The comparatively large amounts of uranium and the form of the curve suggest that chemical combination and perhaps solvation of metallic ions contribute to the high uranium content. More work will be needed before definite conclusions can be drawn.

TABLE I

Metallic Content of Emulsion Fractions

Metals	Oil	Vegetation water	Membranes
Iron, p.p.m.	1.9	54	3890
Copper, p.p.m.	0.02	8.6	1300
Zinc, p.p.m.	0.1	19.9	3915
Manganese, p.p.m.	0.015	3.3	53.4
Potassium, p.p.m.	0.00	8000	1950
Ash, %	0.014	1.97	9.2

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The Temperature Dependence of Micellar Solubilization

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The temperature dependence of micellar solubilization was determined in the 180°–140°F. temperature range by using a dye solubilization technique with built and unbuilt solutions of three high-cloud point, commercial surfactants, one anionic of the alkylaryl sulphonate type and two types of nonionic agents. It was found that the logarithm of solubilization in both built and unbuilt solutions was directly proportional to temperature (solubilization was an exponential function of temperature) and that the log solubilization-temperature slopes of the built and unbuilt solutions of each surfactant were approximately parallel.

MICELLAR SOLUBILIZATION is considered by some investigators to be one of the first actions of the detergency mechanism (1). It is therefore important to know how solubilization varies with temperature under field conditions. While hard surface, aqueous cleaning is usually carried out at elevated temperatures, most of the literature data on solubilization are in the low 77°–122°F. (25°–50°C.) range (2,3,4,5,6,7). These data are not complete enough to permit the derivation of solubilization-temperature functions. But it is possible to postulate that in this range solubilizing activity increases with increasing temperature and the temperature coefficient of solubilization varies with the surfactant (5).

This paper deals with the temperature dependence of the micellar solubilizing power of three important types of surfactants in the 180°–140°F. temperature range. Solutions of all three surfactants, two nonionic (including a polyoxyethylated alkyl phenol) and one anionic, possessed high-cloud points and were clear in the temperature range studied. A dye solubilization technique was used with built and unbuilt surfactant solutions. Surfactant and builder concentrations were those obtaining in practical detergency.

Materials

Surfactants. Those used in this investigation were 100% active, commercial products. Two were nonionic agents, polyoxyethylene sorbitan monolaurate (PSML) with a molecular weight of 1226 (according to the manufacturer) and pentadecaethylene glycol nonyl phenyl ether (PGNPE), molecular weight 880. The third surfactant was an anionic agent of the alkyl arylsulphonate type, sodium dodecyl benzene sulphonate (SDBS), molecular weight 346.

Dye. Used in the as-received condition, this was Orange OT, 1-O-tolylazo-2-naphthol.

Builders. These were A.C.S. Na_2SO_4 and technical grade $Na_5P_3O_{10}$.

Experimental

The experimental technique was that used in a previous study of micellar solubilization (8), with the following changes primarily because of the higher temperatures.

a) Preheating time in the water bath prior to addition of dye was increased to 35 min. The interaction period remained 25 min.

b) The interaction test tubes were given a repetition of the initial mixing at 8 and 16 min. after addition of dye to surfactant solution.

c) Filtration was into a receiver placed in the thermostated water-bath.

d) Aliquots of the filtrate were diluted with 1:1, acetone-water mixture prior to determination of optical density at a wavelength of 425 millimicrons. The dilution was made by pouring slightly less than 5 ml. of the hot filtrate into an ice-cooled, 25-ml. glass-stoppered type of graduated cylinder containing 20 ml. of 1:1, acetone-water mixture measured at room temperature. The cylinder was stoppered, the contents were mixed and brought to room temperature, and the volume was noted. The size of the aliquot was given by the difference in volume.

Results and Discussion

Table I gives the solubilization of Orange OT (each value the average of at least two determinations) at temperatures of 180°, 160°, and 140°F. in solutions of surfactants PGNPE, PSML, and SDBS in distilled water and in 0.025M and 0.05M Na_2SO_4 and $Na_5P_3O_{10}$, respectively. For each temperature, solubilizations are given for three concentrations of each surfactant. Some of the data are plotted in Figure 1. The data and graphs indicate that in the 180°–140°F. range the logarithm of solubilization is directly pro-

TABLE 1

Micellar Solubilization *versus* Temperature

Temperature °F.	Surfactant	Surfactant molarity	mg Orange OT Solubilized per 100-ml. Solution				
			No builder	.025M Na_2SO_4	.05M Na_2SO_4	.025M $Na_5P_3O_{10}$	.05M $Na_5P_3O_{10}$
180	PGNPE	.025	50.1	48.3	48.1	54.6	insolubles
		.02	36.4	36.0	35.0	38.9	41.6
		.01	19.5	19.1	19.1	20.0	20.5
160	PGNPE	.025	33.9	33.4	34.4	35.6	36.8
		.02	27.8	27.0	27.0	28.8	29.4
		.01	14.3	14.3	14.3	15.5	15.7
140	PGNPE	.025	23.2	23.4	23.7	24.1	25.6
		.02	19.7	19.4	18.8	20.2	21.3
		.01	10.3	10.0	10.2	11.6	11.6
180	PSML	.0145	30.5	32.6	32.9	30.1	33.6
		.00725	16.6	18.6	19.3	16.3	16.3
		.00363	9.4	9.4	9.3	9.1	cloudy
160	PSML	.0145	21.1	21.1	21.5	21.5	22.2
		.00725	11.1	11.4	11.9	11.7	12.0
		.00363	6.3	6.4	6.5	6.5	6.9
140	PSML	.0145	15.1	15.1	15.3	15.2	15.9
		.00725	8.3	8.1	8.3	8.5	8.9
		.00363	4.5	4.4	4.4	4.9	5.2
180	SDBS	.0434	11.0	13.0	13.6	12.8	13.7
		.0289	6.7	8.4	9.0	8.5	9.3
		.0145	2.9	3.8	4.1	4.2	4.7
160	SDBS	.0434	8.6	9.6	10.5	10.1	10.7
		.0289	5.0	6.2	6.9	6.8	7.2
		.0145	2.1	2.9	3.3	3.4	3.8
140	SDBS	.0434	6.9	7.8	8.5	7.7	8.5
		.0289	4.2	5.1	5.5	5.3	5.9
		.0145	1.7	2.4	2.7	2.8	3.2

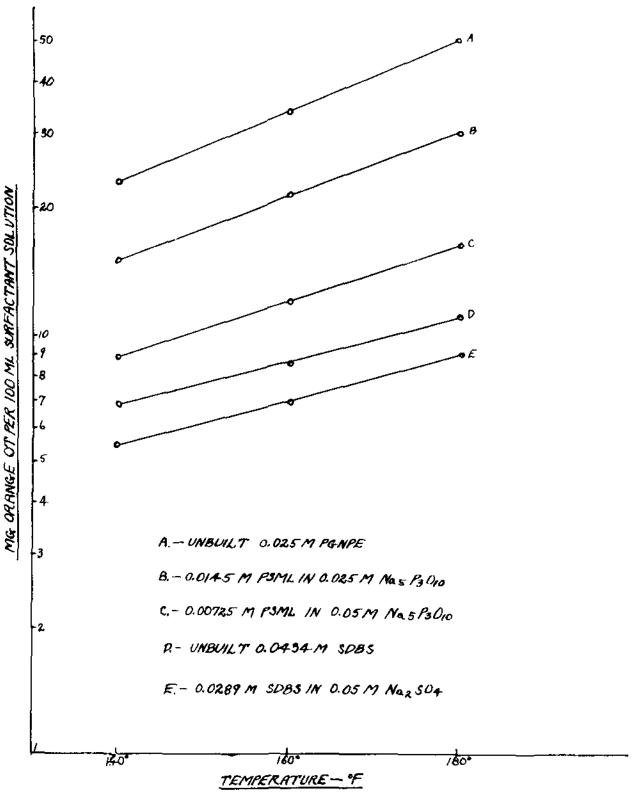

FIG. 1. Solubilization—Temperature function.

portional to temperature (solubilization is an exponential function of temperature) and that the log solubilization-temperature slopes of built and unbuilt solutions of each surfactant are substantially parallel. The calculated values of the slopes are given in Table II.

Further examination of the data reveals that the log solubilization-log concentration function for built and unbuilt surfactants is linear in the 180°–140°F. range as well as at lower temperatures (8).

Several effects of builders on micellar solubilization in the important 180°–140°F. range are also apparent from the data of Table I. This is particularly true of built solutions of the anionic surfactant SDBS. It is well known that solubilization by anionic surfactants is increased by the addition of inorganic builders. Now Table I indicates that for 0.58:1 to 1.73:1 mole ratios of builder-SDBS (covering 0.0289–0.0434M SDBS concentrations) the increased solubilization is independent of the type of builder (neutral Na_2SO_4 or polyphosphate $Na_5P_3O_{10}$), that is, equimolar amounts of Na_2SO_4 or $Na_5P_3O_{10}$ increase solubilization by SDBS equally. Since molar solutions of Na_2SO_4 and $Na_5P_3O_{10}$ contain considerably different sodium contents (46 g./l. and 115 g/l., respectively), the data do not support the theory that solubilizing power of a built anionic surfactant is a logarithmic function of the sodium content of the builder (9).

It is of interest that the data of Table I do not

TABLE II

Log Solubilization—Temperature Slopes Between 140° and 180°F.

Surfactant	Surfactant molarity	Slope				
		No builder	.025M Na_2SO_4	.05M Na_2SO_4	.025M $Na_5P_3O_{10}$	.05M $Na_5P_3O_{10}$
PGNPE	.025	.0084	.0079	.0077	.0089	.0079
	.02	.0067	.0067	.0068	.0071	.0073
	.01	.0069	.0070	.0068	.0059	.0062
PSML	.0145	.0076	.0084	.0083	.0074	.0081
	.00725	.0075	.0090	.0092	.0071	.0066
	.00363	.0080	.0082	.0081	.0067	.0061
SDBS	.0434	.0051	.0055	.0051	.0055	.0052
	.0289	.0051	.0054	.0053	.0051	.0049
	.0145	.0058	.0050	.0045	.0044	.0042

show an uniform trend in the 180°–140°F. range for the effect of builders on the solubilization of the two nonionic agents. Nonionic concentration, builder-nonionic mole ratio, temperature, and builder type appear to exert specific influences on the solubilization of specific builder-nonionic combinations. Previous work at this laboratory had shown that builder additions to 0.0062M octyl phenyl decaethylene glycol ether decreased Orange OT solubilization at 122°F. for 4.6 : 1 to 11.4 : 1 mole ratios of Na_2SO_4-surfactant and for 2.4 : 1 to 6.1 : 1 mole ratios of $Na_4P_2O_7$-surfactant (7). Similar decreased solubilization by the related nonionic PGNPE was obtained in this investigation in 0.01–0.025 M PGNPE at 1 : 1 to 5 : 1 mole ratios of Na_2SO_4-surfactant at 180°F. At 160° and 140°F. there was substantially no effect on solubilization by added Na_2SO_4 at the same builder and PGNPE concentrations. At 180°, 160°, and 140°F. additions of $Na_5P_3O_{10}$ increased solubilization by 0.01–0.025M PGNPE at 1 : 1 to 5 : 1 mole ratios of $Na_5P_3O_{10}$-surfactant.

Similarly in previous work with 0.0033M PSML at this laboratory (7) it was found that the Orange OT solubilization at 122°F. was substantially unaffected by additions of Na_2SO_4 and $Na_4P_2O_7$ at 8.7 : 1 to 21.6 : 1 mole ratios of Na_2SO_4-surfactant and at 4.6 : 1 to 11.7 : 1 mole ratios of $Na_4P_2O_7$-surfactant. In this investigation the solubilization of 0.00725–0.0145M PSML was increased by 0.025–0.05M additions of Na_2SO_4 at 180°F. while these additions had no substantial effect at 160° and 140°F. The same builder additions to 0.00363M PSML had no effect on solubilization at 180°, 160°, and 140°F.

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• *Letter to the Editor*

Triglyceride Elution by Gas Chromatography

WE WISH TO REPORT a new development in gas-liquid phase chromatography (GLPC) analysis of fats and oils, not previously reported in the literature. We have successfully eluted triglycerides, through tristearin, with quantitative interpretation through trimyristin, and qualitative through tristearin, including most common edible oils (Figure 1).

Our initial studies gave us separation of the simple triglycerides, with both quantitative and qualitative interpretation, tributyrin through tripalmitin in polyester-packed columns ["Craig" polyester—ethylene glycol-succinate MW∼1000, 30% on Chromosorb "W" (30/60 mesh), 18-in. column, operating at 250°C., 50 ml./min. He flow]. Because of the degradation of the polyester we have not attempted to operate these columns higher than 300°C.

We have extended the elutions through tristearin, using a silicone liquid phase at temperatures up to 350°C. The silicone used was fractionated from Dow Corning high-vacuum grease dispersed in ethyl acetate. A typical column used in this phase is an 18-in. stainless steel tube, packed with 30% silicone on Chromosorb "W" (30/60 mesh), operating at 300 to 350°C. with 50 to 200 ml./min. He flow. Table I shows a typical duplicate analysis of a synthetic mixture. Figure 2 shows typical log-retention plots for the columns used.

TABLE I
Quantitative Interpretation of GLPC Elution.
Tributyrin Through Trimyristin

Triglyceride	Standard Mixture		Curve I area %	Curve II area %
	Mole %	Weight %		
Butyric	14.9	8.11	8.15	12.2
Hexanoic	10.3	7.18	11.2	11.8
Octanoic	8.54	7.25	14.2	10.0
Decanoic	17.9	17.93	21.2	23.4
Lauric	22.3	25.71	29.7	26.0
Myristic	25.9	33.82	15.3	16.4

Despite what appears to be moderate degradation we have repeatedly reproduced the "fingerprint" of edible oils, and the curves given in Figure 1 appear as excellent qualitative elution curves.

The edible oils containing a preponderance of lower-molecular-weight fatty acids (butter and coconut) give elution curves without degradation problems. It is interesting to note that butter oil shows 17 peaks, all reasonably symmetrical, and coconut 15 peaks, indicating 17 and 15 different molecular-weight triglycerides for these oils, respectively.

The triglycerides used in this work were prepared by standard $ZnCl_2$ catalyzed esterification, followed by distillation and/or crystallization.

The instrument is based on the Aerograph (Wilkins Instrument Company) circuitry with conventional oven and cell geometry. The cell is Gow-Mac TEIII Model 9230, with four tungsten filaments operating at ≃ 200 ma, 12 volts DC.

Column temperatures for the work ranged from 229 through 350°C., cell temperatures were kept at or slightly above column temperatures, injection and