some organic residue transparent to UV absorption could be present.

The data obtained in this study indicate that benzene ring biodegradation is obtained with all of the aromatic sulfonates shown in Table III.

Foster et al. (6) have reported that benzene ring biodegradation occurs with commercial LAS compounds. This data, coupled with our results on hydrotrope degradation, indicate that benzene ring residual material is not a problem with biodegradable aromatic sulfonates.

During the biodegradation of these hydrotrope compounds the expected changes in the UV spectrum indicating formation of biological intermediates was not generally observed. It is probable that the transition from initiation of oxidation to ring cleavage is very rapid—some evidence for this was shown in Figure 2 where toluene sulfonate dropped from a level of 75% of its original concentration to zero concentration with an essentially transparent UV spectrum, in one day. It is also quite possible that biological intermediates might not be released from the oxidizing microorganisms after their formation. Cell extracts will be examined in future studies to explore this possibility.

A special effort was made to detect intermediate compounds by UV analysis in an experiment using a flowing cell arrangement with the DB spectrophotometer. The sample contained in a glass fruit jar was pumped into a second jar from which the solution flowed by gravity through the UV cell and returned to the sample jar. This arrangement prevented the pumping surge through the cell which caused large recorder deflections.

The DB spectrophotometer was allowed to operate continuously through its full cycle, which required about 18 min. The UV span between 300–200 mμ occupied 2 min of this 18-min cycle time.

A reference solution containing medium and sewage inoculum without added detergent was placed in the reference beam of the spectrophotometer using a standard 1 cm cell.

A sample of toluene sulfonate was prepared, inoculated with sewage microorganisms previously adapted to the toluene sulfonate, and the system placed in operation as described above.

The UV spectra indicates a change occurred in 3 hr, and a slight additional change in 20 hr. However, some sample turbidity had developed causing background interference, and since the change between 3 hr and 20 hr appeared to be relatively small, the experiment was discontinued. This study is described principally to indicate this potential application of UV spectrophotometry for the study of transient intermediate compounds.

Dagley et al. (7) mention a biological mechanism involving replacement of an aromatic functional group with hydrogen. If this were the mechanism of biodegradation with these hydrotrope compounds, the resulting hydrocarbons would probably not be detected in the UV analysis at the concentrations employed in this study, due to the decreased absorptivity of both the K and B band systems and the shift to a very short wave length of the sensitive K band.

However, this mechanism is considered to be unlikely with these compounds. When sulfonate group cleavage does occur, it is expected that the mechanism would follow one of the well-known aromatic pathways involving hydroxylation, and subsequent ring cleavage.

It does appear that the biodegradation of the compounds reported in this study provide little or no extracellular build-up of an aromatic biological intermediate, indicating a quick benzene ring cleavage once bio-oxidation has been initiated, or a retention of the intermediates by the microorganisms.

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Performance Evaluation of Selected Fabric Softeners

M. E. GINN, T. A. SCHENACH and ERIC JUNGERMANN, Armour Grocery Products Company, Household Products Research and Development Department, Chicago, Illinois

Abstract

Some methods and variables of importance in softener evaluation were examined. A subjective, paired-comparison panel method is recommended for softening measurement, and a dye wicking method seems most reliable for rewettability measurement. Use of these methods shows that softening tends to decrease and rewettability to increase with unsaturation and introduction of ether groups in bridging radicals and with reduction of alkyl chain length, in a word with increasing hydrophilicity of various radicals. Rewet data are particularly sensitive to these effects. For excellent softening, two long chain alkyl groups are apparently required, and these should be at least C_{16} and more preferably C_{18} in length.

Introduction

CATIONIC SOFTENERS are in widespread use for the treatment of fabrics in commercial laundries and hospital institutions, and are now available in household products. These agents are added to the rinse water during normal laundering to impart softness, fluffiness, and antistatic qualities to the fabric (1,2,3). Agents may be included in softener products to change antibacterial effect (4). Cationic softeners are usually quaternary ammonium compounds such as dialkyldimethylammonium chloride (DADMAC), where the alkyl group is derived from hydrogenated tallow, ethoxylated analogues and imidazolinium salts. These compounds are highly substantive on cotton and rayon fabrics and when absorbed, produce desired effects (5).

Excluding germicidal properties, the criteria of importance in evaluation of fabric softeners are listed as follows: 1) dispersibility in rinse or wash liquor; 2) substantivity on fabric load, notably cotton; 3) impartment of softness, fluffiness, lubricity (without greasiness) and antistatic effects to improve fabric handle; 4) nonyellowing and nongraying in effect; preferably brightening; 5) fabric rewettable after treatment.

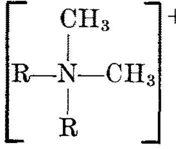
An effective softener must be readily dispersible in the rinse water and rapidly sorbed so that uniform deposition on fabric can occur within the relatively short exposure times. Exhaustion must occur within 5 min in order for the softener to be effective and economically useable. The softener must impart softness, fluffiness and lubricity to treated cloth and reduce static charges particularly in the case of hydrophobic fabrics such as Nylon, Dacron, Orlon and acetate cotton (1,6). These effects should be achieved without loss of fabric whiteness or brightness, and treated cloth should retain its ability to absorb water in subsequent use for drying the body and other surfaces.

Measurement of softness and rewettability are considered the most important criteria for primary screening of softeners. These two aspects are the main subjects of this paper, which will be limited to quaternary ammonium salts. Other softeners, such as amine oxides (7) or nonionics, will not be covered.

Experimental

Cationic softeners employed in this study are quaternary ammonium salts:

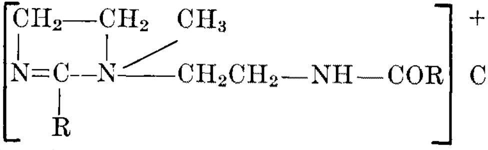
(1) *Dialkyldimethylammonium chloride* (DADMAC)



$$\left[\begin{array}{c} CH_3 \\ | \\ R{-}N{-}CH_3 \\ | \\ R \end{array}\right]^{+} Cl^{-}$$

Cl—; R = Alkyl group derived from hydrogenated tallow.

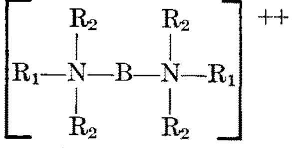
(2) *Quaternized imidazoline*



$$\left[\begin{array}{l} CH_2{-}CH_2 \quad CH_3 \\ | \qquad\quad | \diagup \\ N{=}C{-}N{-}CH_2CH_2{-}NH{-}COR \\ \quad | \\ \quad R \end{array}\right]^{+} CH_3SO_4^{-};$$

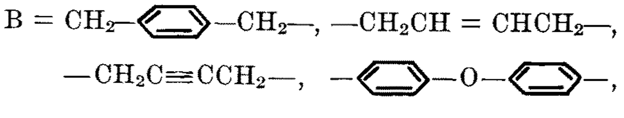
R = Alkyl group derived from partially hydrogenated tallow.

(3) *Bisquaternaries*



$$\left[\begin{array}{c} R_2 \qquad R_2 \\ | \qquad\quad | \\ R_1{-}N{-}B{-}N{-}R_1 \\ | \qquad\quad | \\ R_2 \qquad R_2 \end{array}\right]^{++} 2\ Cl^{-};$$

$R_1 = C_{12}H_{25}—, C_{14}H_{29}—, C_{16}H_{33}—, C_{18}H_{37}—$
$R_2 = CH_3—, HOCH_2CH_2—,$



$B = CH_2{-}C_6H_4{-}CH_2—, —CH_2CH = CHCH_2—,$

$—CH_2C{\equiv}CCH_2—, —C_6H_4{-}O{-}C_6H_4—,$

$—CH_2CH_2—O—CH_2CH_2—$

Preparations

Dialkyl dimethyl ammonium chloride (DADMAC, alkyl groups from hydrogenated tallow).

This was obtained from Armour Industrial Chemical Company as a white crystalline powder, 98–100% active (Arquad 2HT).

2-Butene-bridged bis-quaternaries

These were prepared by quaternization of the appropriate amine with 1, 4-dichloro-2-butene (DuPont, 95% *trans* isomer). The following preparation is representative:

2-Butene-1, 4-bis (dimethyl dodecylammonium chloride). A one-liter round-bottom flask was charged with 226 g (1.05 moles) dimethyl dodecylamine and 500 ml of acetone. 1, 4-Dichloro-2-butene, 63 g (0.5 moles) was cautiously added and the mixture refluxed gently with stirring. In 3 hr, a heavy white precipitate of the *bis*-quaternary was formed. It was filtered, washed twice with acetone, and air-dried. A yield of 232 g (83%) of 99% active product was obtained.

Diphenyl oxide bridged bis-quaternaries

These were prepared from p, p′-*bis*-(chloromethyl) diphenyl oxide (Dow Chemical Company's "DiCM-DPO") as illustrated below:

p,p′-Oxydibenzyl-bis(N, N-dimethyl-N-tetradecylammonium chloride). A 500 ml round-bottomed flask was charged with 37 g (0.15 moles) of dimethyl tetradecylamine, 150 ml of ethyl acetate, and 20 g (0.075 moles) p,p′-*bis* (chloromethyl) diphenyl oxide. The mixture was refluxed 1.5 hr, at the end of which time a white precipitate had formed. The reaction mixture was cooled, diluted with ethyl ether, and the resulting precipitate filtered, washed with cold ethyl acetate, and air-dried. The yield was 45 g (80%) of 97% active product.

Diethylene oxide-bridged bis-quaternaries

2,2′-Oxydiethyl-bis(N,N-dimethyl-N-octadecylammonium chloride). A mixture of 75 g dimethyl octadecylamine, 50 ml isopropanol, and 100 ml (excess) *bis* (2-chloroethyl) ether was refluxed for 6 hr, then allowed to cool. The resulting white precipitate was filtered, washed with acetone, and air-dried. The yield was 82 g (88%) of product titrating 88% active.

p-Xylylene bridged bis-quaternaries

p-Xylylene-bis (dimethyl octadecylammonium chloride). A mixture of 0.275 moles dimethyloctadecylamine, 0.25 moles p-xylylene dichloride, 300 ml n-propyl alcohol, and 20 ml of water was refluxed 4 hr. The solvent was removed under vacuum and the residue was recrystallized from a 4:1 mixture of ethyl acetate-isopropanol. The white crystalline product was filtered, washed with petroleum ether, and air-dried. Yield 99% of 99.5% active product.

2-Butyne-bridged bis-quaternaries

2-Butyne-1, 4-bis(dimethyl octadecylammonium chloride). To a mixture of 0.2 moles dimethyl octadecylamine, 400 ml n-propyl alcohol, and 25 ml of water was cautiously added 0.1 moles 1,4,-dichloro-2-butyne. The mixture was refluxed 8 hr, the solvent removed under vacuum, and the residue was recrystallized from ethyl acetate. The resulting white crystalline product was filtered, washed with petroleum ether, and air dried. Yield, 87.5% of 100% active product.

2-Heptadecyl-1-methyl-1-stearamidoethyl-imidazolinium methyl sulfate (quaternized imidazoline). This was obtained from Armour Grocery Products Company.

Evaluation

Softeners were usually tested at 0.1% active concentration on cloth, applying the softeners as 100

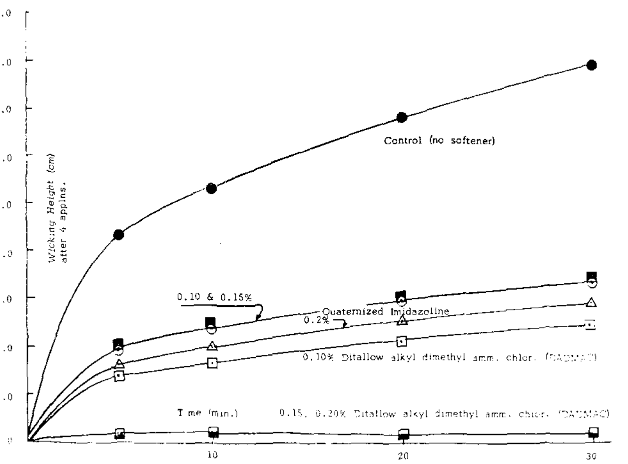


FIG. 1. Effect of concentration basis fabric for the bisquaternary, p-xylylene bis (octadecyl dimethyl ammonium chloride).

ml aqueous dispersions at the beginning of the deep rinse, and evaluating them according to the multiwash dummy bundle technique described below:

Multiwash Softener Evaluation

Top-loading automatic washers and machine dryers were used in these tests. Each softener was applied four times to a wash load consisting of the following: 1) a 6-lb dummy bundle of desized mixed cottons; 2) four terrycloth swatches for softness measurement (two swatches were withdrawn for panelling after the first and fourth application of softener); 3) one diaper for rewettability testing (three 1½ in. widths were removed after the first and the fourth applications).

The following wash schedule was carried out. 1) desize with soap and metasilicate and machine dry; 2) wash with household laundry detergent; 3) apply softener at beginning of deep rinse; 4) machine dry; 5) repeat steps 2 to 4 until four applications of the softener have been made. (Test swatches conditioned overnight at 75F, 40% relative humidity before testing.)

Terry cloth swatches were found to be excellent fabric for evaluating softness, and diapers for subsequent testing of rewettability. Since softeners will build up on cloth after repeated application, swatches were evaluated after both one and four applications of softener. The wash schedule included a detergent wash prior to each softener addition so that home use procedures were approximated. Soil was omitted to avoid erratic results.

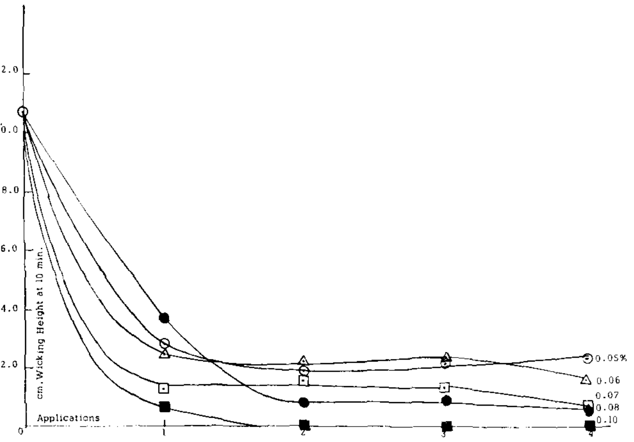


FIG. 2. Rewettability for tallow dialkyl dimethyl ammonium chloride (DADMAC) and a quaternized imidazoline.

TABLE I

Softener Panel Data Related to Concentration

% Conc.[a] based on cloth	Cumulative panel votes from paired Comparisons after applications: 1	4	Softness rating
0.05	8	6	Fair
0.06	17	6	Good
0.07	18	22	Excellent
0.08	22	18	Excellent
0.10	15	28	Excellent

[a] Softener: p-xylylene bis (octadecyldimethylammonium chloride).

Softness Evaluation

Following overnight conditioning at 75F and 40% relative humidity, terry cloth swatches were evaluated for softness by a small expert panel using a paired comparison technique. The usual softener panel involved the following: 1) four expert panelists; 2) five systems (softeners, controls, or blanks) usually evaluated (A–E); 3) two terry cloth swatches (1 and 2) per system or softener. Each panelist makes the following comparisons and selects the softest swatch in each pair, e.g. for softeners A–E: (repeated with the duplicate swatches)

A_1 vs B_1
A_1 vs C_1 B_1 vs C_1
A_1 vs D_1 B_1 vs D_1 C_1 vs D_1
A_1 vs E_1 B_1 vs E_1 C_1 vs E_1 D_1 vs E_1

So for five systems there are $10 \times 4 \times 2 = 80$ total votes. There are 8 votes maximum possible for one softener in each paired comparison, and 32 votes maximum possible for any given softener.

Five softeners including controls are usually evaluated by one panel. Each swatch is compared against another swatch and a preference or vote is made. Two swatches are tested for each softener at each application to check variability in wash load. Softeners are then ranked according to the number of votes received. This technique is found more reliable and less confusing to the panelists than the series ranking method.

A typical score sheet for two hypothetical test softeners A and B is shown below:

Softener Panel Score Sheet

(One application)

Sample	Votes when compared with Control (0.1%)	A (0.1%)	Control (0.05%)	B (0.1%)	Blank	Total	Rank
Control (0.1%)	..	4	6	7	8	25	1
A (0.1%)	4	..	7	5	8	24	2
Control (0.05%)	2	1	..	6	8	17	3
B (0.1%)	1	3	2	..	6	12	4
Blank (no softener)	0	0	0	2	..	2	5
						80	

(Scores are sums for series 1 and series 2 swatches; similar data would be obtained after four applications).

It is useful to include as controls swatches treated with 0.1 and 0.05% (basis cloth) of some reference softener such as dioctadecyldimethylammonium chloride (DADMAC) and also a blank swatch to which no softener has been applied. In this way, the performance of test softeners A and B can be described in terms of the performance of a well-known softener. In this case, "A" would be considered highly effective and equal to the reference softener. "B" at the 0.1% level has some effect over no softener but is inferior to the reference material at 0.05% level. It is pointed out however, that care must be employed

TABLE II

Rewet Data Comparing Method Reproducibility Data for Replicates Within One Wash Load

Secs. swatch sinking time[a]	Secs. tape sinking time[b]	Cm. dye wicking height[c]
79	21	6.2
45	146	6.1
65	75	6.0
45	29	5.8
31	47	5.6
240	159	5.5

[a] Terry cloth. [b] Cotton tape. [c] Curity diaper (20 min. readings).

in expressing results since softening is not linearly but rather is apparently logarithmically related to softener concentration.

Rewettability Measurements

Three methods were studied for measuring fabric rewettability. The first two involve measuring sinking times in water for treated terry cloth swatches or cotton tapes (1). The third method, found most reliable and quantitative, measured the rate of wick-up of an aqueous dye solution along a suspended strip of treated diaper cloth (8–10). A 0.18% aqueous solution of FD & C Acid Red (e.g. Azo Phloxine, General Dyestuff Corp.) is prepared and an aliquot placed in a graduated cylinder. One- to two-inch wide strips of treated diaper material are suspended into the dye solution, using a glass rod sewn into the strip at the bottom for weight and a slitted cardboard at the top of the cylinder so that with the aid of paper clamps, the strip could be immersed to a depth of 3 cm in the dye solution. A stopwatch is started as soon as the strip is immersed and centimeter height of dye solution was recorded at 5, 10, 20 and 30 min.

Data and Discussion

Variables in Measurement

1) *Softener Concentration.* Data given in Table I for a bisquaternary show the nonlinearity of preferred softness with respect to softener concentrations. Apparent for this softener is a critical concentration range on cloth between 0.05 and 0.07% in which softening increases very rapidly with concentration, moving from fair to excellent at 0.07% and remaining essentially unchanged up to 0.1% concentration. It would seem logical that once a monolayer or near fraction thereof on cloth is realized, further increase in softener level may not increase softness (but rather greasy feel).

TABLE III

Relative Agreement Between Swatch Sinking and Dye Wicking Methods

Test method	Sample	Data for applications					
		0	1	2	3	4	5
					secs:		
Swatch sinking	DADMAC[a]	8	140	106	23	57	34
	Quaternized Imidazoline	8	33	16	32	48	14
	Bisquat. from p-xylene[b]	6	292	300	300	252	300
					cm		
Dye wicking	DADMAC[a]	10.7	5.4	4.6	4.3	3.4	
	Quaternized Imidazoline	10.7	5.9	5.4	4.9	4.8	
	Bisquat. from p-xylene[b]	10.7	2.2	0.8	0.9	0.0	

[a] DADMAC = dialkyldimethylammonium chloride, alkyl groups from hydrogenated tallow.

[b] p-xylylene bis(octadecyldimethyllammonium chloride).

[c] Terry cloth swatch sinking times given in seconds. Values increase with decreasing rewettability.

[d] Diaper strip wicking heights at 10 min. Values decrease with decreasing rewettability.

TABLE IV

Effect of Unsaturation of Alkyl Groups on Rewettability from Quaternized Imidazoline Treatment

Iodine value of alkyl group R	cm wicking after 10 min for applns,				
	0	1	2	3	4
30–32	10.6	5.9	4.5	4.4	4.1
40	10.7	6.4	5.4	5.4	4.7

Figure 1 shows the rewet data corresponding to these softening results. Wicking heights after 10 min are plotted as a function of application number for each softener level. These data suggest that with multiple application, rewettability tends to decrease with increasing softener level. Discrepancies in the concentration effect are particularly evident after only one application, suggesting that data from multiple treatments, e.g. 4, are considerably more reliable than from single treatments.

2) *Fabric Rewettability Measurement.* If water repellant films build up on treated cloth, the cloth may become unable to sorb water in use. A reliable measurement of this key property is therefore needed.

Data comparing the reproducibility of the three rewet tests are listed in Table II. These results show that highly erratic values can arise in either of the sinking methods. The dye wicking method, on the other hand, is considerably more reproducible.

Table III shows that the dye wicking data are in good relative agreement with swatch sinking data and therefore do not introduce artificial results. Thus, both the dye wicking and swatch sinking yielded the same relative ranking for three softeners; i.e., ranked them in order of decreasing wettability as follows: 1) Quaternized imidazoline; 2) dialkyldimethylammonium chloride; 3) bisquaternary derivative of p-xylene.

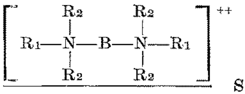
Results for Various Softeners

The quaternized imidazoline yields very slightly lower softening but rewettability is higher than from the dialkyldimethylammonium chloride. The p-xylylene bridged "bisquaternary" equals DADMAC in softening but treated cloth becomes essentially nonwettable within four applications (Table III). These results show that we can have essentially equal softening in a given case, but sharply different rewet properties.

The higher rewettability from the quaternized imidazoline compared to the DADMAC was confirmed by testing at higher levels of 0.15 and 0.2% basis cloth. Figure 2 shows that while the quaternized

TABLE V

Softening by Bisquaternaries
(4-Applications)

	 $\left[R_1-\overset{R_2}{\underset{R_2}{N}}-B-\overset{R_2}{\underset{R_2}{N}}-R_1\right]^{++}$		2 cl⁻		
Bridging moiety B	R_1	R_2	Softness rating[a]	Relative rank	Rewet[b]
p-xylylene:	$C_{18}H_{37}$—	CH_3—	E[b]	..	0.0
2-butene:	$C_{18}H_{37}$—	CH_3—	E	2	0.2
	$C_{16}H_{33}$—	CH_3—	E	1	1.3
	$C_{14}H_{29}$—	CH_3—	E	3	4.0
	$C_{12}H_{25}$—	CH_3—	VG	4	15.0
2-butyne:	$C_{18}H_{37}$—	CH_3—	E	1	2.2
	$C_{18}H_{37}$—	$HOCH_2CH_2$—	E	2	0.5
diphenyl oxide:	$C_{16}H_{33}$—	CH_3—	G	2	7.3
	$C_{14}H_{29}$—	CH_3—	VG	1	8.0
	$C_{12}H_{25}$	CH_3—	F	3	12.0
diethylene oxide:	$C_{18}H_{33}$—	CH_3—	VG	..	3.9
(Arquad control			E	..	4.1)

[a] Ratings: E = Excellent; VG = Very Good; G = Good; F = Fair.

[b] cm height wick-up after 30 min.

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.

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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-

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