imidazoline yields equal rewets at 0.1 and 0.15% and is only slightly reduced at 0.2%, the DADMAC yields essentially zero rewets at 0.15% and 0.20%.

Level of use of the DADMAC is therefore more critical and overuse will present rewet problems. Such problems are commonly overcome in practice by incorporating suitable rewet agents, e.g. ethoxylated quaternaries.

With the quaternized imidazoline the unsaturation present in alkyl groups affects rewettability. Table IV shows that rewettability increases slightly with the iodine value of the tallow employed for alkylation.

A summary of data for the various bisquaternaries tested is given in Table V.

Considering the effect of bridging moiety, p-xylylene, 2-butene, and 2-butyne bridges yield very good to excellent softeners, and with dialkyl groups of C_{18}, give softening essentially equal to DADMAC. However, rewettabilities become extremely low with these materials. With the 2-butene, a series for study of alkyl chain length indicated that softening does diminish but only to a slight extent on reducing the chain from C_{18} to C_{12}. Rewettability of these samples does increase dramatically with reduction of alkyl chain length.

With the 2-butyne bridge, replacement of methyl with hydroxyethyl groups did not alter softening, but unexpectedly reduced rewet. This may be caused by an increased dispersibility of the sample with hydroxyethyl groups which may have produced a more uniform coverage of the fabric surface.

The ether bridged samples tend to give lower softening and higher rewettabilities than the alkene or alkyne-bridged samples.

On examining results for compounds with equal or similar alkyl chain lengths, it is evident that rewettability tends to increase on going from bridging groups of p-xylylene to 2-butene, to 2-butyne, to diphenyl oxide and finally to diethylene oxide. Thus as the bridging unit becomes more unsaturated or more hydrophilic, rewettability increases. The trend of concurrently reduced softening is much less marked, being only apparent on introducing ether linkages.

REFERENCES

1. Linfield, W. M., J. C. Sherrill, G. A. Davis and R. M. Raschke, JAOCS *35*, 590 (1958).
2. Merz, A., Kunstoffe Plastics *8*, 36–45 (1961).
3. Saville, D., Bulletin B-584, Oklahoma State University, July 1961.
4. Linfield, W. M., et al, JAOCS *37*, 248 (1960).
5. Ginn, M. E., F. B. Kinney, and J. C. Harris, JAOCS *38*, 138 (1961).
6. Turer, J., and J. K. Smith, Amer. Dyestuff Reptr. p. 21–24, Jan. 22, 1962.
7. Jungermann, E., and M. E. Ginn, Soap Chem. Spec. *40*, 59 (1964).
8. Minor, F. W., et al. Textile Res. J. *29*, 931, 940 (1959).
9. Onyx Chemical Corp., Technical Bulletin on Laundry Softener, 1963–1964.
10. Holland, V. B., Am. Dyestuff Reptr. *32*, 167 (1943).

[Received May 21, 1965—Accepted October 20, 1965]

Micelle Formation of Polyoxyethylene-Polyoxypropylene Surfactants[1]

IRVING R. SCHMOLKA and ARTHUR J. RAYMOND
Wyandotte Chemicals Corporation, Wyandotte, Michigan

Abstract

Contradictory literature references on their micelle formation led to an investigation of block copolymers of ethylene and propylene oxides. By means of differential absorbance measurements of the dye-surfactant complex, critical micelle concentrations (CMC's) for these polyols were determined. CMC values for surfactants with a molecular weight range of 1,100 to over 15,000 varied from 3.0 to 11.1 μmoles per liter, which are much lower than for other nonionics normally encountered. Corroborative data were obtained by the surface tension depression method. An increase in temperature below the cloud point or the addition of sodium chloride resulted in an increase in the CMC, which is not usual for many nonionics.

Introduction

ALTHOUGH NONIONIC surfactants, which are block copolymers of propylene and ethylene oxides, have been commercially available (1) for a number of years, only scattered references to their micellar nature have been made, and even these few reported results are contradictory. Thus, Mankowich, in a study (2) on the determination of micellar molecular weights of selected surface active agents by the use of light-scattering methods, was led to the conclusion that micelles did not form. He obtained, with a polyoxyethylene-polyoxypropylene glycol of 7200 to 7700 molecular weight, an uncorrected micellar molecular weight of 8400, indicating an aggregation number of about 1.1. The other surfactants which were studied had molecular weights only 1/10 to 1/20 of that of the EO-PO block copolymer.

The second recorded reference to the failure of EO-PO surfactants to form micelles, is the work of Bell (3). In a plot of surface tension depressions vs. concentrations of Pluronic L44, by the duNouy method, over the concentration range of 10 to 1,000 ppm, he reported that the surface tension depression continued to rise with increasing concentration and concluded micelles did not form. However, a similar curve for an octylphenol polyoxyethylene glycol with 9.5 moles of ethylene oxide reached a maximum at 220 ppm.

The analytical ultracentrifuge has also been utilized in an investigation of the micellar character of nonionic detergent solutions. Dwiggins and co-workers reported (4) that Pluronic polyol L64 does not exhibit micelle formation, whereas three other nonionics simultaneously investigated, each of which was less than one fourth of the molecular weight of the polyol, had micellar properties. Dwiggins also reported failure to obtain a break in the surface tension vs. concentration curve.

Although some investigators (5,5a) of the EO-PO block copolymers have attributed solubilization phenomena as due to micellar formation, the first pub-

---

[1] Presented at the AOCS meeting, Houston, April, 1965.

lished mention of this type of surfactant forming micelles is that by Becher (6). It was stated that Pluronic polyol L64 has a CMC of about 260 gamma per gram, or 0.026%. Although not details were reported, it has been learned (7) that the iodine solubilization method was used.

Shortly thereafter Ross and Olivier (8) using the iodine solubilization technique disclosed that the CMC of Pluronic polyol L62 occurs at 2.40 g/dl, or 2.40%. It is interesting to note that the CMC reported for this polyol is far greater than for all but one of the other ten nonionics simultaneously examined. It should be pointed out that at room temperature, a 2.4% solution of Pluronic polyol L62 is not clear, but is faintly opalescent and is just at or below its cloud point of 26C. It was this background of contradictory results that prompted this investigation.

Experimental

A newly described method reported by Becher (9) appeared to offer a facile way to undertake this investigation. It is based upon measuring the change in the absorption spectrum of a dye that occurs as the result of complex formation between the dye and the surface-active agent. Benzopurpurin 4B, a biological stain from Matheson, Coleman and Bell, was used as received. A 0.5% solution of the dye in freshly distilled water was prepared; a freshly prepared dye solution was used each week. Commercial and semicommercial polyoxyethylene-polyoxypropylene block copolymers, Pluronic and Tetronic polyols, from the Wyandotte Chemicals Corporation, were used as the surfactants. All other reagents used were CP grade. Aliquots of a standard surfactant solution were added to 100 ml volumetric flasks, 1 ml of dye solution was added to each, and the flasks were diluted to mark with freshly distilled water. The flasks were shaken, stored in the dark at 25C overnight and then examined the next morning. The total visible absorption spectrum was first obtained on the complex formed between the dye and the surface-active agent over a concentration range of 5x10^{-4} g/dl to 1.0 g/dl, by recording the spectrum on the Perkin-Elmer Spectracord 4000 in a one-centimeter cell. Maximum absorbance was found to occur at 540 mμ. The data were plotted as a function of the logarithm of the concentration vs. the differential absorbance at 540 mμ, giving a curve with a pronounced break at the CMC. The same method was used in all experiments except where indicated. In addition, one set of absorbance measurements was simultaneously checked in the Beckman model DU spectrophotometer, at 540 mμ, and a good agreement was obtained between the two instruments.

Initially an EO-PO block copolymer of 3900 molecular weight, which had no cloud point up to the boiling point of water, and which contains about 60% by weight of ethylene oxide was examined over a wide concentration range, from 5x10^{-5} g/dl through 10 g/dl. The data obtained are shown as the solid line in Figure 1. There appear to be two points of inflection, the first at about 0.0025 g/dl and the second at about 0.01 g/dl. A similar examination of the 23-mole ethylene oxide adduct of lauryl alcohol, which had been used in describing the original method, was carried out over a narrower concentration range, from 5x10^{-4} to 0.1 g/dl. It, too, showed two points of inflection. The first one corresponds to the reported (9) CMC value of 10x10^{-3} g/dl.

It was suggested (7) that the second point of inflection is due to partial exhaustion of the dye. That this appears to be the case was revealed when three times the dye concentration was used. Three milliliters of the 0.5% dye solution was added to each surfactant aliquot. A marked change was noted in the differential absorption, using the original EO-PO surfactant. This is shown as the broken line in Figure 1. We are therefore led to the conclusion that the first point of inflection represents the CMC.

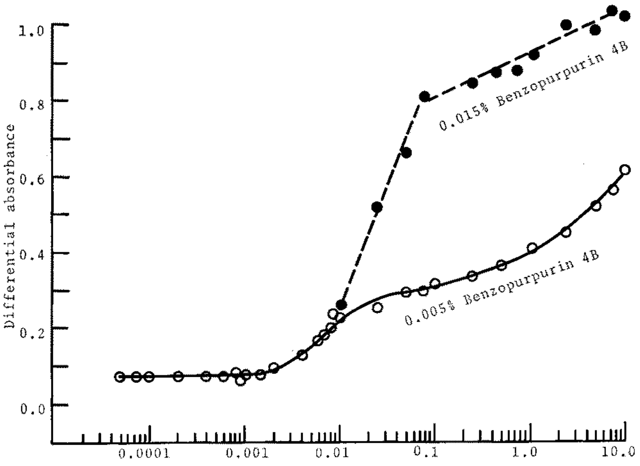

FIG. 1. Differential absorbance of benzopurpurin 4B at 540 mμ as a function of the concentration of an EO-PO block surfactant of 3900 molecular weight, containing 60% EO.

Discussion

Seventeen different block copolymers of propylene and ethylene oxides, derived from a propylene glycol initiator and having a molecular weight range of 1,100 to over 15,000, were studied in a similar fashion. One block copolymer based on an ethylenediamine initiator was also examined. Each surfactant was found to exhibit micelle formation as shown by a plot in the change of absorption spectrum vs. a log of the concentration.

In Table I is a list of the data obtained at 25C, using freshly prepared surfactant solutions. The values obtained, which cover a range of 3.0 to 11.1 μmoles per liter, are much lower than those of other nonionic surfactants. Oxyethylated nonyl phenols, for example, are reported (10) to have CMC values of 75 to 280 μmoles per liter, where the ethylene oxide content ranges from 10 to 50 moles. The so-called "low" CMC for a 100 mole ethylene oxide adduct of octadecanol is reported to be 20 μmoles per liter (10) which is about double that of the highest values obtained in this investigation. Two different lots of

TABLE I

Typical CMC Values of EO-PO Block Surfactants, 25C

Pluronic polyol	Mol. wt.	g/dl	μm/liter
L31	1100	.0033	3.0
L35	1890	.0018	9.5
F38	5020	.0026	5.2
L42	1620	.0018	11.1
L44	2200	.0019	8.6
L61	2000	.0014	8.0
L62	2500	.0017	6.8
L64	2875	.0016	5.6
P66	3915	.0025	6.4
F68	8000	.0055	6.9
P75	4160	.0038	9.1
P84	4520	.0040	8.9
P85	4600	.0037	8.1
F88	10750	.0055	5.1
L92	3480	.0019	5.5
P104	6050	.0044	7.3
F108	15550	.0073	4.7
Tetronic polyol	Mol. wt.	g/dl	μm/liter
707	12250	.0050	4.1

TABLE II

Typical CMC Values of EO-PO Block Surfactants, 25C, μmoles/liter

Hydrophobic base molecular weight	% Oxyethylene content					
	10–20	20–30	40–50	50–60	60–70	80–90
3250			7.3			4.7
2750		5.5				
2250			8.9	8.1		5.1
2050				9.1		
1750	8.0	6.8	5.6		6.4	6.9
1175		11.1	8.6			
940	3.0			9.5		5.2

the same polyol were examined to determine the variation from lot to lot. Reproducible data were obtained with both a hydrophobic and a hydrophilic surfactant.

In Table II, the data are arranged on the basis of their oxypropylene-base molecular weights and their oxyethylene contents. This more readily enables us to make a comparison among the various polyols. The polyols on the right side of Table II, those with an oxyethylene content of 80–90%, are more hydrophilic than those on the left, which have a lower ethylene oxide content. The nonionic polyols represented in the top row, those with the highest base molecular weight of 3250, are more hydrophobic than the corresponding surfactants below them. Although those polymers having polyoxypropylene glycol base molecular weights of 2250 and 3250, exhibit a decrease in CMC as the polyols increase in ethylene oxide content, polymers having lower molecular weights do not follow this trend. Those with a base molecular weight of 1750 decrease, and then increase, as the EO content increases. A plot of CMC values vs. % EO, on a mole basis, gave no clear trend. Therefore, it appears that no valid conclusion can be drawn which would correlate the CMC and a change in oxyethylene or oxypropylene content.

CMC values of several of the polyols were corroborated by surface tension depression measurements over a concentration range of 2.5 to 25,000 ppm. Further substantiation was obtained when we received the unpublished CMC data, on several Pluronic polyols, of Williams and Graham (11). They had measured surface tensions as part of an investigation into detergency (12). Their data, together with our corresponding values from the dye-solubilization technique, are shown in Table III. Agreement between the two methods is good, especially when one considers the results reported by other investigators. The dye absorption method is preferred in that the change in slope of the curve at the CMC is more pronounced than it is with the surface tension method.

To exclude the possibility that the presence of electrolyte from unremoved neutralized catalyst was responsible for these phenomena, a specially clarified sample of surfactant, which contained less than 1 ppm Na and K ion, was studied. The same type of curve was obtained. A few experiments were carried out to determine the effect of added electrolyte. The specially clarified polyol, of 2000 molecular weight, was studied in an aqueous system containing 500 ppm sodium chloride (.0224 N NaCl). In a second experiment, a more hydrophilic polyol, with a 2875 molecular weight, containing about 40% ethylene oxide, was studied in a 0.1 normal saline solution. The data, shown in Table IV, indicate an increase in the CMC of the nonionic polyol as a result of the added electrolyte. Just the opposite effect, namely a decrease in CMC upon the addition of sodium chloride, is reported (10,17) with oxyethylated alkyl phenols. On the other hand, the addition of saline to n-octadecanol + 100 EO is reported (10) to result in little or no change in the CMC value. The data for the more hydrophilic polyol were checked by surface tension measurements. The agreement with the dye absorbance data, as shown in Table IV, is satisfactory.

TABLE III

Comparison of Critical Micelle Concentrations of EO-PO Block Surfactants by Dye Absorption and Surface Tension Measurements at 25C, μmoles/liter

Pluronic polyol	Dye absorption	tension Surface
L44	8.6	9.0 [a]
L62	6.8	7.0 [a]
F68	6.9	7.0 [a]
P75	9.1	9.0 [a]
L64	5.6	4.2

[a] Williams, J. L. and H. D. Graham (11).

TABLE IV

Effect of Added Electrolyte on CMC of EO-PO Block Surfactant Solutions

Method	Pluronic polyol	Solvent	CMC, g/dl	CMC, μmoles/liter
Dye absorption	L61	Water	0.0014	8.0
	L61	0.0224 N NaCl (500 ppm)	0.0023	11.5
Dye absorption	L64	Water	0.0016	5.6
	L64	0.1 N NaCl	0.0030	10.4
Surface tension	L64	Water	0.0012	4.2
	L64	0.1 N NaCl	0.0032	11.1
Surface tension	L64	0.125% $Na_5P_3O_{10}$ 0.050 % Na_2CO_3 0.025% Na_2SiO_3	0.0010	3.5

Because of the excellent detergency properties of the latter surfactant (13), it was of interest to determine whether or not detergent power occurred at the low concentrations at which micellization was found. Dilute solutions were prepared in the presence of the alkaline builders as shown in Table IV. The same ratios of alkaline builders were used as are found in a built heavy-duty detergent. This electrolyte concentration is equivalent to that of a 0.25% solution of a standard detergent formulation containing: 20% polyol, 50% $Na_5P_3O_{10}$, 20% Na_2CO_3 and 10% Na_2SiO_3. A value of 3.5 μmoles per liter was obtained as the CMC under these conditions, which is a slight decrease from the value found in distilled water.

The detergency properties of dilute solutions of this surfactant were studied in the presence of the same alkaline builders. The method involves the removal of an oily tagged clay (Ca^{45}) soil from Indianhead cotton swatches in a miniature washing machine as a basis for evaluation (14). Tests were carried out using tap water at 25C. Detergency properties at or even slightly above the CMC were not found. We are therefore led to the conclusion that for this surfactant, detergent power does not occur at 25C, at the low concentration at which micelles form. This corroborates what has been reported (15) for other nonionic surfactants.

In order to determine the effect of temperature, a comparison was made of the CMC's of the same surfactant at 25C and at 40C. As shown in Table V, a temperature increase of 15C resulted in an increase in the critical micelle concentration from 5.6 to 11.5 μmoles per liter, using the dye-solubilization method.

TABLE V

Effect of Temperature on CMC of EO-PO Block Surfactant Solutions [a]

Method	Temp., C	CMC, g/dl	CMC, μmoles/liter
Dye absorption	25	.0016	5.6
Dye absorption	40	.0033	11.5
Surface tension	25	.0012	4.2
Surface tension	40	.0040	13.9

[a] Solutions of Pluronic polyol L64.

By the surface tension depression method, the same conditions resulted in an increase from 4.2 to 13.9 μmoles per liter. This is in contrast to the data obtained by Schick (16) and by Ginn and co-workers (18). They reported that CMC values of oxyethylated alkanols and alkyl phenols, in general, decreased with increasing temperature.

After this investigation had been completed, it was reported (19) that the CMC's of Pluronic polyols L62, L64 and F68 were 2.40, 2.20 and 0.1 g/dl, respectively. We are unable to account for the discrepancy in the data.

ACKNOWLEDGMENT

T. Kalis and G. Kabalka prepared solutions; R. Seaton carried out the detergency measurements.

REFERENCES

1. "Pluronics—A New Series of Nonionic Surface Active Agents," Form 3013, July 1957, Wyandotte Chemicals Corporation.
2. Mankowich, A., J. Phys. Chem. *58*, 1028 (1954).
3. Bell, W. E., *Ibid*, *63*, 299 (1959).
4. Dwiggins, C. W., Jr., R. J. Bolen and H. N. Dunning, *Ibid. 64*, 1175 (1960).
5. Marcus, A. D., E. Wetstein and M. Ruderman, J. Am. Pharm. Assoc. *17*, 453 (1956).
5a. Blang, S. M., and S. S. Ahson, J. Pharm. Sci. *50*, No. 5, 441 (1961).
6. Becher, P., J. Phys. Chem. *63*, 1615 (1959).
7. Becher, P., private communication.
8. Ross, S., and J. P. Olivier, *Ibid. 63*, 1671 (1959).
9. Becher, P., *Ibid. 66*, 374 (1962).
10. Schick, M. J., S. M. Atlas and F. R. Eirich, *Ibid. 66*, 1326 (1962).
11. Williams, J. L., and H. D. Graham, private communication.
12. 6th Report on Research, The Petroleum Research Fund—482-A1, B, American Chemical Society, 1961, by Williams, J. L., and H. D. Graham, "Study to Correlate Surface Tension Measurements with Detergency."
13. "Pluronic Surfactants for Laundry Formulations," Technical Bulletin, Wyandotte Chemicals Corporation, January, 1962.
14. Hensley, J. W., and C. G. Inks, "Applied Radiation and Radioisotope Test Methods, "STP No. 268, p. 27 (1959).
15. Lange, H., Fette, Seifen, Anstrichmittel *64*, 457 (1962), through Chem. Abs., *57*, 9976 (1962).
16. Schick, M. J., J. Phys. Chem., *67*, 1796 (1963).
17. Hsiao, L., H. N. Dunning and P. B. Lorenz, *Ibid. 60*, 657 (1956).
18. Ginn, M. E., F. B. Kinney and J. C. Harris, JAOCS *37*, 183 (1960).
19. Saski, W., and S. G. Shah, J. Pharm. Sci., *54*, 71 (1965).

[Received July 14, 1965—Accepted September 28, 1965]

Neutral Oil in Linear Alkyl Benzene Sulfonate Slurries: Determination and Composition

K. KELLENBACH, E. EMERY and E. W. BLANK, Colgate-Palmolive Research Center, New Brunswick, New Jersey

Abstract

A method of improved accuracy and acceptable precision for the determination of neutral oil in detergent slurries is described. The increase in accuracy results from minimizing loss of highly volatile constituents of the neutral oil.

The composition of the neutral oil in linear alkyl benzene slurries has been determined utilizing infrared and mass spectrometry techniques.

Highly branched, saturated aliphatic hydrocarbons constitute the principal portion of the neutral oil. Traces of aromatic hydrocarbons are also present. The balance of the neutral oil comprises dialkylsulfones together with trace quantities of unidentified sulfur containing components.

Analogies are drawn between the composition of neutral oil from linear alkyl benzene sulfonates and branched alkyl benzene sulfonates.

Introduction

IN A STUDY OF THE COMPOSITION of neutral oil from linear alkyl benzene sulfonate detergent slurries, it was necessary to isolate a large quantity of the neutral oil without loss of components. An attempt was made to isolate it by scaling up AOCS Tentative Method Dd 4-60 (1). Low recoveries of neutral oil indicated that highly volatile materials are present and lost by volatilization during evaporation of the petroleum ether extract. Weeks et al. (2) describe the determination of unsulfonated oil [1] by distillation of neutralized sulfonate (slurry) with ethylene glycol. The distillation operation is quite rapid, requiring approximately 10 min, and there is no loss of volatile materials. In their opinion the primary properties influencing the quality of alkyl benzene sulfonates are: (a) the amount of unsulfonated oils and (b) product color. For this reason they are not particularly interested in the sulfone content of the neutralized sulfonates except to note that sulfones can be recovered from the still residue by extraction of the latter with petroleum ether. However, in our view, the amount of sulfone present in slurries designated for detergent formulation is considered significant since it exerts a deleterious effect on the performance of formulated products.

Part I of this paper presents evidence that the method of Weeks et al. (2) for the determination of neutral oil when performed in two operations (distillation and extraction) yields results of the same degree of precision but of vastly improved accuracy over the results obtained by use of AOCS Tentative Method Dd 4-60. Part II incorporates a discussion of the composition of neutral oil isolated from typical commercial linear alkyl benzene sulfonate slurries.

Part I—Determination of Neutral Oil

AOCS Tentative Method Dd 4-60 yields results for neutral oil which include such sulfones as may be present. However, inadvertent losses of neutral oil are occasioned in the performance of this method during the operation of evaporation to constant weight. It will be shown in Part II of the present paper that some of the constituents of neutral oil are highly volatile and evaporate spontaneously at room temperature. By determining the volatile constituents of the neutral oil by distillation with ethylene glycol and determining the sulfones and other nonvolatile organic constituents by petroleum ether extraction of the residue in the distillation flask as described by Weeks et al. (2) and combining the two quantities, a result can be obtained for neutral oil which is independent of the variable loss of highly volatile con-

---

[1] Unsulfonated oil is frequently confused with neutral oil and free oil. The term unsulfonated oil is specific but all three have been used interchangeably. In this paper neutral oil refers to material which may consist of unsulfonated oil, sulfones and other concomitant organic constituents in admixture.