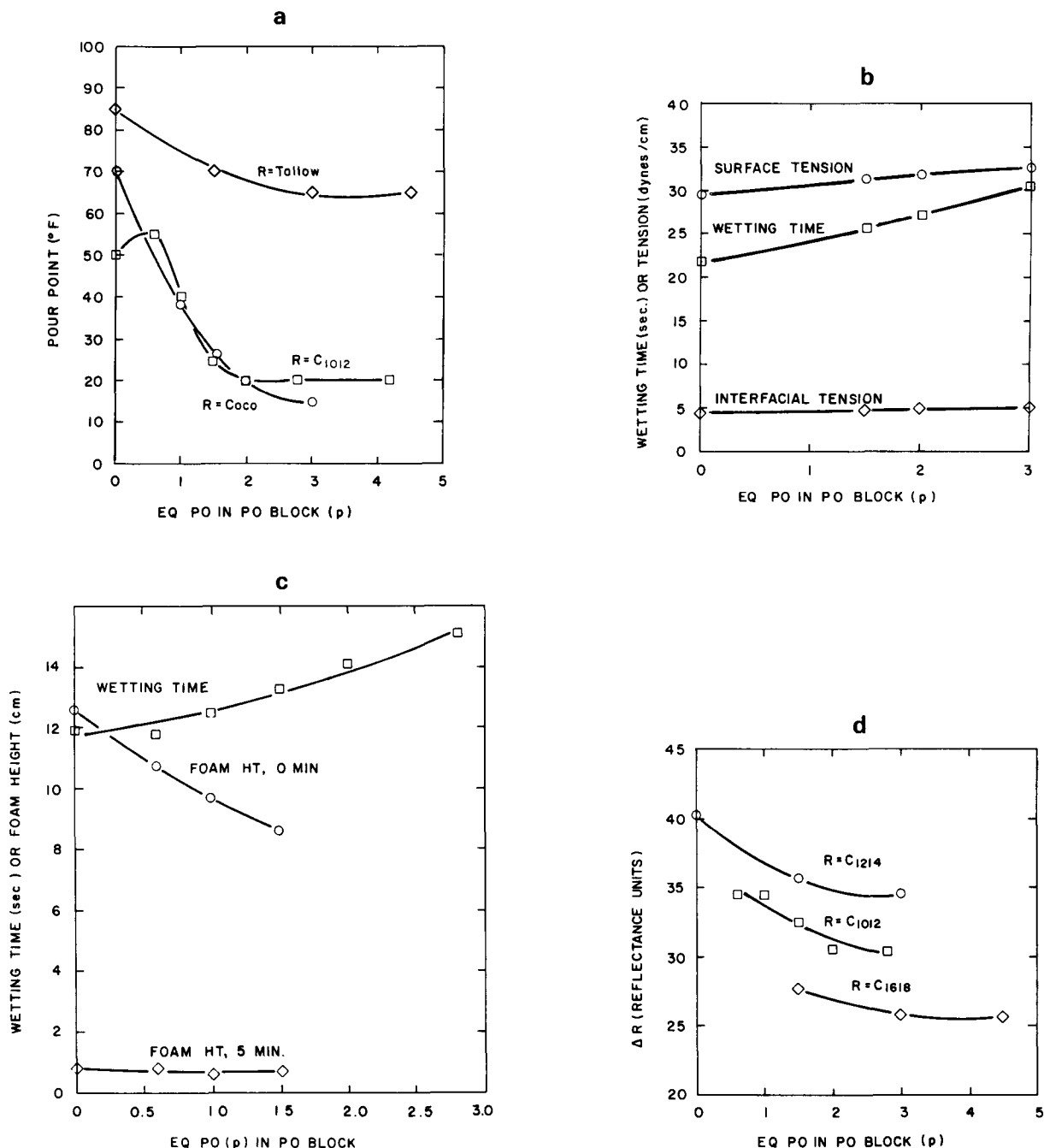
FIG. 3. Effect of PO block size (p) in $RO(EO)_{n/2}(PO)_p(EO)_{n/2}H$ on a, pourpoint; b, wetting and tensions (R = Coco, n = 8); c, wetting and foaming (R = $C_{10\ 12}$, n = 7.4), and d, detergency.

propylene oxide was added all in one block rather than being broken up into two or more smaller blocks. A series of four adducts (Table 2) was made in which propylene oxide was added in 1, 2 or 3 separate blocks without complete digestion before EO addition began ("overlapping" blocks). The object was to widen the distribution of PO along the polyoxyethylene chain. While the extent of randomization of PO and EO groups was not quantified, the distribution of EO and PO can be

related qualitatively to primary hydroxyl.

Primary hydroxyl content declined as the EO/PO mixing increased (Fig. 4a). This is reasonable because the final EO block decreased in size from sample 1 to sample 5. The only exception to the pattern was sample 5. It had the same size (2.7 equiv.) final EO block as sample 4, but had higher primary hydroxyl, probably because the last PO block was smaller (0.5 equiv. vs. 0.75 equiv. for sample 4); consequently, less PO was present

during the final EO reaction step.

Pour points showed an upward trend with increased EO/PO mixing. The important conclusion from this trend is that increasing the EO/PO randomness does not decrease the pour point below the case where the PO is one discrete block; rather, there is a definite increase.

Wetting power (Fig. 4b) showed little effect due to increased PO/EO mixing until the last point (sample 5), where the wetting power improved slightly (i.e., wetting time was shorter). Surface tension also showed little effect, the final point having the lowest surface tension value. Interfacial tensions were virtually unchanged. Foaming (Fig. 4c) as expressed by initial Ross-Miles foam height showed a slight maximum at sample 3 of uncertain significance. Five-min foam heights showed no trend.

Thus, there is no compelling reason, aside from shortening the time of preparation, to increase the randomness of the EO and PO groups within the polyether chain. None of the physical or surfactant properties benefit significantly from this technique.

Surfactants based on nonylphenol. Nonylphenol ethoxylates have low pour points as well as excellent detergency and wetting properties. A series of nonylphenol ethoxylates containing propylene oxide, all with cloud points in the range of 55-60 C, were prepared to assess the effect of PO. The propylene oxide was added in a manner to maximize the EO/PO mixing, i.e., in three overlapping blocks separated by three overlapping blocks of ethylene oxide. The total amount of propylene oxide was varied from 1 to 5 mol. In addition, one sample was prepared in which a discrete block of 2 mol of propylene oxide was located in the middle of the polyoxyethylene chain.

As the amount of propylene oxide increased, the pour points declined steadily (Fig. 5a) from an initial value of 40 F (no PO) down to 0 F (5 PO). The sample with the single 2-mol PO block had a very low pour point of 5 F compared to 25 F for the sample containing 2 mol of PO randomly mixed with EO.

Wetting times steadily increased as the amount of propylene oxide increased (Fig. 5a). The first sample with 1 mol of propylene oxide had the same wetting time as the ethoxylate without any propylene oxide. The sample with the 2-mol block of propylene oxide had the same wetting time as the sample with 2 mol of PO more thoroughly mixed. Foaming (Fig. 5b) showed little influence due to the amount of propylene oxide for initial foam heights. But 5-min foam heights showed a steady decrease in foam stability as the amount of propylene oxide increased.

A second series of nonylphenol ethoxylates modified with propylene oxide had cloud points of 80-85 C. The 12-mol ethoxylate (Surfonic N-120) has a pour point near room temperature, and the material is commonly a slush. Figure 6 shows that addition of up to 1 mol of propylene oxide had virtually no effect on the pour point, but caused the wetting power to deteriorate significantly.

The three samples which contained 0.25, 0.5 and 1.0 equivalent of propylene oxide had the PO introduced as a single overlapping block after 1/3 of the ethylene oxide had been added, so the propylene oxide was somewhat more mixed than had it been a discrete block (open
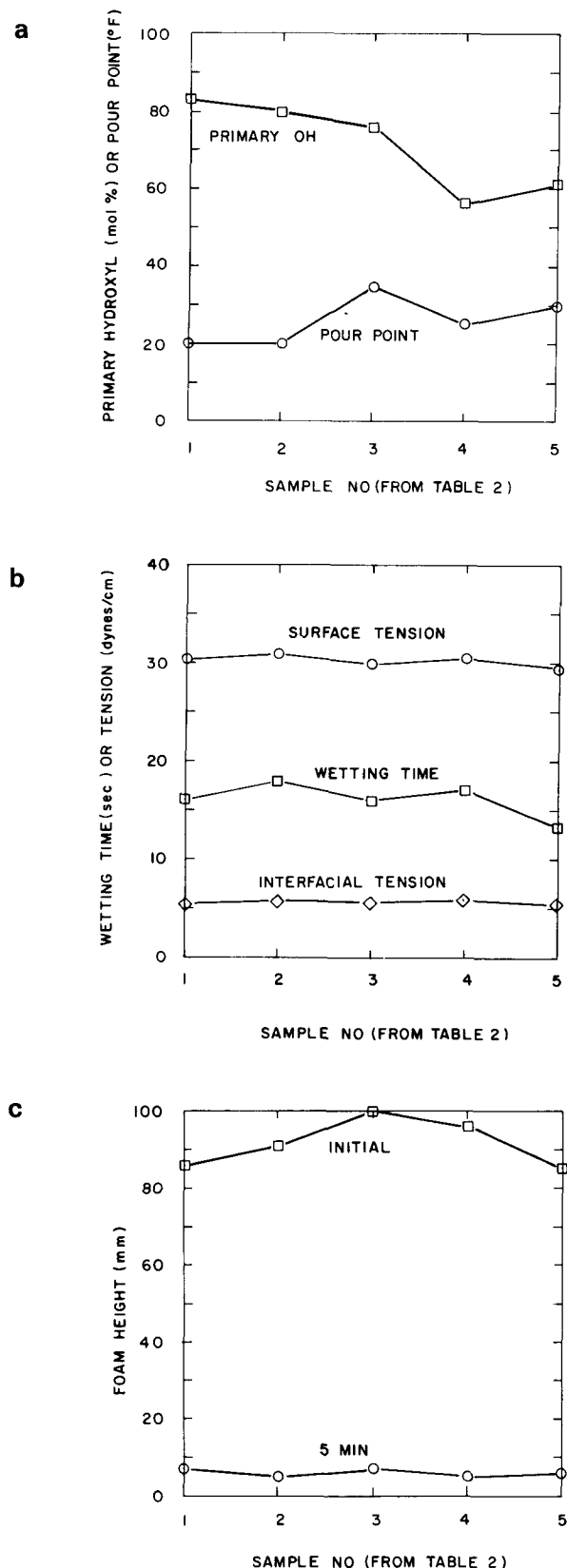
FIG. 4. Effect of PO distribution in $C_{10\ 12}O(7.5\ EO, 1.5\ PO)H$ on a, primary hydroxyl value and pour point; b, wetting and tensions, and c, foaming.

TABLE 2

Increased PO/EO Mixing

| Sample	Structure	Mode of Addition
1.	$C_{10\ 12}O(EO)_3\ _7(PO)_1\ _5(EO)_3\ _7H$	Digested blocks
2.	$C_{10\ 12}O(EO)_2\ _7(PO)_1\ _5(EO)_5\ _2H$	Overlapping blocks
3.	$C_{10\ 12}O(PO)_0\ _{75}(EO)_3\ _7(PO)_0\ _{75}(EO)_3\ _7H$	Overlapping blocks
4.	$C_{10\ 12}O(EO)_2\ _5(PO)_0\ _{75}(EO)_2\ _5(PO)_0\ _{75}(EO)_2\ _5H$	Overlapping blocks
5.	$C_{10\ 12}O(PO)_0\ _5(EO)_2\ _5(PO)_0\ _5(EO)_2\ _5(PO)_0\ _4(EO)_2\ _5H$	Overlapping blocks
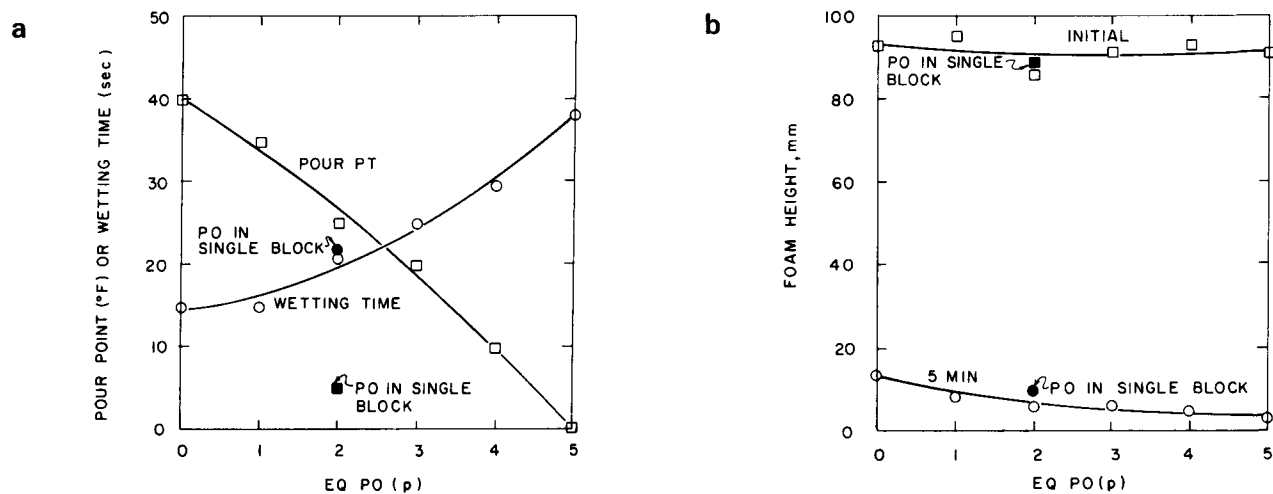
FIG. 5. Effect of PO in $C_9PhO(nEO,pPO)H$ with 55-60 C cloud points on a, pour point and wetting, and b, foaming.

symbols in Fig. 6). The 2-mol PO adduct contained the propylene oxide as a discrete block in the middle of the EO chain (solid symbols). This last sample did have a much lower pour point of 35 F, but its wetting time was much longer than those of the other adducts. Surface tension appeared to increase in direct proportion to the amount of propylene oxide regardless of mode of addition (from 33 to over 35 dynes/cm for 0 PO to 2 PO).

These two latter studies make clear that inclusion of propylene oxide within nonylphenol ethoxylates has an adverse effect on surfactant properties which is not outweighed by the benefits of having lower pour points.

Gelling of PO-containing alcohol ethoxylates. Gelling tendencies of ethoxylates containing a central PO block are reduced compared to conventional ethoxylates. This property is an advantage for the preparation of aqueous formulations by allowing the use of cooler blending temperatures.

The beneficial effect of PO was quite substantial with the $C_{10\ 12}$ alcohol adducts (Table 3); gel temperature (i.e., where gel "melts" on warming) dropped from 32 C to 16 C as 1.0 equivalent PO was inserted into the polyoxyethylene chain. Coconut alcohol adducts showed much less drop in gel temperature: from 41 C to 35 C (3 eq. PO).
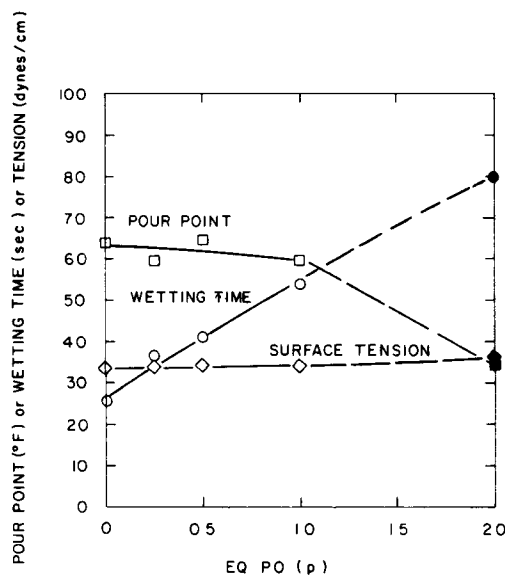
FIG. 6. Effect of PO in $C_9PhO(nEO,pPO)$ with 80-85 C cloud points on surfactant properties.

TABLE 3

Effect of PO Block Size on Gel Temperature RO(EO)$_{n/2}$(PO)$_p$(EO)$_{n/2}$H

| R	n, eq.	p, eq.	Cloud pt.	Gel temp. 50% aq. solution
C$_{10\ 12}$	6.5	0	63 C	32 C
	7.1	1.0	56 C	16 C
	7.2	1.5	59 C	16 C
Coco (C$_{12\ 14}$)	7.3	0	59 C	41 C
	7.1	1.0	57 C	39 C
	8.0	2.0	58 C	37 C
	8.3	3.0	57 C	35 C

Figure 7 is a phase diagram of C$_{10\ 12}$ alcohol-EO-PO-EO adducts and water. Narrowing of the gel region and lowering of the gel temperature as the PO block size was increased from 0 to 2 equiv. are readily apparent.

Odor reduction. An unexpected advantage of PO incorporation is the virtual elimination of fatty alcohol odor in the adducts. The PO acts as a scavenger of unreacted alcohol which in conventional ethoxylates may be present to the extent of several percent. The 1-PO adducts of the alcohols have much lower vapor pressure and hence much less odor.

Lack of odor is especially welcome in aerosol and pump spray liquid cleaning products. Less fragrance is required, and less remains on the treated fabric or hard surface.

REFERENCES

1. Schmolka, I.R., in *Nonionic Surfactants*, edited by M.J. Schick, vol. 1, Surfactant Science Series, Marcel Dekker, Inc., New York, NY, 1967, p. 300.
2. Schmolka, I.R., *Ibid.*, p. 308.
3. Decker, Q.W., E. Martin and R.J. Morlino, European Patent 51,878.
4. O'Connor, J.M., M. Scardera and F.R. Grosser, European
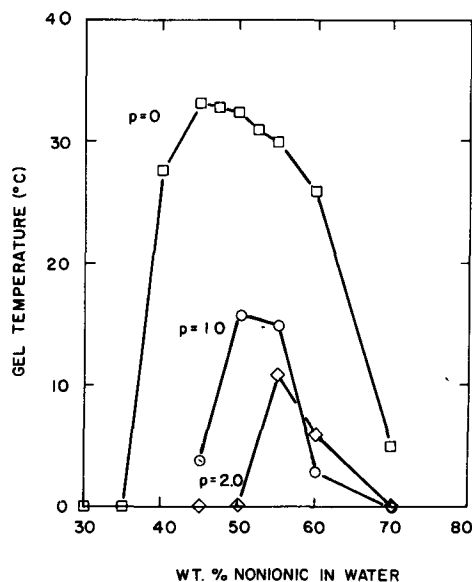
FIG. 7. Gel points of nonionics C$_{10\ 12}$O(EO)$_{n/2}$(PO)$_p$(EO)$_{n/2}$H.

patent 129,328.
5. Stahel, F.H., U.S. patent 4,299,994.
6. Kiessling, D., et al., European patent 19,193.
7. Nippon Shokubai Kagaku Kogyo Co. Ltd., Japan patent 59 164,743 (CA 102:26884).
8. Arai, K., and T. Baba, Japan patent 53 58,508 (CA 89:181497).
9. Scardera, M., and R.N. Scott, U.S. patent 3,956, 401.
10. Scardera, M., and F.R. Grosser, U.S. patent 4,317,940.
11. Wiedemann, A., U.S. patent 4,115,457.
12. Tsatsos, W.T., R.F. Schimbor and R.C. Morris, U.S. patent 3,567,784.
13. Milligan, J.G., U.S. patent 3,752,857.
14. Milligan, J.G., U.S. patent 4,134,854.
15. LeBas, C.L., and P.A. Turley, *J. Cell. Plast.* May-June 1984, p. 194.