

11%. The range was 0.32 ppm for a series of nine determinations.

At the 20.0 ppm concn level, the standard deviation was 0.76 ppm, giving a relative standard deviation of 3.8%. The range was 2.7 ppm in this series of 17 determinations.

#### ACKNOWLEDGMENT

Analyses in support of this work by J. O. Rider, Surfactants Laboratory.

#### REFERENCES

1. Barber, A., C. C. T. Chinnick and P. A. Lincoln, *Analyst* **81**, 18-25 (1956).
2. Brown, E. G., and T. J. Hayes, *Ibid.* **80**, 755-67 (1955).
3. Crabb, N. T., and H. E. Persinger, paper presented at the AOCs Meeting, New Orleans, 1964.
4. Davis, B. F., K. E. Wattman and H. C. Speel, *Soap* **31**, No. 12, 73, 75, 77, 79 (1955).
5. Gnam, H., "Die Losungs und Weichmachungsmittel," Wissenschaftliche Verlagsgesellschaft, Stuttgart, 1941.
6. Huddleston, R. L., and R. C. Allred, "Developments in Industrial Microbiology," Vol. 4, in press.
7. Karabinos, J. V., *Soap* **31**, No. 6, 50-51 (1955).
8. Kurata, M., *J. Japan Oil Chemists' Soc.* **4**, 293-298 (1955).
9. Oliver, J., and C. Preston, *Nature* **164**, 242-3 (1949).
10. Schoenfeldt, N. J., *JAOCs* **32**, 77-79 (1955).
11. Shaeffer, C. B., and F. Critchfield, *Anal. Chem.* **19**, 32-34 (1947).
12. Stevenson, D. G., *Analyst* **79**, 504-7 (1954).
13. Stewart, R. G., *Ibid.* **88**, 468-70 (1963).
14. Van der Hoeve, J. A., *Rec. Trav. Chim.* **67**, 649-64 (1948).
15. Van der Hoeve, J. A., *Soc. Dyers Col.* **70**, 145-54 (1954).
16. Weber, J. R., E. F. Degner and K. S. Bahjat, *Anal. Chem.* **36**, 678-79 (1964).
17. Wurzschnitt, B. Z., *Ibid.* **130**, 105-85 (1950).
18. Staff Report, *Chem. Eng. News* **41**, No. 25, 50-51 (1963).
19. Private communication from Nissan Chemical Industries, Ltd., April, 1963.
20. Work of the Nonionic Detergents Analytical Subcommittee, The Soap and Detergent Assoc.

[Received June 15, 1964—Accepted October 19, 1964]

## The Energetics of Micellar Solubilization

A. M. MANKOWICH, U.S. Army Coating and Chemical Laboratory, Aberdeen Proving Ground, Maryland

### Abstract

Micellar solubilization, an action of the detergency mechanism, is considered from the standpoint of quasi-thermodynamics. The basis of the approach was suggested by the similarity of micellar solubilization and Freundlich adsorption isotherms. Free energy change ( $\Delta G$ ), heat of solubilization ( $\Delta H$ ) and change in entropy ( $\Delta S$ ) for the micellar solubilization of Orange OT are calculated using two-phase theory and the Gibbs-Helmholtz equation. It is postulated that the dye concn in the solution (monomer) phase is that at the critical micelle concn. The dye concn in the solubilized phase is computed for the dye-penetrated portion of the micellar volume. Calculated values of  $\Delta G$  in anionic and nonionic surfactants are of the order of magnitude of a physical adsorption. The positive  $\Delta H$  values indicate the process is not an adsorption. The positive  $\Delta S$  values point to increased randomness or possibly to decreased energy effects due to iceberg water molecule structure surrounding the hydrophobic dye molecules. The loss of the water structure around the latter in the solubilization process would result in their acquiring increased configurational entropy.

### Introduction

ALTHOUGH MICELLAR solubilization is usually assigned a minor role in the detergency mechanism (1), research at this Laboratory has indicated that an important empirical relation exists between this physicochemical factor and hard surface detergency in the practical soil removal range of ca. 90-100% (2). Establishment of the relation, a linear function, made it desirable to investigate the energetics of the variable, the micellar solubilization of the water-insoluble dye, Orange OT.

Some years ago, Lambert and Busse called attention to the correspondence of dye solubilization—concn functions and Freundlich adsorption isotherms (3). Work at this Laboratory revealed no correlation of polarity of dye with the log-log slope of the function nor with the magnitude of solubilization (4). However, Harkins's speculation (5) on the existence of an adsorption type of solubilization suggested that treatment of the process as an adsorption would permit

thermodynamic constants to be calculated, and that the latter would give a clue to the validity of the postulation. Accordingly, the free energy change for micellar solubilization could be calculated by the equation:

$$\Delta G = -2.3 RT \log \frac{C_s}{C_L} \quad [1]$$

Where  $C_s$  = the concn of dye in the adsorbed, micellar phase, and  $C_L$  = the dye concn in the non-micellar, monomer phase. The heat of micellar solubilization,  $\Delta H$ , could then be determined by the Gibbs-Helmholtz equation with the slope of the  $\left(\frac{\Delta G}{T}\right)$  vs.  $\left(\frac{1}{T}\right)$  function giving  $\Delta H$  directly. The change in entropy,  $\Delta S$ , for the process would follow from the equation:

$$\Delta S = \frac{\Delta H - \Delta G}{T} \quad [2]$$

This paper calculates the free energies, heats, and entropy changes of the micellar solubilization of Orange OT in aqueous solutions of an anionic and a nonionic surfactant.

### Theory

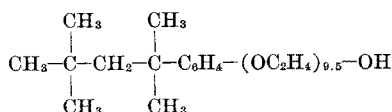
Several assumptions must be made in order to utilize equation 1. First, we accept Shinoda's model of micellization as an equilibrium between micellar and monomer phases (6), the latter being the maximum molecular concn, the so-called critical micelle concn (CMC). It is reasonable then that  $C_L$  should be taken as the dye concn at the CMC. Such a solubilization is small, and has been attributed to the adsorption of single dye molecules on single surfactant molecules by Klevens (7).  $C_L$  is expressed as "molecules Orange OT per  $\text{\AA}^3$ ," a unit into which the conventional "mg Orange OT/100 cc solution" is readily converted.  $C_s$ , the dye concn in the micellized phase, is expressed in the same units. However, the calculation of  $C_s$  involves a different treatment of the data. While  $C_L$  is a value based on the bulk surfactant volume,  $C_s$  is based on the part of the micellar volume available for solubilization of dye molecules. In this study we also accept Klevens' postulate (7) that dye solubilization consists of the incorporation of the solubilized molecules into the micelle with their long axes lying approx parallel to those of the adjacent detergent monomers, oriented as the latter with respect to the hydrophilic and hydrophobic ends, and with the dye

TABLE I  
 Micellar Solubilization

Surfactant	% Concn. w/v	mg Orange OT/100 cc					
		25C	30C	35C	42.5C	46C	50C
OPE	1.00	5.86		7.79	10.1		12.0
	0.80	4.72		6.30	8.50		9.91
	0.40	2.43		3.33	4.47		5.58
	0.20	1.33		1.82	2.42		3.16
	0.10	0.66		0.98			
	0.015—CMC	0.053		0.053	0.068		0.068
SDBS	0.80	2.02	2.14	2.43	2.97	3.19	3.49
	0.60	1.44	1.61	1.81	2.07	2.37	2.58
	0.40	0.91	1.05	1.16	1.41	1.51	1.53
	0.20	0.38	0.44	0.47	0.52	0.55	0.55
	CMC	0.20 at 0.123%	0.21 at 0.135%	0.21 at 0.148%	0.30 at 0.166%	0.35 at 0.172%	0.42 at 0.185%

molecules extending about 7 Å into the micelle from its charged surface. From the known bond distances, the lengths of the surfactant and Orange OT molecules can be calculated. Assuming a spherical micelle, the space therein available to the solubilized Orange OT molecules will be equal to the difference in volume of two spheres whose radii are ( $L_{DET} - 7$ ) and ( $L_{DET} - 7 - L_{OT}$ ), where  $L_{DET}$  and  $L_{OT}$  are the lengths of the surfactant and Orange OT molecules in Å, respectively.

The solubilization in "molecules Orange OT/surfactant micelle" is readily calculated from the conventional value of "mg Orange OT/100 cc solution" and the aggregation number of the surfactant. It is to be noted that since  $C_s$  is part of a large logarithmic term, errors in its determination do not have an appreciable effect on the calculated value of  $\Delta G$ . For example, in determining  $\Delta G$  for the solubilization in a 1% (w/v) solution of a commercial, 100% active, 9.5 ethylene oxide mole ratio adduct of octylphenol,



the solubilization is 5.86 mg Orange OT/100 cc at 25C; and it is 0.053 mg Orange OT/100cc at the CMC of 0.015% (w/v) at 25C. Since the mol wt of the dye is 262,

$$C_L = \frac{.000053}{262} \times 10^{-26} \times 6.02 \times 10^{23} = 12.1779 \times 10^{-10} \frac{\text{molecules Orange OT}}{\text{\AA}^3}$$

With the theoretical monomer wt of 624, and the aggregation number of 118 at 25C as determined in this Laboratory (8),

$$\text{solubilization} = \frac{.00586}{262} \times \frac{624}{1} \times 118 = 1.64689 \frac{\text{molecules Orange OT}}{\text{micelle}}$$

Now, taking Kushner's value of 43 Å for the length of the monomer molecule (9), calculating a length of 10.3 Å for the dye molecule from the bond radii (10), and assuming a spherical micelle whose radius is 43 Å, the volume available to solubilized Orange OT molecules in the micelle is, according to our postulation, equal to:

$$V = \frac{4}{3} \pi (43-7)^3 - \frac{4}{3} \pi (43-7-10.3)^3 = 124,495 \text{ \AA}^3$$

$$\therefore C_s = \frac{1.64689}{124,495} = 1.32286 \times 10^{-5} \frac{\text{molecules Orange OT}}{\text{\AA}^3}$$

$$\begin{aligned} \therefore \Delta G &= -1.987 \times 298 \times 2.3 \log \left( \frac{1.32286 \times 10^{-5}}{12.1779 \times 10^{-10}} \right) \\ &= -5.5 \text{ kcal/mole Orange OT.} \end{aligned}$$

If the solubilized dye molecules occupy a 25% greater micellar volume, 155,619 Å<sup>3</sup>, it can be shown that  $\Delta G = -5.4$  kcal/mole Orange OT, a difference of less than 2%.

In using the Gibbs-Helmholtz equation to obtain  $\Delta H$  by a plot of  $\frac{\Delta G}{T}$  vs.  $\frac{1}{T}$  micellar solubilization,

CMC, and micellar mol wt data are required over a temp range. Micellar solubilizations over the 25–50C temp range covered in this study are readily determined, as are the CMC and micellar mol wt data at 25C. However, obtaining CMC and micellar size data at the elevated temp is a laborious task. In this study these data were obtained by applying temp coefficients from the literature to 25C values, as follows:

**CMC Temperature Dependence.** Ginn et al. found that branch-chain alkylbenzene sulphonates have a positive CMC temp coefficient (11). Their graphical representation of the temp dependence of the CMC of sodium dodecylbenzene sulphonate (SDBS), with a CMC of .005M at 25C, revealed a coefficient of +2%/degree C in the 25–50C range. This figure was applied to the CMC of the branched chain SDBS used in this investigation, .123% w/v (.00353M) at 25C, to obtain the CMC values at the elevated temp. Ginn et al. also found that in general the CMC of nonionics decreases with increasing temperature (11). However, important specificities were obtained with branch-chain alkylphenol ethylene oxide adducts. In the 25–50C range, temp sensitivity decreased with decreasing hydrophobe chain length. The nonylphenol adducts showed anomalous effects, the CMC of the 9.8 ethylene oxide mole ratio (R) adduct increasing slightly and the 15.4R and 20R adducts being temp independent. It was therefore considered legitimate in this investigation to assume that the CMC of the closely-related 9.5R adduct of isoctylphenol was temp independent in the 25–50C range.

**Micellar Size Temperature Dependence.** Kuriyama's work indicates that the micellar mol wt of anionic surfactants have a negative temp coefficient (12). A typical value of -0.55%/degree C can be calculated from his data for sodium dodecyl sulphate in the 30–50C range. This coefficient was used in computing the micellar weights of SDBS in the 35–50C range. Kuriyama also found, in accordance with the inverse solubility of polyethenoxy-ethers of alkylphenols and alcohols and the expectation of increased micellar size with increasing temp, that such nonionics have a positive micellar size temp coefficient, a typical value calculated from his data being +0.45%/degree C in the 20–60C range for dodecaethylene glycol monomethyl monododecyl ether (13). This coefficient was used in calculating the micellar wt in the 35–50C range of the 9.5R adduct of isoctylphenol used herein. As in the other instances in this study involving esti-

TABLE II  
Micellar Data

Surfactant <sup>a</sup>	°C	CMC, % w/v	Monomer length, Å	Micellar wt	Available micellar vol, <sup>1</sup> Å <sup>3</sup>
OPE	25	.015 <sup>b</sup>	43 <sup>c</sup>	73,500 <sup>b</sup>	124,500
	35	.015 <sup>c</sup>		76,800 <sup>g</sup>	
	42.5	.015 <sup>c</sup>		79,300 <sup>g</sup>	
	50	.015 <sup>c</sup>		81,800 <sup>g</sup>	
SDBS	25	.123 <sup>b</sup>	17.9 <sup>f</sup>	31,600 <sup>b</sup>	5,390
	35	.148 <sup>d</sup>		30,200 <sup>h</sup>	
	42.5	.166 <sup>d</sup>		29,200 <sup>h</sup>	
	46	.172 <sup>d</sup>		28,700 <sup>h</sup>	
	50	.185 <sup>d</sup>		28,100 <sup>h</sup>	

<sup>a</sup> OPE = 9.5 mole ratio ethylene oxide adduct of isoocetylphenol; SDBS = sodium dodecyl (branch chain) benzene sulphonate.

<sup>b</sup> Reference (8), this laboratory.  
<sup>c</sup> Temp independent, reference (11).  
<sup>d</sup> Temp coeff. of +2%/°C in 25-50C range, reference (11).  
<sup>e</sup> Reference (9).  
<sup>f</sup> Calc from bond radii (reference 10).  
<sup>g</sup> Temp coeff. of +0.45%/°C in 20-60C range for ethylene oxide adduct, reference (13).  
<sup>h</sup> Temp coeff. of -0.55%/°C in 30-50C range for anionic surfactant, reference (12).  
<sup>1</sup> Occupied by solubilized dye molecules; based on 7 Å penetration into spherical micelle, reference (7).

mated values of CMC and micellar size, small errors in their estimation have no appreciable effect on the calculated values of ΔG because of their appearance in large (ca. 10<sup>4</sup>) logarithmic terms.

**Experimental**

**Materials.** The surfactants were commercial, 100% active materials. The anionic agent was a branch-chain sodium dodecyl benzene sulphonate (SDBS). The nonionic was a 9.5 ethylene oxide mole ratio adduct of isoocetylphenol (OPE).

**Methods.** Micellar solubilization was determined by a modification of the dynamic method of Lambert and Busse (3), the details of which have been described previously (4,14).

Micellar mol wt of the SDBS and OPE at 24-26C were determined in a previous investigation at this Laboratory (8). Absolute turbidities were measured with a Brice-Phoenix light scattering photometer using 5460 Å radiation. Refractive index increments were obtained with the same radiation using a Rayleigh interferometer. Details of the techniques have been reported (15). Micellar wt of 73,500 (aggregation number = 118) and 31,600 (aggregation number = 91) were obtained for OPE and SDBS, respectively. Aggregation numbers were based on theoretical monomer wt.

CMC values of OPE and SDBS at 25C were determined graphically from surface tension-log concentration plots in a previous investigation (8). Values of 0.015% and 0.123% were obtained for OPE and SDBS, respectively.

**Calculation of ΔG.** The calculation of the free energy

TABLE III  
ΔG, ΔH and ΔS of Micellar Solubilization (OPE)

Surfactant	% Concn w/v	° Kelvin	kcal/mole Orange OT		cal./mole deg. ΔS
			ΔG	ΔH	
OPE	1.00	298	-5.5	+4.0	+31.9
		308	-5.9	+4.0	+32.1
		315.5	-6.1	+4.0	+31.9
		323	-6.3	+4.0	+32.0
	0.80	298	-5.5	+4.4	+33.2
		308	-5.9	+4.4	+33.4
		315.5	-6.1	+4.4	+33.2
		323	-6.4	+4.4	+33.2
	0.40	298	-5.5	+5.0	+35.3
		308	-5.9	+5.0	+35.4
		315.5	-6.1	+5.0	+35.2
		323	-6.4	+5.0	+35.3
	0.20	298	-5.6	+5.2	+36.1
		308	-6.0	+5.2	+36.1
		315.5	-6.2	+5.2	+36.0
		323	-6.5	+5.2	+36.1

TABLE IV  
ΔG, ΔH and ΔS of Micellar Solubilization (SDBS)

Surfactant	% Concn, w/v	° Kelvin	kcal/mole Orange OT		cal./mole deg. ΔS
			ΔG	ΔH	
SDBS	0.80	298	-5.6	+2.4	+26.7
		303	-5.7	+2.4	+26.6
		308	-5.8	0	+19.0
		315.5	-5.8	-5.9	-0.3
		319	-5.8	-5.9	-0.3
		323	-5.8	-5.9	-0.3
	0.60	298	-5.5	+2.9	+28.3
		303	-5.7	+2.9	+28.3
		308	-5.8	0	+19.0
		315.5	-5.8	-6.0	-0.6
		319	-5.8	-6.0	-0.6
		323	-5.8	-6.0	-0.6
0.40	298	-5.5	+3.7	+31.0	
	303	-5.7	+3.7	+31.0	
	308	-5.8	0	+18.9	
	315.5	-5.8	-6.9	-3.5	
	319	-5.8	-6.9	-3.5	
	323	-5.8	-6.9	-3.5	
0.20	298	-5.4	+2.9	+28.0	
	303	-5.6	+2.9	+28.0	
	308	-5.7	0	+18.5	
	315.5	-5.6	-8.6	-9.4	
	319	-5.6	-8.6	-9.3	
	323	-5.5	-8.6	-9.4	

change of micellar solubilization, ΔG, by equation 1 has already been indicated. Tables I and II give the necessary solubilization and micellar data in the 25-50C range studied.

**Calculation of ΔH.** The Gibbs-Helmholtz equation is given by

$$\Delta H = \Delta G - T \left[ \frac{\partial \Delta G}{\partial T} \right]$$

It follows (reference 10, page 284) that

$$\frac{\Delta G}{T} = \frac{\Delta H}{T} + \frac{\partial \Delta G}{\partial T}$$

and,

$$\frac{\partial \left( \frac{\Delta G}{T} \right)}{\partial (1/T)} = - \frac{\Delta H}{T^2}$$

Hence,

$$\frac{\partial \left( \frac{\Delta G}{T} \right)}{\partial \left( \frac{1}{T} \right)} = \Delta H$$

Therefore, the slope of the  $\left( \frac{\Delta G}{T} \right)$  vs.  $\left( \frac{1}{T} \right)$  function gives ΔH. Table III contains the calculated ΔG data at the various surfactant concn studied. Figures 2 and 3 are graphical representations of the  $\left( \frac{\Delta G}{T} \right)$  vs.  $\left( \frac{1}{T} \right)$

TABLE V  
Sample Calculation

Given: S, 1% OPE at 25C = 5.86 mg Orange OT/100 cc  
 S, 0.015% OPE at 25C = 0.053 mg Orange OT/100 cc  
 Mol wt Orange OT = 262  
 Mol wt OPE = 624  
 Aggregation number OPE = 118 at 25C  
 L<sub>OT</sub> = 10.3 Å  
 L<sub>OPE</sub> = 43 Å

$$V = \frac{4}{3} \pi (43 - 7)^3 - \frac{4}{3} \pi (43 - 7 - 10.3)^3 = 124,495 \text{ Å}^3$$

$$C_L = \frac{.000053}{262} \times 10^{-26} \times 6.02 \times 10^{23} = 12.1779 \times 10^{-10} \text{ molecules Orange OT } \frac{1}{\text{Å}^3}$$

$$C_s = \frac{.00586}{262} \times \frac{624}{1} \times \frac{118}{1} \times \frac{1}{124,495} = 1.32286 \times 10^{-6} \text{ molecules Orange OT } \frac{1}{\text{Å}^3}$$

$$\therefore \Delta G = -2.3 \times 1.987 \times 298 \log \frac{1.32286 \times 10^{-6}}{12.1779 \times 10^{-10}}$$

$$= -5.5 \text{ kcal/mole Orange OT}$$

If V is 25% greater, or 155,619 Å<sup>3</sup>, then  
 ΔG = -5.4 kcal/mole Orange OT

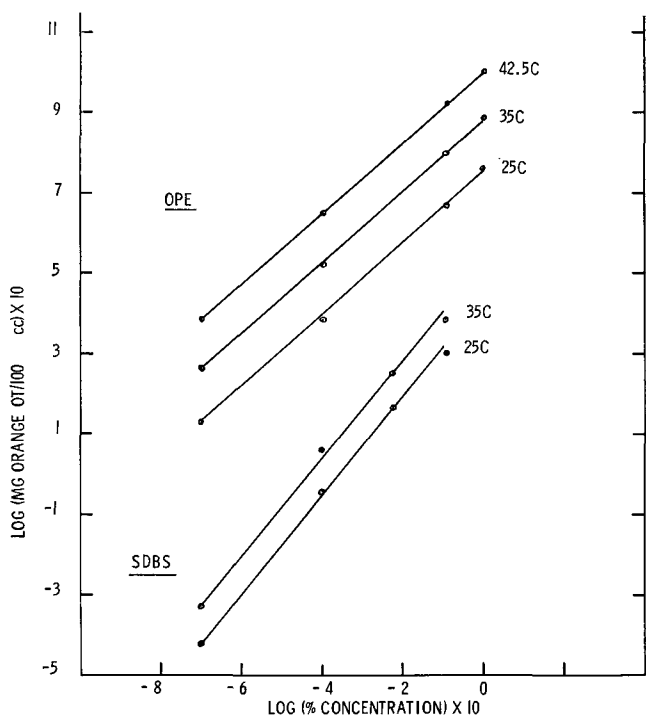


FIG. 1. Micellar solubilization isotherms, OPE and SDBS.

functions based on these data. The slopes of the lines, obtained by least squares treatments, give the corresponding  $\Delta H$  values which are also shown in Table III.

**Calculation of  $\Delta S$ .** Change in entropy,  $\Delta S$ , is calculated by equation 2, and results are given in Table III.

### Results

Micellar solubilization values are given in Table I. Figure 1 shows that log solubilization-log concn plots of these data are linear in the 25–50C range. It is to

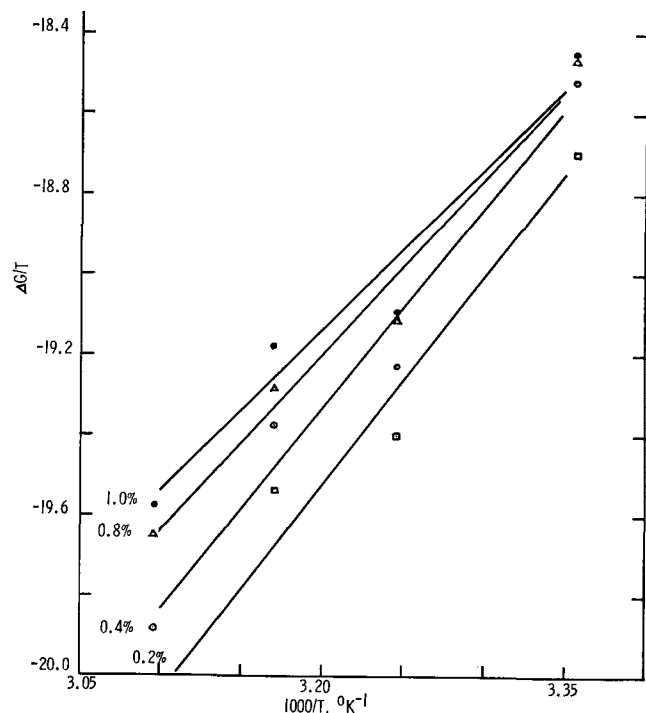


FIG. 2. Gibbs-Helmholtz  $\Delta H$  functions for OPE, showing least squares lines.

□, 0.2%; ○, 0.4%; △, 0.8%; ●, 1.0%.

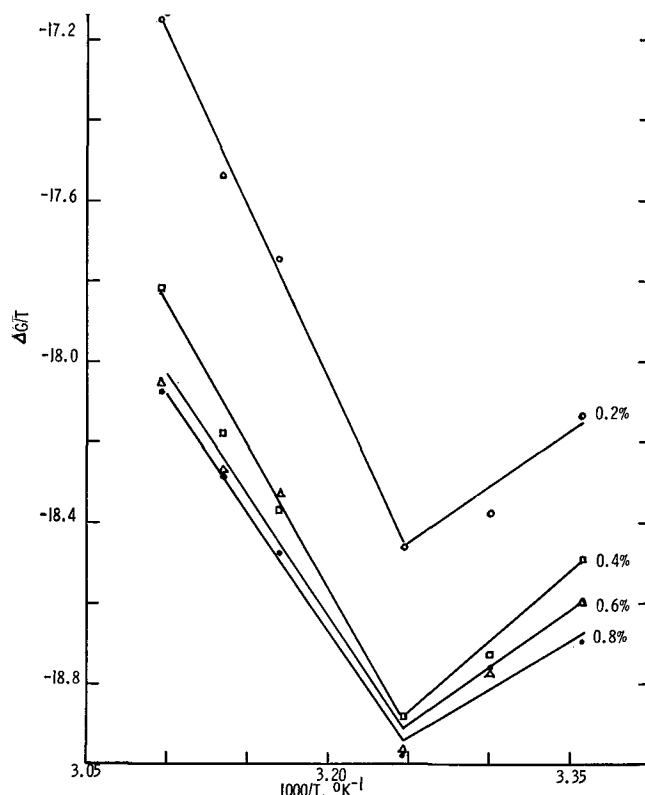


FIG. 3. Gibbs-Helmholtz  $\Delta H$  function for SDBS, showing least squares lines.

be noted that for each surfactant the slopes at the various test temp are substantially equal.

Table III gives the calculated thermodynamic constants for the Orange OT micellar solubilization process. In the nonionic OPE solutions,  $\Delta H$  and  $\Delta S$  are positive in the 25–50C range, with both values decreasing as the stoichiometric surfactant concentration increases. Mean values of  $\Delta G$  in this temp range are constant at  $-6.0$  kcal/mole as the surfactant concn varies from 0.2–1.00% w/v. For the anionic surfactant SDBS, mean values of  $\Delta G$  in the 25–50C range are practically constant at  $-5.7$  kcal/mole in the 0.20–0.80% concn range. Figure 3 indicates that  $\Delta H$  for all concn of SDBS is positive between 25 and 35C, and that it is negative in the 35–50C range. The change in slope of the  $\left(\frac{\Delta G}{T}\right)$  vs.  $\left(\frac{1}{T}\right)$  function occurs at ca.

35C. Positive values of  $\Delta S$  are obtained at 25–35C for all concn of SDBS with negative values at all concn in the 42.5–50C range.

### Discussion

The free energy changes obtained for the micellar solubilization of Orange OT are of the order of magnitude of a physical adsorption. However, the positive  $\Delta H$  values, at 25–50C for nonionic OPE and at 25–30C for anionic SDBS, indicate the process is not a true adsorption. Since adsorption is characterized by considerable packing or crowding of adsorbed molecules into an adsorbed film, the attendant restriction in movement should result in a negative  $\Delta S$ , and therefore (by equation 2) in a negative  $\Delta H$ . It would seem reasonable to expect the micellar solubilization process also to occur with a negative entropy change because of the crowding of dye molecules into the surfactant micelle, and to also expect the process to be exothermic. The positive  $\Delta S$  values indicate that the expected nega-

tive entropy effect is more than counteracted by increased randomness or increased configurational entropy of the solubilized dye molecules. Several investigators, notably Frank and Evans (16) and Nemethy and Scheraga (17), have postulated water molecule structures partially surrounding nonpolar hydrocarbon molecules or groups, with van der Waals interactions lowering the energies of both hydrocarbon and water molecules. The breakup of this structure about surfactant monomers in the micellization process with consequent increased configurational entropy of the monomers in the micelle has been suggested as the cause of positive entropy changes in micellization by Schick (18) and by Goddard et al. (19). It is suggested now that the positive  $\Delta H$  values of micellar solubilization may be attributed in part to similar water structure effects about the dye molecules.

The mean values of  $C_s$ , the dye concn in the micellar phase, for both surfactants give a possible clue to the cause of the negative entropy changes of the anionic SDBS in the 42.5–50C range. The maximum value of  $C_s$  for the nonionic OPE is  $3.39 \times 10^{-5}$  molecules Orange OT/ $\text{\AA}^3$  at 50C. This concn does not involve enough crowding to make the concomitant negative  $\Delta S$  predominate over the positive entropy change effects previously mentioned.  $C_s$  values for SDBS are considerably larger, i.e., 6.05, 6.86 and  $7.59 \times 10^{-5}$  molecules Orange OT/ $\text{\AA}^3$  at 35, 42.5 and 50C, respectively. One can speculate, therefore, that at a micellar packing of  $6.86 \times 10^{-5}$  dye molecules/ $\text{\AA}^3$  ( $\Delta S$  negative), the negative entropy change due to restricted movement becomes larger than the positive entropy change effects involved. It is of interest to estimate the degree of packing at this point by determining the volume actually occupied by the micellized dye molecules. The molecular volume of Orange OT

may be calculated from its mol wt and bulk density, as follows:

$$\text{Molecular volume, Orange OT} = \frac{10^{24} \times 262}{6.02 \times 10^{23} \times .54} = 810 \text{ \AA}^3$$

The volume of ( $6.86 \times 10^{-5}$ ) Orange OT molecules is then  $0.055 \text{ \AA}^3$ . Hence, it seems that the negative  $\Delta S$  effect begins to predominate when solubilized dye molecules with a volume of  $0.055 \text{ \AA}^3$  are contained in a  $1 \text{ \AA}^3$  space.

It is of interest to note that the reversal of sign in  $\Delta H$  and  $\Delta S$  with increasing temp for the micellar solubilization of Orange OT by anionic SDBS duplicates similar sign reversals in the micellization of ionic surfactants as reported by Goddard and Benson (20) and Floekhart (21).

#### REFERENCES

- Harris, J. C., *JAOCs* **35**, 428 (1958).
- Mankowich, A. M., *Ibid.* **39**, 206 (1962); **40**, 674 (1963).
- Lambert, J. M., and W. F. Busse, *Ibid.* **26**, 289 (1949).
- Mankowich, A. M., *J. Colloid Sci.* **14**, 131 (1959).
- Harkins, W. D., "The Physical Chemistry of Surface Films," Reinhold Publ. Corp., New York, 1952, p. 321.
- Shinoda, K., and E. Hutchinson, *J. Phys. Chem.* **66**, 577 (1962).
- Klevens, H. B., *JAOCs* **26**, 456 (1949).
- Mankowich, A. M., *Ibid.* **41**, 499 (1964).
- Kushner, L. M., and W. D. Hubbard, *J. Phys. Chem.* **58**, 1163 (1954).
- Daniels, F., "Outlines of Physical Chemistry," John Wiley & Sons, Inc., New York, 1953, p. 92.
- Ginn, M. E., F. B. Kinney and J. C. Harris, *JAOCs* **37**, 183 (1960).
- Kuriyama, K., *Kolloid-Z.u.Z. Polymere* **180**, 55 (1962).
- Kuriyama, K., *Ibid.* **181**, 144 (1962).
- Mankowich, A. M., *Ind. Eng. Chem.* **44**, 1151 (1952).
- Mankowich, A. M., *J. Phys. Chem.* **58**, 1027 (1954).
- Frank, H. S., and M. W. Evans, *J. Chem. Phys.* **13**, 507 (1945).
- Nemethy, G., and H. A. Scheraga, *Ibid.* **36**, 3401 (1962).
- Schick, M. J., *J. Phys. Chem.* **67**, 1796 (1963).
- Goddard, E. D., C. A. Hoeve and G. C. Benson, *Ibid.* **61**, 593 (1957).
- Goddard, E. D., and G. C. Benson, *Can. J. Chem.* **35**, 986 (1957).
- Floekhart, B. D., *J. Colloid Sci.* **16**, 484 (1961).

#### ACKNOWLEDGMENTS

Most of the data used obtained by Troy Nichols and Allan Potter.

[Received October 1, 1964—Accepted November 27, 1964]

## The Effect of Tallow-Based Detergents on Anaerobic Digestion<sup>1</sup>

E. W. MAURER, T. C. CORDON, J. K. WEIL, M. V. NUÑEZ-PONZOA, W. C. AULT, and A. J. STIRTON, Eastern Regional Research Laboratory,<sup>2</sup> Philadelphia, Pennsylvania

### Abstract

Eight anionic detergents from three general classes (alcohol sulfates,  $\alpha$ -sulfo fatty acid esters and alkylbenzenesulfonates) were tested for biodegradability under anaerobic conditions of sludge digestion. The alcohol sulfates were found to be readily and completely degraded. The  $\alpha$ -sulfo fatty acid esters did not degrade but had no adverse effect on bacteriological digestion while the alkylbenzenesulfonates used for control purposes did not degrade and disrupted the normal digestion process.

Preliminary lysimeter studies showed that sodium isopropyl  $\alpha$ -sulfofostearate is completely degraded, linear alkylbenzenesulfonate 83%, and ABS 35%.

### Introduction

Recent studies by this laboratory have reported on

the biodegradation of some tallow-based surface active agents in river water (9) and in activated sludge (1). The present study is concerned with the effect of tallow-based surfactants on the anaerobic digestion process. Two preliminary approaches have been made. First, the use of anaerobic sludge digesters and second, the use of lysimeters utilizing local soil.

The effect of detergents on the anaerobic biodegradation process is an important consideration in septic tank operation and seepage from a septic tank to saturated soil.

### Experimental

#### Materials

The preparation of sodium isopropyl  $\alpha$ -sulfofostearate  $C_{16}H_{33}CH(SO_3Na)CO_2CH(CH_3)_2$ , disodium 2-sulfoethyl  $\alpha$ -sulfofostearate  $C_{16}H_{33}CH(SO_3Na)CO_2C_2H_4SO_3Na$ , sodium methyl  $\alpha$ -sulfofostearate  $C_{16}H_{33}CH(SO_3Na)CO_2CH_3$ , sodium 9,10-dichlorooctadecyl sulfate  $C_8H_{17}CHClCHCl(CH_2)_7CH_2OSO_3Na$  and hydrogenated tallow alcohol sulfates (HTAS) has been

<sup>1</sup> Presented at the AOCS meeting, Chicago, 1964.

<sup>2</sup> E. Utiliz. Res. Devel. Div., ARS, USDA.