ductance results can be explained on the basis of Ostwald's formula and Debye-Huckel's theory of weak electrolytes.

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Cobaltothiocyanate Colorimetric Analysis for Homologous Polyoxyethylated Alkyl Amides

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Cobaltothiocyanate colorimetry has been used for quantitative analysis of polyethoxylates in biodegradation and environmental studies. Usually, the calibration parameters (slope and intercept of a calibration line) for the cobaltothiocyanate colorimetry are dependent on ethylene oxide chain length. To make the colorimetric method useful for polyoxyethylated surfactant mixtures, where the average chain length is polydispersed, a condition was found yielding parameters independent of chain length in a homologous series of polyethoxylates within a limited chain length range. The dependency can be correlated to the thermodynamics of the ethylene oxide-cobaltothiocyanate complexation and the solvent extraction.

Recently, Micich and Linfield (1) developed a series of polyoxyethylated alkyl amides with outstanding wetting properties (see Table 1 for structured diagram). To evaluate their products as soil conditioners the adsorption of these nonionic surfactants on clay particles was studied. Such a study requires the measurement of the surfactant concentration in serum separated from the clay particles.

Polydispersity of the chain length distribution often prevents quantitative analysis of polyethoxylate surfactants. To be precise, two complimentary analytical methods must be devised, one for the hydrophobic head group and the other for the hydrophilic polyethoxylate chain, since the average chain length may change in the serum after adsorption. In our case, UV-VIS spectro-

TABLE 1

Cobaltothiocyanate Colorimetric Absorptivity of Homologous Polyoxyethylated Alkyl Amides[a]

	EO = 5	EO = 10	EO = 15	EO = 20
methyl chloride				
a[b] · 10^{-4}	1.71 ± 0.01	4.87 ± 0.01	7.27 ± 0.03	9.44 ± 0.12
a′[c] · 10^{-3}	3.41 ± 0.02	4.87 ± 0.01	4.85 ± 0.02	4.72 ± 0.06
f[d]	99.0 ± 0.5	98.2 ± 0.5	97.0 ± 0.5	97.5 ± 0.5
benzene				
a[b] · 10^{-4}	1.58 ± 0.01	0.84 ± 0.03	0.08 ± 0.02	—
a′[c] · 10^{-3}	3.16 ± 0.02	0.84 ± 0.03	0.05 ± 0.01	—
f[d]	97.5 ± 0.5	<31	—	—

[a] The homologous polyoxyethylated alkyl amide has a structure as $RCON(CH_2R)(C_2H_5O)_nH$, where R is $-CH(C_4H_9)(C_2H_5)$ and n is the average E.O. chain length.
[b] a is apparent molar absorptivity in unit of mole^{-1} · cm^{-1}.
[c] a′ is apparent molar absorptivity per E.O. in unit of equivalent^{-1} · cm^{-1}.
[d] f is the extraction efficiency.

photometry was applied for the alkyl amide group analysis, while a cobaltothiocyanate colorimetric method was used for ethylene oxide quantitative analysis.

The colorimetric cobaltothiocyanate analysis of polyethoxylates has been investigated extensively since van der Hoeve (2) reported that polyethoxylates form a blue insoluble complex with ammonium cobaltothiocyanate. Brown and Hayes (3) then developed a quantitative method based on this reaction. They extracted the complex into chloroform and measured the concentration photometrically. Since then, there have been several modifications of this method to increase its sensitivity (4–6). Recently, the Chemical and Environmental Research Committee of the Soap and Detergent Association (SDA) recommended the cobaltothiocyanate method for quantitative analysis of the nonionic surfactant in biodegradation and environmental studies (7).

Usually, the concentration of nonionic surfactant in parts per million (ppm) is determined from a calibration curve derived with the same nonionic surfactant as is suspected (known) in the sample. Because of nonspecificity, the method is suspect whenever applied to adsorption studies. The problem is: Does this method correctly assay the ethylene oxide content in post-adsorption serum if the average chain length differs from that in the calibrated original solution? Since the cobaltothiocyanate colorimetry involves both a complexation reaction between ethylene oxide chain and cobalt ion (the actual chromophor), and extraction of the complex from aqueous phase into organic phase, this technique is applicable to adsorption studies if and only if the following assumptions hold: (i) The stoichiometric ratio of E.O. group to Co^{++} in the complex is independent of E.O. chain length; and (ii) the extraction efficiency is constant.

When the above assumptions are satisfied, one can evaluate the number of equivalent E.O., [N], in an unknown sample from its apparent absorbance, A, according to Eq. [1]:

$$[N] = A/a'l \qquad [1]$$

where a′ is the apparent equivalent absorptivity per E.O., and l is the optical path length. The apparent equivalent absorptivity per E.O. can be obtained from a surfactant with known apparent molar absorptivity, a, and known average E.O. chain length, n, according to Eq. [2]:

$$a' = a/n \qquad [2]$$

Depending on the experimental conditions, a constant value of a′ may not be attainable. For instance, Greff et al. (5) found that a homologous series of branched nonylphenol ethoxylates with average E.O. chain length 4, 6, 9.5 and 10.5 gave apparent molar absorptivities of 800, 2234, 2639 and 2109 (l/mol·cm), respectively. These data give a′ values of 200, 372, 278 and 201 (l/equivalent·cm). In their case, benzene was the solvent for extraction. They pointed out that the extraction efficiencies differed with the average chain length of the samples. On the other hand, Zoller et al. (8) reported that nonylphenol ethoxylates with E.O. chain lengths of 10 and 12 gave apparent absorptivities of 0.152 and 0.172 (Ab. unit/mg), respectively. Calculated from their data, the apparent equivalent absorptivities per E.O. are 1.00×10^4 and 1.07×10^4 (Ab. unit/equivalent), respectively. These two figures are about the same. Methylene chloride was used in their experiment.

The object of our work is to find conditions yielding a′ values that are chain length-independent. Realizing that solvent plays an important role in the extraction process, we will attempt to apply thermodynamic principles and to develop a criteria for choosing an extraction solvent which minimizes the dependence on ethylene oxide chain length in the cobaltothiocyanate colorimetric analysis of homologous polyoxyethylenated compounds.

EXPERIMENTAL PROCEDURES

To prepare ammonium cobaltothiocyanate solution, dissolve 30.0 g of cobalt nitrate hexahydrate crystals and 200.0 g of ammonium thiocyanate crystals to make a one-l solution. Next, add methylene chloride to extract the organic solvent-soluble impurities. For the cobaltothiocyanate colorimetric method:

(i) Take a known volume of surfactant solution. Dilute to 15 ml with DI- water. The final concentration is in the range of $0.1 \sim 3 \times 10^{-4}$ mol/l.

(ii) Add the solution to a 125-ml separatory funnel containing 25 ml of methylene chloride.

(iii) Add 25 ml of cobaltothiocyanate solution to the mixture.

(iv) Add 10.00 g of NaCl crystals.

(v) Shake the mixture for 3 min. All NaCl should dissolve in the aqueous phase.

(vi) Let the mixture stand for 4 min. The organic phase which settles at the bottom is then separated for spectrophotometry.

(vii) Measure the absorbance at 624 nm. (We used a Perkin-Elmer UV-VIS spectrophotometer, model 559.)

To study the effect of solvent, benzene was used in another experiment as the extracting solvent.

RESULTS AND DISCUSSION

Linear calibration curves were obtained when methylene chloride was used in the cobaltothiocyanate colorimetry. Solid lines in Figure 1 are calibration curves for the homologous series of N-poly(oxyethylenated) octyloctamides with E.O. average chain lengths of 5, 10, 15 and 20. Their apparent molar absorptivities, a, and apparent equivalent absorptivities per molar E.O., a′, are listed in Table 1. (Note these data are not "true absorptivities" because the single extraction does not remove all of the nonionic surfactant-cobaltothiocyanate complex.)

Except for the surfactant with EO = 5, which has much lower a′ value, the other three surfactants have a′ values which are practically identical to each other when methylene chloride is used. Initially, we thought that the slight decrease in a′ as E.O. chain length increases was due to the difference in extraction efficiencies. Because EO = 10 is more hydrophobic than EO = 15 or EO = 20, it is reasonable to assume that their cobaltothiocyanate complexes had hydrophobicities in the same order. Therefore, a favorable extraction efficiency for EO = 10 results in an apparent equivalent absorptivity 0.4%

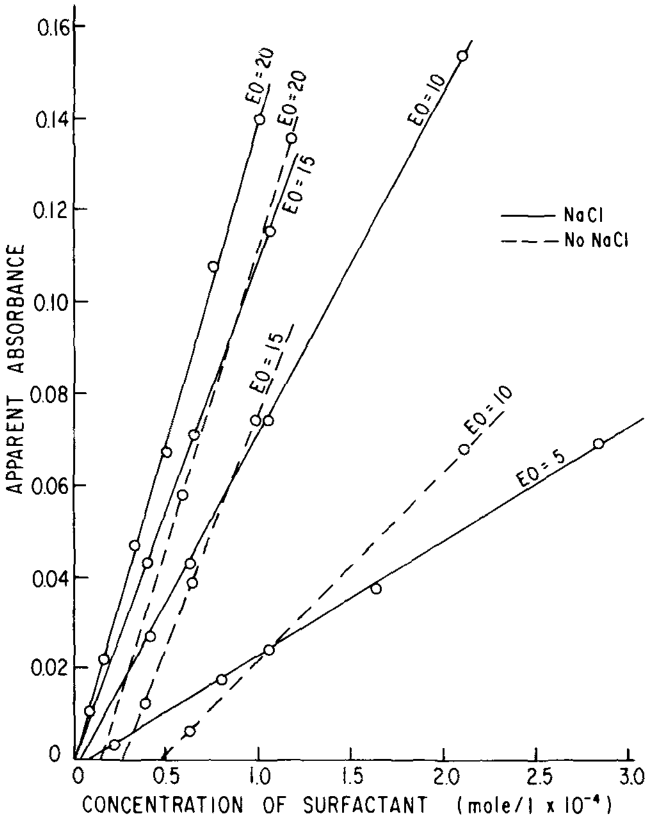

FIG. 1. Apparent absorbance of cobaltothiocyanate colorimetry of solutions (15 ml) of surfactants with various chain lengths.

and 3% higher than EO = 15 and EO = 20, respectively. However, multiple extraction studies reveal that surfactants with EO = 10, 15 and 20 have about the same extraction efficiency, f, within experimental error. Therefore, the extraction efficiency is not the reason for deviation of a′ value. It is our belief that the low a′ value for EO = 20 is due to an overestimation of the average EO chainlength for the surfactant. During ethoxylation, loss of ethylene oxide may occur and result in the overestimation of EO chainlength. This is more likely to happen for long-chain polyethoxylates because the reaction time is longer. Nevertheless, the apparent equivalent absorptivity, a′, changes only slightly as the E.O. chain length changes in such a wide range, we can then justify the cobaltothiocyanate method for adsorption studies. Multiple-extraction technique could in principle reduce the deviation of the a′ value, but the color strength, and therefore the colorimetric sensitivity, would be reduced by the volume of solvent. The volume of solvent could be reduced but multiple extraction is not necessary because the simple, single extraction already gave satisfactory results for our work.

When benzene is used as extracting solvent, the apparent equivalent absorptivity, a′, is dependent on the E.O. chainlength of surfactant. This is due to the fact that the extraction efficiency decreases as the E.O. chainlength increases, as shown in Table 1. For the EO = 20 sample, the extraction efficiency is so low no absorbance due to surfactant could be detected.

For single extractions, therefore, one should choose an organic solvent which is nonselective regarding the variation of chain length. Hildebrand's solubility parameter theory (9) and Hansen's partial solubility parameter version (10) offer a guide in selecting the right solvent. According to Martin's (11) additivity of group interactions theory, the distribution (or partition) coefficient, P, in two phases for a homologous series with chain length n can be written as

$$\log P = A + B \cdot n \qquad [3]$$

Here A is a thermodynamic constant related to the hydrophobic group, whereas constant B is related to the ethylene oxonium-cobaltothiocyanate ion-pair segment in the complex. As the chain length changes, the oil/water distribution coefficient changes according to the following equation, neglecting the entropy effect of chain length on P:

$$\Delta \log P = B\Delta n \qquad [4]$$

$$= [(h_{oxonium\text{-}aqueous} - h_{oxonium\text{-}org\ solv})/2.3\ RT]\Delta n$$

$$= (\bar{v}_i/2.3\ RT)\ [(\delta_{oxo} - \delta_{aq})^2 - (\delta_{oxo} - \delta_{org})^2]\Delta n$$

where h represents the group interaction enthalpy between ethylene oxonium and solvent (aqueous or organic); $\bar{v}_i$ is the partial molar volume of the oxonium group, and δ's are solubility parameters (12). Equation [4] suggests that the change in distribution coefficient with n can be minimized if the difference in group interaction enthalpies is minimized by proper choice of solvent. The argument also implies that the solubility parameter of the organic solvent should be close to that of water, as long as the solvent-water system does not form a single phase. In Eq. [4], the interaction enthalpy between oxonium and aqueous, $h_{oxonium\text{-}aqueous}$, should be disregarded if the oxonium group in the ion-pair is nonsolvated. In that case, the deviation of P is determined mainly by the difference in solubility parameters of oxonium and organic solvent. Due to the ionic nature of the ethylene oxonium, we assume that the group is polar; therefore, a polar solvent should dissolve it when the solubility parameters are close. The dipole interaction is the dominating factor in determining the solubility of a polar solute in polar solvent. Thus, nonpolar benzene, with dipole interaction solubility parameter $\delta_{dipole} = 0$ (12), is expected to give a low solubility for the oxonium complex and a larger deviation of distribution coefficients for ethoxylates with various chain lengths. Methylene chloride, with $\delta_{dipole} = 5.5$ (12), should dissolve the oxonium complex better and also give a fairly constant P value, judging from the a′ values in Table 1. Such is the case for ethylene oxide with chain lengths in the range of 10-20.

Comparing the a′ values in the experiments using methylene chloride as extracting solvent, the EO = 5 ethoxylate has the lowest a′ value because the chain length is too short. Greff et al. (5) reported that ethoxylates with less than 2.5 mol of ethylene oxide were not detected by the cobaltothiocyanate method. On the other hand, Crabb et al. (13) reported that ethoxylates with less than 6 mol of E.O. did not form a color with cobaltothiocyanate. Despite the discrepancy, it is clear that when the ethoxylate chain length is less than a critical number, the ethylene oxide group is nonactive to cobaltothiocyanate. It is reasonable to deduce furthermore that, if an ethoxylate has a chain length just barely greater than the critical number, the marginal E.O. segments are also nonactive. Since most ethoxylates have polydisperse chain length distribution, a significant number of molecules in a low average chain length sample might have chain lengths shorter than or only barely greater than the critical number. Therefore, short-chain ethoxylates have a lower cobaltothiocyanate activity.

Some experiments were carried out that omitted the addition of NaCl in experiment procedure step (iv). Their apparent absorbances vs. molar concentration of ethoxylates are also shown in Figure 1 with dotted lines. They have lower slopes than their solid-line counterparts (with NaCl added), which is obvious for EO = 10 but is also true for EO = 15 and 20. Furthermore, by Eq. [1], the slopes of the dotted lines do not yield a constant a′ value. This implies that the extraction efficiency, f, the percentage of solute extracted into the organic phase in these systems is chain-length dependent. Since

$$f = \frac{P}{P+1} \qquad [5]$$

it may be shown that the change of extraction efficiency, Δf, with respect to the change of chain length, Δn, can be written as:

$$\begin{aligned} \Delta f &= f(1-f)\Delta \log P \\ &= f(1-f)B\Delta n \end{aligned} \qquad [6]$$

As NaCl is added (to salt out the cobaltothiocyanate-oxonium complex), the absolute value of B decreases and f approaches unity. As a consequence, f becomes less dependent on n, according to Eq. [6].

Each dotted line shows a positive x-intercept. The intercepts are 4.64, 2.80 and 1.43 (× 10^{-5}M) for EO = 10, EO = 15, and EO = 20, respectively. When expressed in terms of number of equivalent E.O., the intercepts are in the same decreasing order for EO = 10 to EO = 20. Also, the intercepts can be related to thermodynamic properties of the cobaltothiocyanate-ethoxylate complexation.

The oxonium ion formation and ion-pair reaction occur in aqueous phase and can be written as follows.

$$-(\mathrm{EO})_2\text{-} + \mathrm{M}^{++} \rightarrow -(\mathrm{oxonium}^{+})_2\text{-M} \qquad [7]$$

$$\text{-}(\mathrm{oxonium}^{+})_2\text{-M} + \mathrm{Co(SCN)}_4^{=} \rightarrow \text{ion-pair}\downarrow \qquad [8]$$

The above mechanisms have been proposed by Wurzschmitt (14) and Crabb et al. (13). Wurzschmitt has proposed that M^{++} can be either H^{+}, NH_4^{+}, or Co^{++}, and on the average two oxoniums form in 5.5 E.O. segments. According to Crabb et al. M^{++} was strictly Co^{++}, and it had to have at least 6 E.O. segments in a single chain to complex with Co^{++} ion.

According to the mass law, we assume the equilibrium concentrations of ethylene oxide and oxonium to be related to equilibrium constants as

$$K_{eq} = [(\mathrm{oxonium}^{+})_2\text{-M}]/[\text{-}(\mathrm{EO})\text{-}_2]\,[\mathrm{M}^{++}] \qquad [9]$$

and

$$K_{sol} = [(\mathrm{oxonium}^{+})_2\text{-M}]\,[\mathrm{Co(SCN)}_4^{=}] \qquad [10]$$

where K_{eq} is the equilibrium constant of Reaction 7, and K_{sol} the solubility product of Reaction 8. As long as $[M^{++}]$ and $[Co(SCN)_4^{=}]$ remain constant due to their swamping amounts in the system, the total number of equivalent of unprecipitated E.O. units (including oxonium), N_i, is a constant according to the Eq. [11], derived from Eqs. [9] and [10].

$$\begin{aligned} N_i/m &= [\text{-}(\mathrm{EO})_2\text{-}] + [\text{-}(\mathrm{oxonium}^{+})_2\text{-M}] \\ &= (K_{sol}/[\mathrm{Co(SCN)}_4^{=}])\,(1 + 1/K_{eq}[\mathrm{M}^{++}]) \end{aligned} \qquad [11]$$

where m = 2-3, is the average number of E.O. segment per oxonium.

Soluble in organic phase, the ion-pair transferred to organic solvent is then proportional to $(N-N_i)P'$ where N is the total ethylene oxide added and P′ is the distribution coefficient of ion-pair in two phases of the extraction system. Obviously, the apparent absorbance vs ethoxylate concentration must be linear with a positive x-intercept.

The N_i values calculated from the x-intercepts of the dotted lines on Figure 1 are 4.63, 4.19 and 2.86 (× 10^{-4} equivalent E.O./L) for EO = 10, EO = 15 and EO = 20, respectively. Since N_i values increas as K_{eq} decreases, it is suggested that the short chain ethoxylate has a lower K_{eq} than that of long-chain ethoxylate. A low K_{eq} value is due to the entropic effect. For example, it takes two molecules of a short-chain ethoxylate to form an $(\mathrm{oxonium}^{+})_2$-M with cobalt ion, while only one molecule of a long-chain ethoxylate is needed to form an oxonium with cobalt ion. The former involves a greater amount of entropy loss, and therefore shows a lower value of the equilibrium constant, K_{eq}.

The x-intercept and slope of the apparent absorbance vs. concentration calibration lines are therefore chain-length dependent. However, by adding NaCl to the system the x-intercept reduced to essentially zero, indicating the solubility product, K_{sol}, becomes negligibly small. In this case, the only parameter which is chain length-dependent causing a deviation in a′ value is the ion-pair distribution coefficient in two phases. However, a characteristic value of a′ obtained for EO = 10 to EO = 20 indicates that even such a deviation of the distribution coefficient is negligible. Therefore, the cobaltothiocyanate method is justified when applied to study the adsorption of ethoxylates with chain length 10 to 20. Equally important, a characteristic a′ value suggests that the cobaltothiocyanate method can be used to determine the average E.O. chainlength of a homologous polyethoxylate.

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Monomeric N-Hydroxyethylated Amides

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Oxyethylated amides that are good wetting agents have been prepared as mixtures by allowing amides to react with ethylene oxide under base catalysis. Individual components of such mixtures can be synthesized by allowing 1-alkylaziridines to react with p-toluenesulfonic acid in monomethylethers of di-, tri- and tetraethylene glycol used as solvents. The aminoethers are then acylated, and the methylether group is removed with trimethylsilyliodide from the resulting amide ethers. The sequence should allow the synthesis of specific wetting agents of quite varied structure (alkyl, aryl groups) with an option for isotopic labeling for more detailed analysis of the wetting properties.

An authoritative review of the status of animal fat feedstocks for oleochemicals (1) served to underline the continuing interest in finding additional uses for these fats and related chemicals. One area of potential use of fatty acid derivatives, for example, is in providing chemicals that have the potential to modify the properties of soil. Soil modification by materials that act to increase watershed, i.e. that impart hydrophobic character to the soil, has been reviewed recently (2). An alternative approach to creating a new market for oleochemicals has involved the preparation and study of certain classes of nonionic wetting agents intended to increase water retentiveness of soil. In particular, Micich and Linfield have described the properties of oxyethylated benzenesulfonamides (3) and secondary amides (4) that are derived from n-alkylamines and fatty acids (Fig. 1). A subsequent study by these authors showed that polydisperse E.O. adducts of hydroxyethyl tertiary amides are outstanding wetting agents for cotton skeins and soil (5).

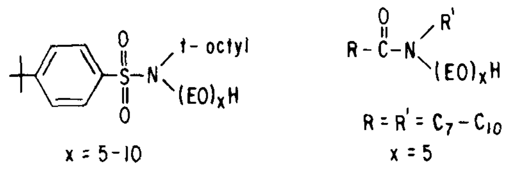

FIG. 1. Structure of fatty amides that have good wetting properties (3-5).

The conversion of a sulfonamide (or carboxamide) to a material with wetting properties has been accomplished by means of a base-catalyzed reaction with ethylene oxide that permitted rapid screening for activity-structure relationships using a fairly broad spectrum of substituents. Optimum wetting properties for benzenesulfonamides were associated with 5-10 ethylenoxy (EO) units, and for secondary amides with about 5 EO units with aliphatic alkyl groups of intermediate (ca. 8) chain length. Apparently one may expect that hydrophilic character will be bestowed on an otherwise hydrocarbon-like material if a suitable number of EO units can be fixed to the central portion of that organic compound. The ability to generate such classes of compounds, which might also effectively tap the reservoir of oleochemicals, seems firmly established. However, the optimum EO count for a particular parent molecule, as well as the details of binding to the soil and to water, remain a matter of conjecture.

A synthetic procedure that allows one to generate selected hydrophilic materials as homogeneous compounds seemed highly desirable at this juncture. In a thorough study of surface and interfacial tension of normal distribution versus homogeneous p, t-octylphenoxy-ethanols (6), similar values of measured physical properties were obtained. This implied that screening the more easily synthesized polymeric mixtures in that series could serve as a useful guide in the search for materials with desirable surfactant properties. The physical properties of the polymeric material and the homogeneous (average) counterpart were not identical, and the disparity between these became greater with increasing average EO chain length. In addition, the degree of divergence may be expected to bear a relationship to the nature of the parent molecule to which the chain is affixed. Thus, examination of a sequence of homogeneous hydrophilic candidates would provide a firmer basis for structure versus activity assessments where a finer tuning was deemed important. Secondly, the studies of oxyethylated amides were troubled in some degree by the presence of byproducts, namely aminoesters derived from N-to-O acyl migra-