TABLE II

	80%			100%		
	Ref. loss	Ref. color	Bl. color	Ref. loss	Ref. color	Bl. color
	%	*red*	*red*	%	*red*	*red*
a) Southeast Expeller Oil (1.6% FFA)						
Refined by hydraulic oil conditions						
12° Bé	8.40	13.53	5.24	......	......	......
16°	8.18	11.98	4.74	8.56	11.20	4.28
Refined by Expeller oil conditions + 22° Bé						
16°	8.63	10.85	4.30	......	......	......
20°	9.52	9.92	3.91	10.14	9.29	3.58
22°	10.16	9.97	3.72	10.47	9.15	3.38
b) Valley Expeller Oil (2.1% FFA)						
Refined by hydraulic oil conditions						
12° Bé	9.04	7.96	3.20	......	......	......
16°	8.05	7.60	3.21	8.97	7.26	2.83
Refined by Expeller oil conditions + 22° Bé						
16°	8.96	7.05	2.66	......	......	......
20°	9.62	6.65	2.57	10.85	6.21	2.22
22°	10.17	6.52	2.35	11.39	6.14	2.09
c) Southwest Expeller Oil (0.8% FFA)						
Refined by hydraulic oil conditions						
12° Bé	6.97	6.50	2.87	......	......	......
14°	6.79	6.46	2.60	......	......	......
Refined by Expeller oil conditions + 22° Bé						
16°	7.25	5.71	2.31	......	......	......
20°	7.28	5.47	2.21	7.97	5.33	2.06
22°	7.53	5.35	2.09	8.41	5.04	1.96
d) West Coast Expeller Oil (1.2% FFA)						
Refined by hydraulic oil conditions						
12° Bé	6.31	6.24	2.21	......	......	......
14°	6.10	5.88	2.11	......	......	......
Refined by Expeller oil conditions + 22° Bé						
16°	6.39	5.13	1.80	......	......	......
20°	6.60	4.78	1.54	7.53	4.61	1.44
22°	6.74	4.85	1.57	7.69	4.47	1.40

A comparison of the settlement results on the four oils, using the hydraulic oil-refining conditions now permitted by the rules, and the criterion of this experiment (the lowest loss with a bleach color within 0.2 red above the lowest bleach obtained) is of interest (Table III).

TABLE III

Oil	Present settlement rule		Experimental settlement criterion		Difference in loss	Difference in bl. color
	Loss	Bl. color	Loss	Bl. color		
	%	*red*	%	*red*	%	*red*
Southeast	8.56	4.28	10.14	3.58	+1.58	−0.70
Valley	8.05	3.21	10.85	2.22	+2.80	−0.99
West Texas	6.79	2.60	7.28	2.21	+0.49	−0.39
West Coast	6.10	2.11	6.60	1.54	+0.50	−0.57

These results confirm the conclusion of the earlier work of the committee, reported in September 1958, that the use of hydraulic oil refining conditions on current Expeller oils for settlement purposes (Rule 150) results in a substantial under-refining of the oil compared to the requirements of commercial practice.

Examination of the individual data reveals that the experimental criterion of adequate refining was met in all cases by the 16° and 20° Bé results, *i.e.*, the current conditions specified for Expeller oil if the seller does not choose the hydraulic oil conditions. This report is published because it is believed that the work will be of general interest.

D. L. HENRY, chairman

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Effect of Temperature on Critical Micelle Concentration

M. E. GINN, F. B. KINNEY, and J. C. HARRIS, Monsanto Chemical Company,
Research and Engineering Division, Dayton, Ohio

REVIEWS of the literature of critical micelle concentration (cmc) and solubilization by Klevens (6, 8) indicated some of the conflicting views concerning the effect of temperature on these measurements. Since no concise collection of the various statements had been made, these are shown in Table I.

Certainly some of the apparent disagreement may be attributed to the method and conditions chosen for measurement of critical concentration and to the samples investigated. Some ionic surfactants measured by conductivity procedures showed cmc increases with increasing temperature while the converse was found when using the spectral dye method. Results with the latter method were attributed to changes in dye aggregation and not to micelle formation (7).

In cases where the same compounds have been used, a difference in method for measurement may affect the magnitude of the change. In general, it appears that the most marked changes in the measurement value and in cmc occur above 40°C. though here a contrary report (2) appears. Another (3) indicates independence of cmc and temperature, and still another points out for organic liquids that their solubilization is reduced by increased temperature (18). However the general consensus for ionic surfactants seems to be that cmc increases with increase in tem-

TABLE I

Literature Values of the Effect of Temperature on cmc

Surfactant	Temperature range, °C.	Procedure	Effect of temperature increase	Ref.
Na Soaps—C_5–C_{18}	20–>40	Refraction	Increase in cmc marked above 40°C.	6
Miscellaneous	30–50	Solubilization (of dimethyl-aminoazobenzene)	Solubilization and cmc increase	10
Lauryl sulfonic acid Potassium laurate	0–90	Conductivity	Above 50°C. cmc increases	1
Na C_{10}–C_{18} alkyl sulfates	....	Visual	Solubilization of organic liquids reduced by increase	18
Na C_{10}, C_{12}, C_{16} sulfonates	40–80	Conductivity	Conductance and cmc increase	19
K acetate and laurate	25–35	Density	cmc lower at 35°, less change in cmc above 35°	2
Na myristate	17–80	Conductivity	Increase in conductance and cmc	4
Na laurate and myristate	17–80	Conductivity	No change	3

perature. Critical micelle values for nonionic surfactants are not extensive, and no work concerning cmc-temperature dependence for them appears to have been made.

The need for studies to clarify the status of temperature dependence of cmc is apparent, particularly as this factor can have considerable practical importance. Measurement of cmc at a variety of temperatures is a tedious operation, and it frequently may be adequate only to estimate the extent of a predictable trend, provided that the trend has been determined. This paper reports the magnitude and direction of change in cmc for several anionic and nonionic surfactants as measured at 25, 50, and 75°C.

Experimental

Since both anionic and nonionic surfactants were to be examined in this study, a method for determination of cmc was required which was applicable to both types, eliminating as possibilities those procedures dependent upon the ionic character of the compound. Chosen was a dye solubilization technic (10, 11, 13, 14, 16, 17). Preliminary evaluation indicated, as others had found (11), that 1-o-tolylazo-2-naphthol (External Orange No. 4, originally Orange OT) was less soluble in these systems than dimethylaminoazobenzene (DMAB) and additionally that slightly better reproducibility was attainable with it.

Procedure. External D & C Orange No. 4 was purified by recrystallization (20 g. from 1,800 ml. of ethanol, followed by vacuum drying at 50°C.). Calibration curves of concentration *versus* optical densities were prepared by replicate measurement at 500 mμ in a ½-in.-diam. test tube, using a Spectronic 20 (Bausch and Lomb) spectrophotometer.

Dye in 25-mg. quantities was transferred to 25 × 95-mm. vials fitted with foil-lined (tin or silver, 10 mil in thickness) screw caps. Stock solution of surfactant was pipetted to the vials, and distilled water was added to provide proper dilution, covering a range of concentrations. The vials were rotated 16 hrs. at 25°C. Following the rotation period, the samples were stored upright for 24 hrs. at 25°C. Three-ml. samples of the supernatant liquid were filtered through small plugs of absorbent cotton, then transferred to photometer test tubes, and diluted with 3 ml. of absolute alcohol. Optical density was measured against a 1:1 ethanol-water solvent blank for zero absorbence. Additional measurements were made at 24-hr. intervals to obtain equilibrium dye solubilities. The dye solubility was then plotted *vs.* surfactant concentration, and the cmc was derived by suitable extrapolation from above and below the region where the greatest change in slope occurred.

Materials Tested. The surfactants used were carefully purified to remove salts or unsulfonated materials resulting from preparation.

Anionics. Shown in Figure 1 for temperatures of 25, 50, and 75°C. are cmc values for five sodium alkylbenzene sulfonates and for sodium n-dodecyl sulfate as a comparison standard. With the exception

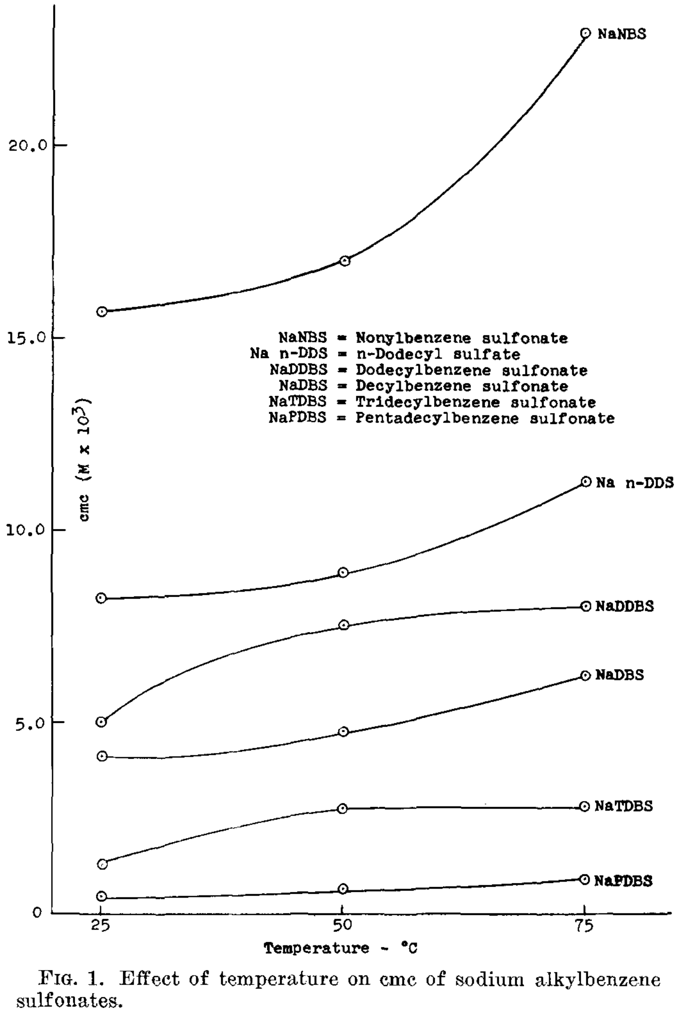

FIG. 1. Effect of temperature on cmc of sodium alkylbenzene sulfonates.

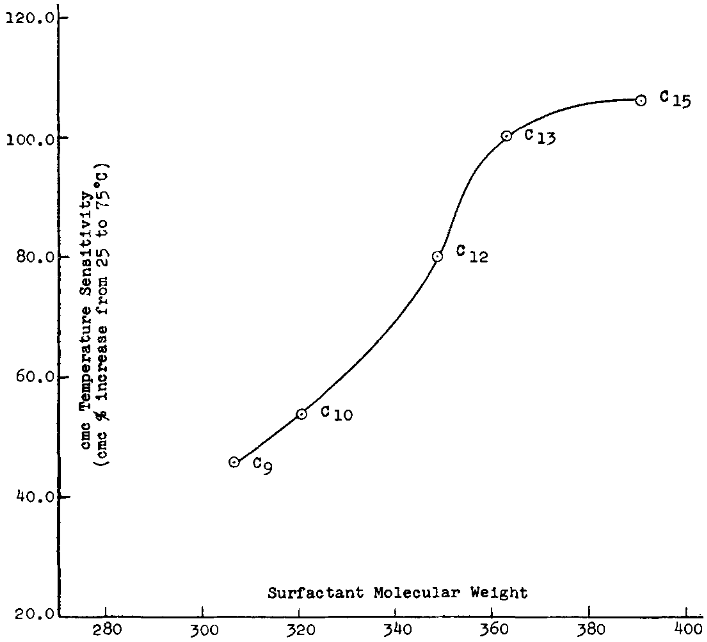

Fig. 2. Temperature sensitivity of cmc values for sodium alkylbenzene sulfonates of varying molecular weight.

of the decylbenzene sulfonate, a keryl-base material, the alkylbenzenes are olefin-derived, hence they are considerably branched in character. Difference in branching helps to explain the apparently anomalous position of the decyl compound.

Temperature sensitivity (percentage change in cmc) of the alkylbenzene sulfonates is plotted in Figure 2 as a function of surfactant molecular weight.

Nonionics. The nonionics tested were laboratory-prepared samples. In each case of varying ethylene oxide (EO) chain length, the same hydrophobe base (alcohol or alkylphenol) was employed. The hydrophobe bases however are not homologous, and this prevents a truly quantitative evaluation of the effect of hydrophobe variation on cmc for these compounds but permits some pertinent conclusions.

Table II shows the cmc data for 5 to 30 mole EO adducts of decanol, tridecanol, nonylphenol, and dodecylphenol; all the hydrophobes are branched-chain compounds.

TABLE II

Fundamental Data for Homologous EO Condensates

Surfactant	Formula weight	Cloud-point (°C.)	cmc—% Concentration		
			25°C.	50°C.	75°C.
Decanol+ 5.0 EO	378	<4	0.063	0.060	0.040
Decanol+10.0 EO	598	88	0.16	0.096	0.085
Decanol+14.9 EO	814	>99.8	0.28	0.144	0.12
Decanol+20.0 EO	1038	>98	0.60	0.29	0.19
Decanol+29.4 EO	1452	>98	0.83	0.45	0.34
Tridecanol+ 5.2 EO	426	<0	0.0058	0.0050	0.0065
Tridecanol+10.1 EO	646	61.3	0.010	0.0078	0.00757
Tridecanol+15.2 EO	866	>98	0.023	0.015	0.010
Tridecanol+20.0 EO	1080	>98	0.030	0.019	0.018
Tridecanol+30.6 EO	1545	>98	0.080	0.046	0.025
Nonylphenol+ 5.0 EO	442	<0	0.0025	0.0010	0.0019
Nonylphenol+ 9.8 EO	651	57.8	0.0040	0.0043	0.0042
Nonylphenol+15.4 EO	851	>98	0.0070	0.0070	0.0092
Nonylphenol+20.0 EO	1100	>98	0.010	0.010	0.012
Nonylphenol+30.2 EO	1550	>98	0.024	0.020	0.019
Dodecylphenol+ 5.0 EO	484	<0	0.00075	0.0005	0.0005
Dodecylphenol+10.2 EO	709	36.8	0.0010	0.0005	0.0005
Dodecylphenol+15.1 EO	939	>98	0.0015	0.0010	0.0010
Dodecylphenol+20.1 EO	1145	>98	0.0020	0.0010	0.0010
Dodecylphenol+30.6 EO	1607	>98	0.0038	0.0010	0.0010

Discussion

Anionics. Figure 1 shows that cmc increases with surfactant concentration for sodium n-dodecyl sulfate and presents the data for the series of sodium alkylbenzene sulfonates. This series shows an increase in cmc with temperature increase, confirming the findings of others.

Change in cmc values can be expressed either in total concentration units or as percentage change from the value at the initial temperature. In the case of the lower cmc range (and thus more effective surfactants), the unit change in cmc is of a low order of magnitude. Expressed as percentage change, the sensitivity of cmc to varying temperature is greatest for the higher molecular weight (low cmc range) compounds. The greatest change in cmc in terms of total concentration units occurs for the lowest molecular weight compound of the series. These comparisons are shown in Figures 1 and 2.

Both dye solubility and dye solubilizing power of the surfactant solutions are increased with increasing temperature. In general, cmc increases with temperature increase and the greatest degree of change seems to occur between 50 and 75°C.

Conclusions of others (2, 3) that cmc is temperature-independent might be arrived at on the basis of unit cmc change by examining surfactants of sufficiently large molecular weight or by having selected a sufficiently narrow temperature range for measurement.

Nonionics. This important class of surfactants has received comparatively little attention in micelle studies for two reasons: a) nonionics are difficult to measure since their unreactivity and nonionic character prevent the use of such popular methods as spectral dye and conductivity, and b) nonionic EO condensates of alcohols, alkylphenols, etc., as normally prepared are impure; each is a mixture of compounds of varying EO chain length, according to the literature (15), approaching a normal distribution. Preparation of, or purification to, single-species compounds is difficult and laborious and rarely has been attempted.

Kushner and Hubbard reported (12) that, in contrast to ionic types, there is no well defined cmc for nonionics (specifically Triton X-100) by turbidimetric measurements. Hsaio *et al.* (5) however found that the surface-tension method, *i.e.*, extrapolation of plots of surface tension *vs.* log concentration, could be applied to nonionics. Our work also showed the applicability of the surface-tension method. However, for many nonionics, particularly higher EO adducts, the change in surface tension with respect to concentration is so gradual and erratic below the cmc that reliable extrapolation was difficult. These difficulties were eliminated by use of the dye solubilization method, which has provided reliable cmc values for the various EO condensate nonionics at 25°C. and elevated temperatures.

Nonionic surfactants offer an extra dimension over anionics since for a given hydrophobe multiples of water-solubilizing groups can be added. This extra-dimensional character offers considerable choice of surfactant feature and obviously affects cmc. Table II demonstrates the effect on cmc of hydrophobe and degree of EO addition. For the several hydrophobes over the 5 to 30 EO adduct types, a considerable change in cmc occurs:

Hydrophobe	cmc (M×10³) at 25°C.	
	Moles EO	
	5	10
Decanol	1.67	5.72
Tridecanol	0.136	0.518
Nonylphenol	0.0567	0.155
Dodecylphenol	0.0155	0.0236

Effect of Hydrophobe Base. Comparison at 25°C., for example, of 10 EO adducts of decanol, tridecanol, nonylphenol, and dodecylphenol shows an increase in dye solubilization and a decrease in cmc values with an increase in number of carbon atoms in the hydrophobe. The cmc ratios are 160, 10, 4, and 1, respectively. Nonylphenol had a lower cmc in relation to tridecanol than expected. This anomaly could result if the nonyl group were less branched than the tridecyl alcohol or if an abnormally low distribution of EO adducts were obtained in synthesis of the nonylphenol-EO compounds.

Calculation of the change in cmc per unit increase in carbon content of the hydrophobe was calculated [1] for the alcohol-EO adducts treated separately from the alkylphenol adducts. In these calculations the values for the three temperatures and the five EO ratios were calculated separately, then averaged. For the decanol-tridecanol and nonylphenol-dodecylphenol adducts these values were 0.307 and 0.278, respectively, for an over-all average of 0.293. By this convention effect of unit change in alkyl carbon chain-length can then be compared with that of EO effect. It can also be used to predict change in cmc upon change in carbon content of the hydrophobe base.

Effect of EO Chain-Length. Inspection of Table II shows that cmc increases (and solubilizing activity decreases) as the EO chain-length is increased for a given hydrophobe base. Plots of cmc percentage concentration against EO chain-length yield fairly smooth curves, showing that sensitivity to added EO increases with increasing EO content of the sample. Plotting cmc molar concentration against EO chain-length also gives the same trend but with greater irregularity, which is probably caused by variations in the distribution of EO chain-lengths within each sample.

Comparison of curves at 25 and 75°C. suggests that sensitivity to varying EO chain-length diminishes with increased temperature and with increasing carbon content of the hydrophobe base. No general mathematical relationship is evident from these data.

Greatest sensitivity to varying EO content occurs at different ranges of EO content, depending on the hydrophobe base and temperature. The general picture between 25 and 75° indicates that as the hydrophobe base size increases, the greatest sensitivity (percentage change) occurs at lower EO contents.

Comparison of results (Table III) shows that these compounds are about 10 times more sensitive to a change in carbon chain-length than to a change in EO content.

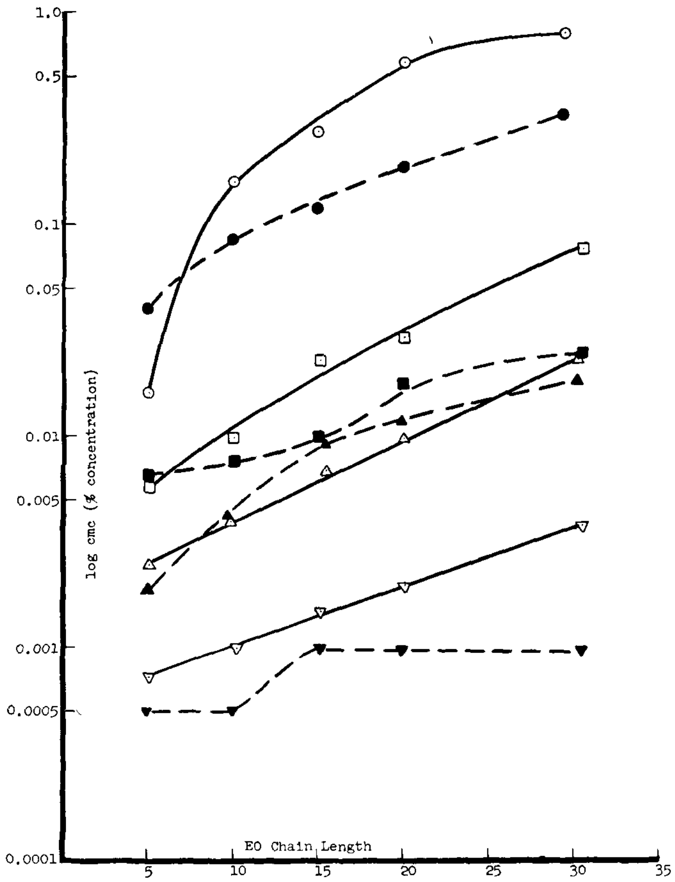

FIG. 3. Log % cmc *vs.* EO content.

25°C.	75°C.	
⊙	●	— Decanol + EO
⊡	■	— Tridecanol + EO
△	▲	— Nonylphenol + EO
▽	▼	— Dodecylphenol + EO

Hsaio *et al.* (5) claimed that cmc varied with EO chain-length according to the expression,

$$\ln \mathrm{cmc}_{(\mathrm{moles/l.})} = 0.56R + 3.87,$$

where R = EO mole ratio for an alkylphenol. Accordingly a plot of log cmc against EO chain-length should yield a straight line. Such plots for our data were usually not linear and therefore do not support the above relation.

Treatment of the data by the Klevens (9) equation, log cmc = A − BL, is not possible since added EO increases the over-all chain length of the molecule, yet reduces cmc. The data suggest that addition of EO to a given hydrophobe at first increases the lipophile length while providing insufficient sites for hydrogen bonding actually to solubilize the molecule. This result may occur between 0 and 5 moles of EO. Fur-

TABLE III

Comparison of Variables

(Temperature, EO chain-length, and hydroprobe carbon atoms)

Sensitivity	Interval measured	Summary value/unit	Ratio
$\frac{(\Delta cmc/cmc)}{\Delta T}$	25–75°C.	0.007	1
$\frac{(\Delta cmc/cmc)}{\Delta EO}$	30–5 EO	0.02	3
$\frac{(\Delta cmc/cmc)}{\Delta C}$	3 Carbons	0.29	40

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[1] Sensitivity is expressed for nonionics as

$$\frac{\Delta cmc/cmc}{\Delta C, \Delta EO, \Delta T}$$

where ΔC = 3 carbon atoms
ΔEO = 25 mole EO units
ΔT = 50°C.
referred to in Table III.

ther addition of EO acts to decrease the net lipophile length even though each EO added supplies two carbon atoms and only one hydrophilic oxygen atom. Also it appears that the more EO incorporated into the molecule, the greater the increase in cmc on adding more EO. Therefore it is inferred that the cloud of hydrogen-bonded water molecules increases for each EO ether oxygen as its distance from the hydrophobe base becomes greater. The number of bound water molecules increases the polar nature of the added EO to such an extent that its net effect is to nullify the EO carbon atoms and make the surfactant more hydrophilic. Our data, because of the mixtures of EO adducts involved, does not permit a clarification of this question.

Behavior of nonionics with respect to temperature is virtually the exact opposite of the result obtained for anionics. The various EO condensate values decrease with increasing temperature. Sensitivity to temperature change diminishes as the temperature is raised; the greatest change in cmc occurs between 25 and 50°C. in most cases. Sensitivity to temperature increases with EO content. The greatest temperature sensitivity occurred for dodecylphenol-EO adducts in the 25–50°C. range and the least sensitivity for the same compounds between 50 and 75°C. The nonylphenol-EO adducts were the least sensitive to temperature change, considering the entire 25 to 75°C. range, and exhibited slight, anomalous rises in cmc between 50 and 75°C. in the cases of the 15 and 20 EO adducts.

The results for nonionics are expected since they are known to have inverse solubility, that is, become less soluble in water as the temperature is raised (see cloud points, Table II). The solubility of EO condensate nonionics is attributed to hydrogen bonding between the ether oxygens of the ethylene oxide chain and water molecules. When the temperature is raised, these bonds are presumably broken and the hydrophilicity of the ethylene oxide chain is reduced. Consequently the relative effect of the hydrocarbon chain becomes more dominant, increasing aggregation and lowering cmc.

Effect of Temperature Compared to Hydrophobe Base and EO Chain-Length. Table III shows that, of these variables, temperature variation has the least influence on cmc, *i.e.,* a unit change in temperature produces about one-third less the change in cmc than does a unit change in EO chain-length, and only one-fortieth of the shift in cmc caused by a change of one carbon atom in the hydrophobe.

Summary

Measurements of cmc changes with temperature increase (at 25, 50, 75°C.) were made by the dye solubilization technique for a series of sodium alkylbenzene sulfonates and several series of nonionic surfactants.

The anionic surfactant series shows an increase in cmc with increasing temperature. This finding is in agreement with those obtained by other investigators who however used different anionic surfactants. The greatest change in cmc in terms of total concentration occurred with alkylbenzene sulfonates of lowest alkyl chain-length, but the greatest change in cmc occurred with those having the longest alkyl chains. Conclusions of other investigators that cmc is temperature-independent may be explained either as a result of investigation of compounds of too low effective carbon chain-length or as the choice of an insufficiently large temperature spread. Dye solubilizing power of surfactant solutions above the cmc is increased with increasing temperature.

The cmc values for ethylene oxide adducts (5 to 30 molar additions) for decanol, tridecanol, nonyl- and dodecylphenol provided the following conclusions.

An increase in carbon chain length for the hydrophobe decreases cmc for any given temperature.

Increase in ethylene oxide content for a given hydrophobe results in cmc increase. No general mathematical relationship for these products was discernible.

Sensitivity to varying ethylene oxide chain-length diminishes with an increase in temperature. A specific effect of hydrophobe chain length on temperature sensitivity was apparent. As hydrophobe size increases, the greatest sensitivity appears to occur at lower ethylene oxide content.

Cmc is approximately 10 times more sensitive to unit change in carbon content of the hydrophobe than to unit change in ethylene oxide chain-length.

Over the ranges tested a ratio of 1:3:40 describes the relative magnitude of changes in cmc for the comparative unit changes in temperature, ethylene oxide chain-length, and carbon chain-length in the hydrophobe base.

The effect of temperature on the cmc of nonionics is virtually the exact opposite of the effect with the anionic surfactants tested: cmc decreases with increasing temperature. Sensitivity of the cmc of nonionic surfactants to temperature change diminishes with temperature increase.

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REFERENCES

1. Brady, A. P., and Huff, H., J. Colloid Sci., *3,* 511 (1948).
2. Bury, C. R., and Parry, G. A., J. Chem. Soc., 626 (1935).
3. Ekwall, P., Kolloid-Z., *101,* 135 (1942).
4. Ekwall, P., and Otterström, B., Z. physik. chem., *A161,* 195 (1932).
5. Hsaio, L., Dunning, H. N., and Lorenz, P. B., J. Phys. Chem., *60,* 657 (1956).
6. Klevens, H. B., J. Phys. and Colloid Chem., *51,* 130 (1947).
7. Klevens, H. B., J. Phys. and Colloid Chem., *51,* 1143 (1947).
8. Klevens, H. B., Chem. Reviews, *47,* 1 (1950).
9. Klevens, H. B., J. Am. Oil Chemists' Soc., *30,* 74 (1953).
10. Kolthoff, I. M., and Stricks, W., J. Phys. and Colloid Chem., *52,* 915 (1948).
11. Kolthoff, I. M., and Stricks, W., J. Phys. and Colloid Chem., *53,* 424 (1949).
12. Kushner, L. M., and Hubbard, W. D., J. Phys. Chem., *61,* 371 (1957).
13. McBain, J. W., and Green, A. A., J. Am. Chem. Soc., *68,* 1731 (1946).
14. Mankowich, A. M., Ind. Eng. Chem., *44,* 1151 (1952).
15. Mayhew, R. L., and Hyatt, R. C., J. Am. Oil Chemists' Soc., *29,* 357 (1952).
16. Merrill, R. C., and Getty, R., J. Phys. and Colloid Chem., *52,* 774 (1948).
17. Rigg, M. W., and Liu, F. W. J., J. Am. Oil Chemists' Soc., *30,* 14 (1953).
18. Winsor, P. A., Trans. Faraday Soc., *44,* 455 (1948).
19. Wright, K. A., Abbott, A. D., Sivertz, V., and Tartar, H. V., J. Am. Chem. Soc., *61,* 549 (1939).

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