could be determined by this procedure (Table III). Averages of the four replicates for each of the two concentrations of the detergent were plotted against the number of soil-wash cycles in Figure 1. This curve shows that the reflectance of the towels gradually decreases after each washing, indicating that some soil remains and has not been removed completely by the previous washing. The slope of this curve also shows that the soil remaining is large, and that there are definite differences between the detergency of both concentrations of the same detergent.

The incremental decrease in reflectance (ΔRd) after each soiling and washing is shown in Figure 2. The ΔRd of soil remaining on the towels and the ΔRd of soil applied after each soiling decreases in the first four cycles, then becomes constant at the fifth cycle. Apparently soil saturation occurs at the fifth cycle, at which point the soil that the towels will permanently retain and which cannot be washed out by the given concentration of detergent becomes constant. Both concentration curves are parallel to each other. The difference between the ordinates of these two curves is a constant and represents the soil removed. The saturation point occurs at the fifth cycle for both concentrations of the same detergent. This suggests that for different concentrations of the same detergent and for the same substrate (Huck towels) and for the same type of soil (mechanical shop soil), the saturation point occurs at the same cycle. Since the ΔRd's of soil applied and soil remaining become constant at the fifth cycle, the Huck towel procedure should be run at least five cycles. However, using six cycles gives greater assurance that a constant residual soil is adsorbed by the towels.

ACKNOWLEDGMENT

J. R. Trowbridge provided the design and the statistical interpretation of the results and V. S. Tarika, R. B. Handler and J. Albano performed various phases of this work.

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A Colorimetric Method for the Determination of Parts/Million of Nonionic Surfactants

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Abstract

A method for the determination of nonionics in low concn (0–20 ppm) has been developed. This method is based on the formation of a blue complex between ammonium cobaltothiocyanate reagent and a polyethoxylated compound. This complex is extracted into benzene from a saturated salt solution and measured with a spectrophotometer at 320 mμ. The absorbance reading is compared to a standard.

The method requires only a single extraction and no preliminary concn step is necessary. It is sensitive to polyethoxylated compounds containing three or more moles of ethylene oxide. We have used this method to detect as little as 0.01 mg of nonionic in 100 ml of sample (0.1 ppm). Reaction conditions, sensitivity differences between compounds, interferences and suitability for use in biodegradation studies have been investigated. The accuracy and repeatability of this method is ±3% relative at 20 ppm concn.

Introduction

A REVIEW OF THE LITERATURE shows few methods for the determination of nonionics in low concn ranges. In higher concn ranges there are methods based on gravimetric, volumetric and colorimetric procedures. Shaeffer and Critchfield (11) described a gravimetric procedure using silicotungstic acid to precipitate the nonionic. They also describe a colorimetric procedure based on a molybdenum determination after precipitation with phosphomolybdic acid. Oliver and Preston (9) used phosphomolybdic acid in a gravimetric procedure. Barber, Chinnick and Lincoln (1) describe a more rapid procedure using phosphotungstic acid. Stevenson (12) developed two colorimetric methods, both based on reaction with phosphomolybdic acid. Schoenfeldt (10) developed a volumetric procedure based on reaction with ferrocyanic acid and determination of the excess reagent with standard zinc sulfate. Karabinos (7) described a phenol titration procedure for determination of ethylene oxide chain length. Ca. 3 moles of phenol are required for each 7–8 ethylene oxide units. Davis, Watman and Speel (4) used the phenol titration for determination of concn. Wurzschmitt (17) describes oxonium ion formation and the development of colored precipitates with reagents such as KI_3 and ammonium cobaltothiocyanate. Two oxonium groups appear to form for each 5.5 ethylene oxide units.

The ammonium cobaltothiocyanate reaction first described by Gnamm (5) was used as a qualitative test for polyethoxylated compounds by Wurzschmitt (17) and van der Hoeve (14,15). In 1955, Brown and Hayes (2) published a method for the quantitative determination of polyethylene glycol mono-oleate using the cobaltothiocyanate reagent of Wurzschmitt to produce a colored complex which is extracted into chloroform and determined absorptiometrically. Also in 1955, Kurata (8) published a review of methods for the analysis of nonionics in which he described a procedure using a concd ammonium cobaltothiocyanate reagent and benzene as the extraction solvent. The nonionic cobaltothiocyanate complex was extracted with benzene from a saturated salt solution. The benzene layer was dehydrated with anhydrous sodium sulfate, centrifuged, and its absorbance measured.

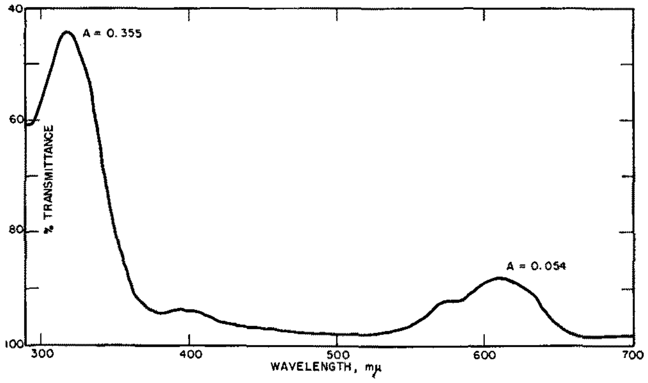


FIG. 1. Spectrum of a polyethoxylated alcohol—cobaltothiocyanate complex in benzene.

Kurata shows data obtained in the concn range of 130–530 ppm (13–53 mg/100 ml). More recently, the Soap and Detergent Assoc. has been working to develop a procedure for the determination of alkylphenol ethoxylates (20). This procedure consists of concn, isolation and measurement of the UV absorption of the aromatic ring. Stewart (13) has published a procedure based on the reduction in absorbance of a solution of dichlorofluorescein by the addition of nonionic detergents. He reports that only nonylphenol ethoxylates can be determined.

In an attempt to develop a method suitable for following biodegradation studies on all types of ethoxylated nonionic surfactants we succeeded in detecting as little as 0.5 mg of nonionic by the method of Brown and Hayes. In 1963 work being done at the Oji Research Institute in Japan (19) came to our attention. Using the method reported by Kurata, they were working in the 10–100 ppm concn range (1–10 mg/100 ml). Since the Japanese procedure is simpler than that of Brown and Hayes, our effort was concd in this direction. We have been able to extend this method to detect as little as 0.01 mg of nonionic in 100 ml of sample (0.1 ppm). A similar procedure has recently been reported by Crabb and Persinger (3). Their method calls for concn of the surfactant by counter current ether extraction, reaction with the reagent of Brown and Hayes (2), and chloroform extraction of the complex which is measured at 620 mμ.

The procedure used in our work is described below. It is presently being used to follow biodegradation studies in several different media, as a matter of routine.

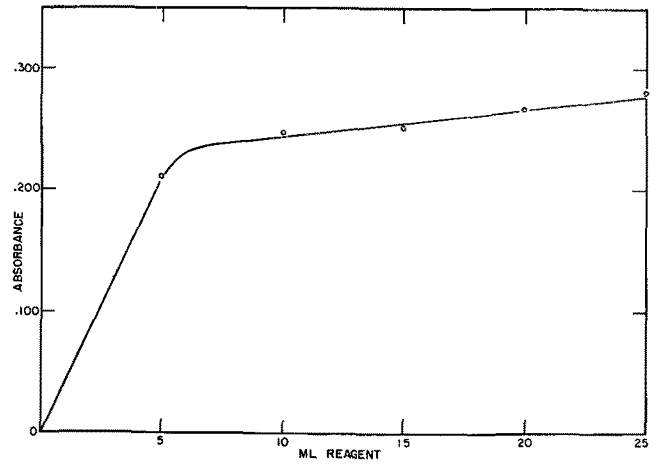


FIG. 2. Effect of reagent volume on absorbance.

TABLE I

Effect of Sodium Chloride on Extraction Efficiency

g NaCl	Absorbance
0	0.231
5	0.253
20	0.286
30	0.284
40	0.287

Experimental

Reagent. Dissolve 620 g of reagent grade ammonium thiocyanate (NH_4SCN) and 280 g of reagent grade cobalt nitrate hexahydrate [$Co(NO_3)_2 \cdot 6H_2O$] in water and dilute to one liter. Extract twice with benzene to lower the blank reading.

Procedure. Place 100 ml of sample solution into a separatory funnel. Add 15 ml of the ammonium cobaltothiocyanate reagent and 35–40 g of sodium chloride. Shake to dissolve the salt. Allow to stand ca. 15 min. Accurately add 25.0 ml of benzene to the funnel. Shake for one min, then let stand to allow the layers to separate. Draw off and discard the lower aqueous layer. Transfer the benzene layer to a centrifuge tube, stopper and spin for 10 min. Using the spectrophotometer, read the peak absorbance at ca. 320 mμ (scan the region between 340 and 315 mμ) against a reagent blank. Compare the absorbance reading to that obtained on a sample of known concn (Figure 1).

This method was developed using a Beckman DB UV Spectrophotometer with a deuterium lamp and 1-cm cells. It was connected to a 100-mv recorder through a Beckman Scale Expander accessory. The Scale Expander accessory is most useful for samples of low concn and/or sensitivity.

Study of Reaction Variables. After assuring ourselves that the method described by Kurata (8) could be extended to the desired 0–20 ppm range, we studied the effect of the following variables on the determination: water removal; sodium chloride addition; reaction time; variation in the volumes of sample, solvent and reagent. The nonionic used in this work was a standard sample obtained from the Nonionic Detergents Analytical Subcommittee, the Soap and Detergent Assoc. This material is one-third Igepal CO 630, one-third Sterox NJ, and one-third Tergitol TP9. It is nonylphenol condensed with an average of 9 moles of ethylene oxide/molecule.

Water Removal. Centrifuging is sufficient to clear the benzene layer; dehydration with anhydrous sodium sulfate is not only unnecessary, but removes some of the nonionic-cobaltothiocyanate complex. (A second dehydration removes nearly all of the complex.)

Sodium Chloride Addition. The effect of sodium chloride, which is added in sufficient quantity to saturate the sample solution, was determined by adding varying amt of sodium chloride to a sample containing 20 ppm of the SDA Nonionic Standard. With this sample, any amount of sodium chloride over 20 g was sufficient to give optimum extraction efficiency.

Sample Volume. Samples containing 2.0 mg of the SDA Nonionic Standard were diluted to 100, 200 and

TABLE II

Effect of Sample Volume on Extraction Efficiency

Sample volume ml	Absorbance	
100	0.274	0.276
100	0.277	
200	0.213	0.213
200	0.213	
300	0.142	0.144
300	0.145	

TABLE III

Effect of Solvent Volume on Extraction Efficiency

ml Benzene	Absorbance	Absorbance × ml
15	0.524	7.86
20	0.418	8.36
25	0.352	8.80
30	0.288	8.64
40	0.205	8.20
50	0.168	8.40

300 ml. Each sample was saturated with sodium chloride and allowed to react with 15 ml of the cobaltothiocyanate reagent. Each was then extracted once with 30.0 ml of benzene. Table II shows the results obtained.

As might be expected, the extraction from larger volumes of sample solution is less efficient. Almost twice as much nonionic was extracted from the 100-ml dilution as from the 300-ml dilution. Therefore, either the sample size must be standardized, or a multiple extraction procedure used. (It is still possible to use smaller than standard size samples, if it is necessary to conserve sample, by diluting to the required volume.)

Solvent Volume. After standardizing on a 100-ml sample size, the effect of variation in the volume of the extraction solvent was studied. All samples contained 2.0 mg of the SDA Nonionic Standard in 100 ml of water. To this was added 35 g of sodium chloride and 15 ml of the cobaltothiocyanate reagent. The volume of extraction solvent (benzene) was varied from 15–50 ml. The data appear in Table III.

It is clear that the extraction efficiency increases as solvent volume is increased, up to ca. 25–30 ml. It then decreases somewhat. We chose 25 ml for our work, since this volume offers the most efficient extraction as well as being a convenient working volume. A smaller volume may be desirable for samples that are relatively insensitive to this method, since it will provide a more concd solution.

Reagent Composition. In most of our work with the cobaltothiocyanate method, the reagent composition and volume reported by Kurata (8) has been used. Most of the other workers (Table IV) have used more dilute reagent solutions. This area of the method should receive further study.

Reagent Volume. A brief study was made of variation in reagent volume, from 5–25 ml. Above 10 ml of reagent, a small continued increase in absorbance with increased reagent volume (Fig. 2) was found. This same occurrence was reported by Brown and Hayes using Wurzschmitt's reagent. We continued to use 15 ml of reagent.

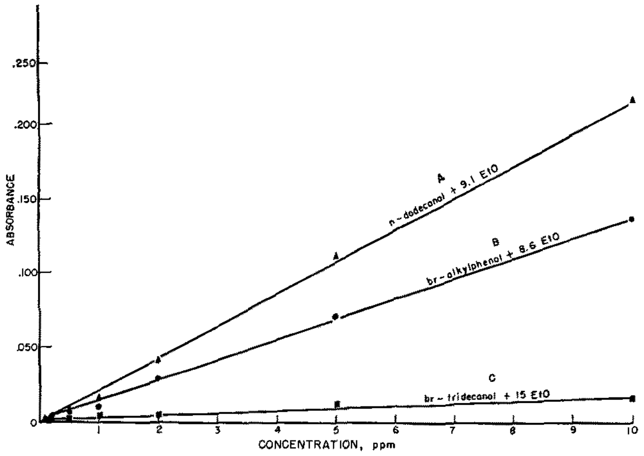


FIG. 3. Calibration curves for three ethoxylated surfactants at low concns.

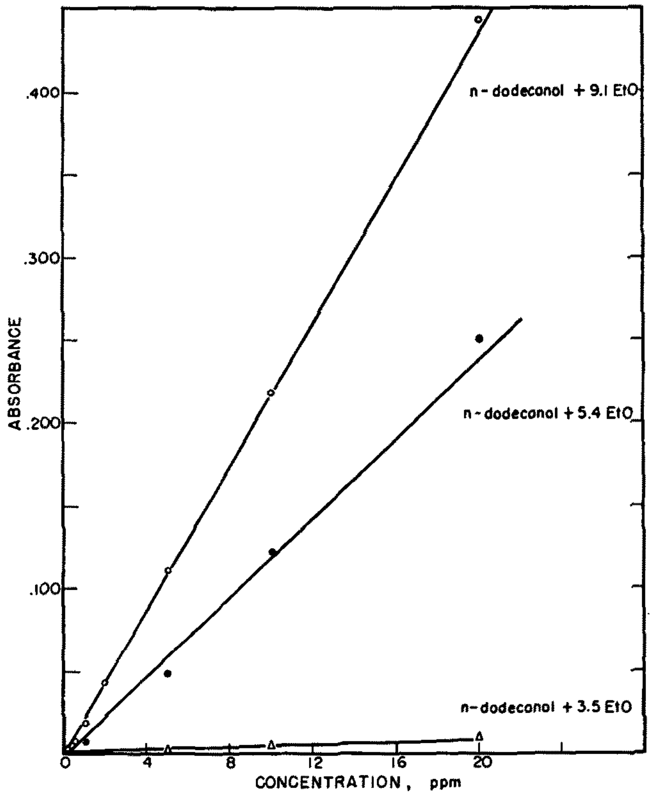


FIG. 4. Effect of ethylene oxide content of the sensitivity of *n*-dodecanol ethoxylates.

Reaction Time. There is relatively little change in absorbance with reaction time. To be consistent we stopper and shake the samples for one min after ad-

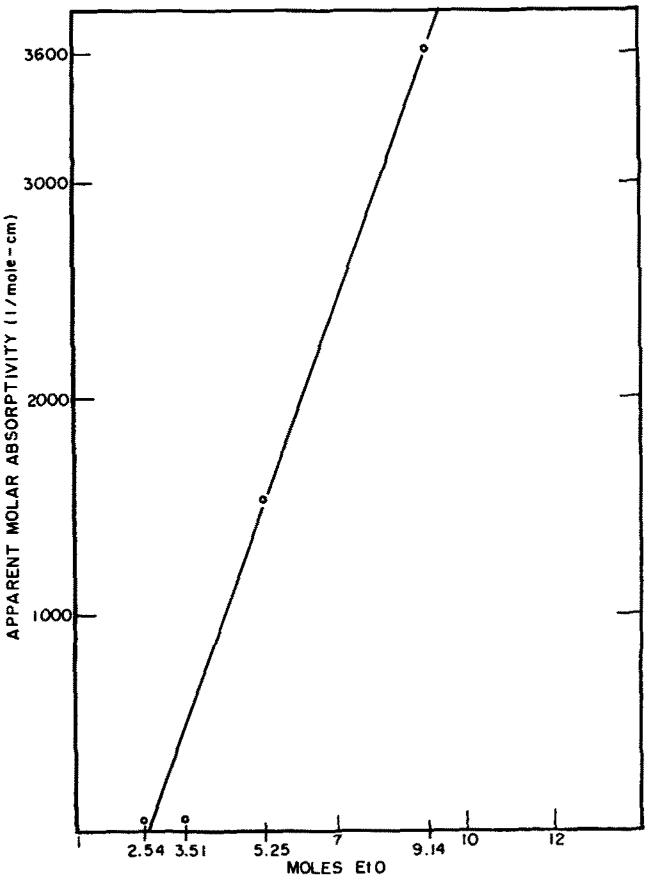


FIG. 5. Moles of ethylene oxide required for complex formation between *n*-dodecanol ethoxylate and ammonium cobaltothiocyanate reagent.

TABLE IV

Proposed Reagent Compositions

Author	Ammonium thiocyanate g/liter	Cobalt nitrate hexahydrate g/liter
Gnamm (5)	347	1.4
Van der Hoeve (14,15)	174	2.8
Wurzschmitt (17)	174	28
Brown and Hayes (2)	200	30
Kurata (8)	620	280

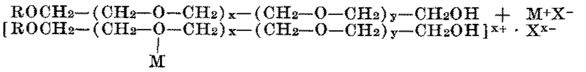
dition of the sodium chloride and the reagent, then set aside for a minimum of 15 min before extraction. Table V shows the results of a reaction-time study using a 20 ppm nonionic solution.

Chloroform and benzene were the only solvents studied. Benzene is much less soluble in water (0.08 g/100 g) than is chloroform (1.0 g/100 g). This provides better phase separation when benzene is used, and a solution that is easier to clear. In addition, the use of a single benzene extraction makes this procedure simple and rapid. A recent paper by Weber et al. (16) on the determination of mg quantities of nonionics, reports the use of ethylene dichloride as the extraction solvent. Its solubility characteristics should be similar to chloroform.

The effect of temp on the reaction was not studied since this is closely controlled in our laboratory. However, we have reason to believe that this can introduce significant errors, as much as 10%, where variations in temp exist. Brown and Hayes (2) recommended that for accurate results solution and room temp should be below 26C and, preferably, nearer to 20C.

Results and Discussion

The reaction of polyethoxylated nonionics with ammonium cobaltothiocyanate reagent probably involves oxonium ion formation, and subsequent precipitation. Wurzschmitt (17) postulates that either hydrogen, ammonium or metal ion is complexed by the ether oxygen of polyethoxylated compounds, forming a cationic oxonium ion. This in turn reacts with suitable anions:



$$\mathrm{ROCH_2{-}(CH_2{-}O{-}CH_2)_x{-}(CH_2{-}O{-}CH_2)_y{-}CH_2OH + M^+X^-}$$
$$\rightarrow \mathrm{[ROCH_2{-}(CH_2{-}\underset{\underset{\displaystyle M}{|}}{O}{-}CH_2)_x{-}(CH_2{-}O{-}CH_2)_y{-}CH_2OH]^{x+}\cdot X^{x-}}$$

He further shows that some reagents not only form the oxonium ion but also furnish the precipitating anion. With ammonium cobaltothiocyanate, the ammonium ion would react to form the oxonium ion, which would then be precipitated by the cobaltothiocyanate anion $[\mathrm{Co(SCN)_4}]^=$.

Sensitivity of Different Structures. Figure 3 shows concn vs. absorbance curves for three ethoxylated materials. Sample A is *n*-dodecanol condensed with 9.1 moles of ethylene oxide. Sample B is the SDA nonionic standard, nonylphenol condensed with 8.6 moles of ethylene oxide. Sample C is a branched tridecanol condensed with 15 moles of ethylene oxide. Although the samples vary in sensitivity to this method, they all show a linear relationship between concn and absorbance. The 0.1 ppm concn level corresponds to 0.01 mg of nonionic in 100 ml of sample.

Figure 4 shows a series of curves obtained by testing a sample of *n*-dodecanol condensed with varying amt of ethylene oxide. The samples show decreasing sensitivity to this test with decreasing ethylene oxide content. Figure 5 shows the "apparent molar absorptivity" vs. moles of ethylene oxide for these same samples. (This is not a true M absorptivity since the single extraction does not remove all of the nonionic-cobaltothiocyanate complex.) This graph shows a linear relationship between ethylene oxide content of *n*-dodecanol ethoxylates and their sensitivity to this reaction. Ethoxylates with less than 2.5 moles of ethylene oxide are not detected by this method. This is in agreement with the report by Wurzschmitt (17) of 2 oxonium groups forming for each 5.5 moles of ethylene oxide. Karabinos (7) reported the same ratio (3/7–8 moles) or, again, about one oxonium group for each 2.5–3 ethylene oxide units.

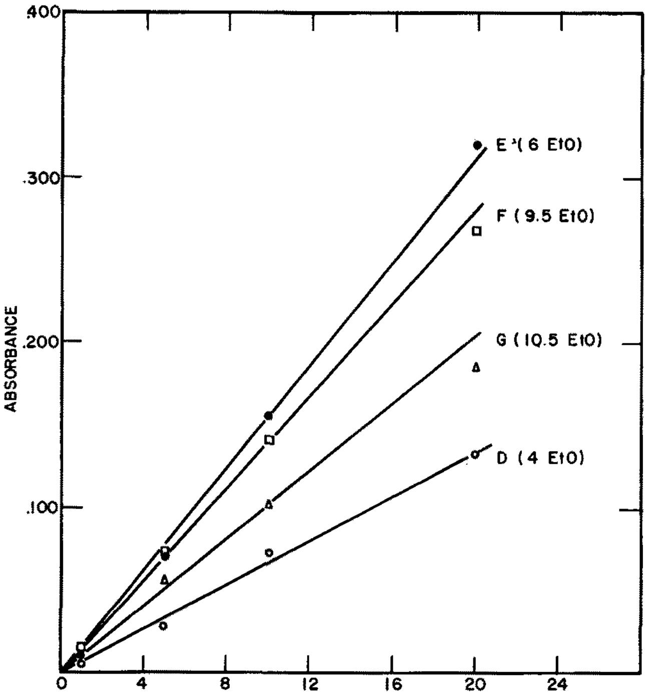


FIG. 6. Calibration curves for a series of branced nonylphenol ethoxylates.

The data shown in Figure 6 were obtained by test-

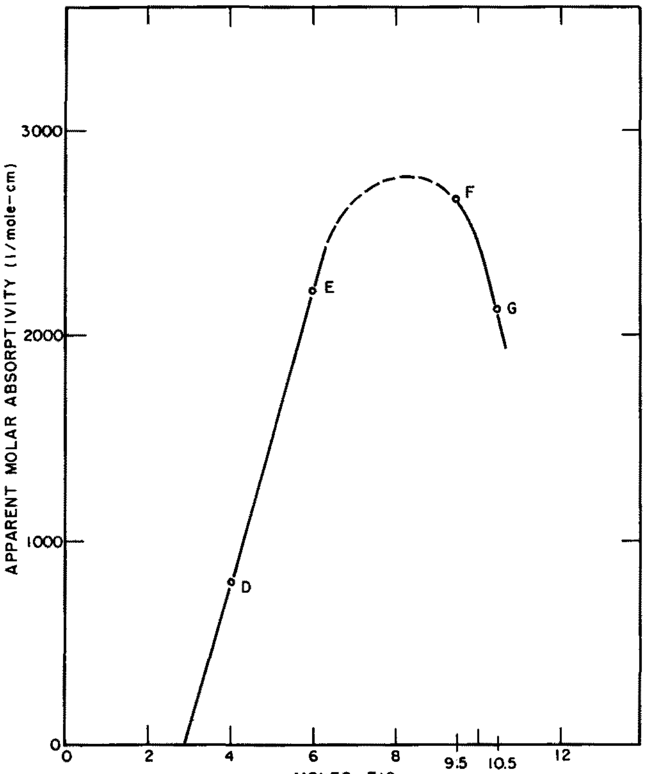


FIG. 7. Effect of ethylene oxide content on the sensitivity of branched nonylphenol ethoxylates.

TABLE V

Effect of Reaction Time on Absorbance

Reaction time (after shaking) min	Absorbance
5	0.259
10	0.262
15	0.268
20	0.268
60	0.273

ing a series of commercial nonylphenol ethoxylates. Samples D,E,F and G contain 4,6,9.5 and 10.5 moles of ethylene oxide/molecule. These samples do not show the expected increased sensitivity with increased ethylene oxide content. We believe this is caused by the great differences in solubility between the ethoxylated alkylphenols. To show this we made multiple extractions on Samples E (6 moles EtO) and G (10.5 moles EtO). The first benzene extraction removed 90% of sample E while removing only 80% of sample G.

Figure 7 is a plot of "apparent molar absorptivity" vs. ethylene oxide content for samples D,E,F and G. This plot also goes to zero just under 3.0 moles EtO/molecule. However, as the ethylene oxide content increases, the "apparent M absorptivity" peaks out and begins to decrease.

Detergent Biodegradation. This method has been used in detergent biodegradation studies with excellent results (Fig. 8). No difficulty was found in river die-away studies or in synthetic medium shake flask (6) studies. Results obtained on runs in a continuous feed activated sludge system (18) show some fluctuation, similar to that reported in sulfonate studies. (This is the nature of a dynamic system, rather than any short-coming of this test.) Of course, proper control samples must be carried along with all biodegradation studies. If it is necessary to preserve samples for analysis at a later time, addition of formaldehyde is a convenient way to do this.

Interferences are cancelled by proper control samples in biodegradation studies. However, interference from polypropylbenzene sulfonate, *n*-alkyl sulfate, an aromatic quaternary ammonium compound, and two polyethylene glycols of differing mol wt (600 and 1000) was determined. The test solutions contained 10 ppm of ethoxylated *n*-dodecanol and 10 ppm of compound under test. Table VI shows the results of this study. The quaternary ammonium compound, as expected, interferes greatly. The sulfonate and sulfate show some positive interference, while the two polyethylene glycols show slight negative interference. The polyglycols, by themselves, show no response; the sulfonate and sulfate by themselves, show a lesser response than they do in mixture with the nonionic. Anionic compounds containing ethylene oxide chains will also interfere, since the cobaltothiocyanate reaction is with this chain.

TABLE VI

Study of Possible Interfering Substances

Nonionic ppm	Test substance		Absorbance	
	ppm	Type		
10	0		0.168	
10	0		.168	
10	0		.166	
10	0		.168	
			0.168	±.001
0	20	polypropylbenzene sulfonate	0.026	
10	10	polypropylbenzene sulfonate	.211	
10	10	polypropylbenzene sulfonate	.198	
10	10	polypropylbenzene sulfonate	.209	
			0.206	±.005
0	20	*n*-alkyl sulfate	0.003	
10	10	*n*-alkyl sulfate	.203	
10	10	*n*-alkyl sulfate	.221	
10	10	*n*-alkyl sulfate	.205	
			0.210	±.008
0	10	quaternary ammonium Cl	0.513	
0	10	quaternary ammonium Cl	.485	
			0.499	±.014
10	10	quaternary ammonium Cl	.694	
10	10	quaternary ammonium Cl	.687	
10	10	quaternary ammonium Cl	.683	
			0.688	±.004
0	20	polyethylene glycol (600)	0.000	
10	10	polyethylene glycol (600)	0.150	
10	10	polyethylene glycol (600)	.155	
10	10	polyethylene glycol (600)	.160	
			0.155	±.003
0	20	polyethylene glycol (1000)	0.000	
10	10	polyethylene glycol (1000)	0.157	
10	10	polyethylene glycol (1000)	.159	
10	10	polyethylene glycol (1000)	.162	
			0.159	±.002

TABLE VII

Separation of Nonionic—Anionic Mixtures

Added anionic	ppm Nonionic found[a]	
	as is	after ion exchange
0		5.2
0	5.7	5.8
0	5.4	5.6
0	5.7	6.1
	5.6 ±0.1	5.7 ±0.3
9.4 ppm LAS	8.5	5.6
9.4 ppm LAS		6.0
9.4 ppm LAS		6.0
		6.1
		5.9 ±0.2
0 ml EtOH	5.6	
1 ml EtOH	6.2	
2 ml EtOH	6.5	
3 ml EtOH	6.7	

[a] All samples contain 5.6 ppm nonionic.

A preliminary separation step is required before this method can be applied to systems containing unknown interferences, as in sewage or river water samples. Even with such a separation, some assumption on sensitivity must be made if this method is to have any application to these systems. We have obtained such a separation by adding a mixed bed ion exchange resin to the sample, agitating, then decanting the solvent and washing the resin with aqueous ethanol. The ethanol is evaporated, the nonionic is washed into the separatory funnel, and the determination carried out as previously described. The data in Table VII were obtained by applying this separation technique to a mixture of 5.6 ppm of ethoxylated alcohol and 9.4 ppm of dodecene-1 LAS. The importance of evaporating all of the ethanol is also shown.

Repeatability data were obtained at concn of 1.0 and 20.0 ppm in water, using the SDA Standard Nonionic. The data were obtained on several different days. The standard deviation at the 1.00 ppm level was 0.11 ppm, giving a relative standard deviation of

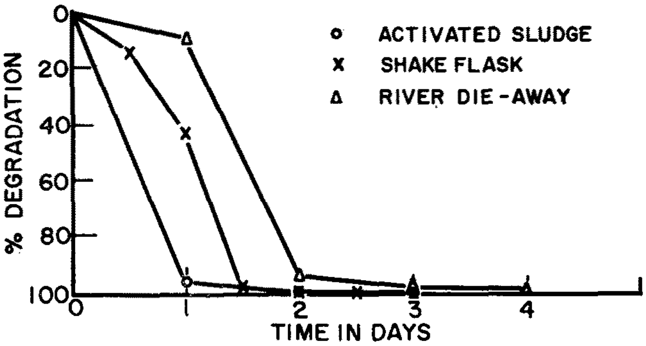


FIG. 8. Degradation of *n*-dodecanol ethoxylate (59% EtO in three different biological media.

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

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The Energetics of Micellar Solubilization

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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 (ΔG), heat of solubilization (ΔH) and change in entropy (ΔS) 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 ΔG in anionic and nonionic surfactants are of the order of magnitude of a physical adsorption. The positive ΔH values indicate the process is not an adsorption. The positive ΔS 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:

$$\Delta G = -2.3\,RT \log \frac{C_S}{C_L} \qquad [1]$$

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, ΔH, 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 ΔH directly. The change in entropy, ΔS, for the process would follow from the equation:

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

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 Å^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