rence of the shifting effect during processing.

GLC of the fatty acid methyl esters derived from an oil obtained by the recommended processing conditions showed the following fatty acid composition for major components: palmitic, 11.9%; stearic, 3.5%; oleic, 22.0%; and linoleic, 61.0%.

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The Effect of Glycols on the Hydrophile-Lipophile Balance and the Micelle Formation of Nonionic Surfactants

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ABSTRACT

The empirical hydrophile-liophile balance (HLB) value of nonionic surfactants is an important parameter used to predict performance as, e.g., emulsifiers, solubilizers and wetting agents. However, the HLB value is based on an original molecular structure and does not take into account all the factors affecting the performance of nonionics, such as presence of additives, type of solvent, temperature, degree of hydration, structural modifications of the surfactant molecule and decomposition of surfactants. On a performance basis, where these factors come into play, a given nonionic surfactant may exhibit a multiplicity of apparent HLB values. Accordingly, we recently introduced the term "effective HLB value" which is a performance value which incorporates into the HLB the parameters listed above. The HLB value thus becomes a variable depending on the physical and chemical conditions at the time of the measurement. In this work, we investigated the effect of adding glycols and diglycols on the HLB using 3 different methods: cloud point, phenol index and critical micelle concentration (cmc). We found that this type of additive increases the cloud point, phenol index, cmc and the "effective HLB" of a polyoxyethylated nonionic surfactant. The effectiveness of the glycols in causing these increases was in the following order; dipropylene glycol > 1,4-butanediol > 1,2-propanediol > diethylene glycol > ethylene glycol. The solvent effect of glycols and diglycols on the hydrophobic and hydrophilic portions of the surfactant molecule are discussed. On the hydrocarbon part of the surfactant molecule, the solvents cause a weakening of the hydrophobic bond and an increase in the cmc. On the polyoxyethylene part of the molecule, the solvent may cause either an increase or a decrease in the cmc. The effect on the hydrophilic portion is related to hydrogen bonding exhibited by the additives. The results obtained again suggest that the effective HLB value, which is a measure of the HLB under operative conditions, may be of greater practical significance than calculated HLB.

INTRODUCTION

Glycols and diglycols are often used in combination with surfactants in pharmaceutical, cosmetic and pesticide formulations. Therefore, an investigation of the effect of these solvents on the physical properties of surfactant solutions is highly desirable.

The hydrophile-lipophile balance (HLB) value of nonionic surfactants not only is used to predict performance as emulsifiers, solubilizers and wetting agents, but also may be used to predict micellization. The micellization of surfactants in an aqueous solution is regulated by the balance between 2 opposing forces: the cohesive force between the hydrophobic groups (which favors micelle formation) and the attractive forces between the hydrophilic group and water molecules (which aids in keeping the nonionic surfactants in solution). Thus, because HLB is a measure of the balance between hydration and cohesion, it also may be used to predict the formation of micelles.

An HLB value of a nonionic surfactant is not a constant but is affected by factors such as additives (1-3), temperature (4,5) and structural modification of the surfactant molecule (6). Therefore, we refer to an "effective HLB value" which is an observed HLB equivalent to a reference surfactant, devoid of additives, having the same physical properties as the one under investigation (7). To estimate the degree and direction of the HLB change (reference HLB to effective HLB) we determined the critical micelle concentration (cmc), phenol index and cloud point of the surfactant measured in the absence and presence of a given additive.

In systems comprising only polyoxyethylated surfactants and water without additives, the following trends have been reported. The cmc increases as the number of ethylene oxide units per molecule is raised and as the hydrocarbon chain length is reduced (8). The cloud point (9) and phenol index (10) values both rise with a corresponding increase in the polyoxyethylene chain length. All additives which affect the surfactant cloud point or surfactant phenol index will affect an experimentally determined HLB value of a nonionic surfactant.

There have been a number of investigations regarding the effect of various organic solvents on micellar properties of nonionic surfactant solutions (11-20) but only Vogt and Dillmann (21) have reported the effect of glycols on the cmc of the heterodisperse-type surfactants such as Tween® 40 and 80.

EXPERIMENTAL

Materials

The polydisperse surfactant used was a polyoxyethylated nonyl phenol (Rewo, Steinau, Germany) nominally containing 8 mol of ethylene oxide/mol of surfactant (abbreviated NPE_8) as previously described (22). The surfactant used in this study exhibits a very small minimum near the cmc in the surface tension vs concentration curve in water. This may be due to the molecular weight distribution of the ethylene oxide in the surfactant molecule (23). We believe that this surfactant has sufficient purity for attaining the aim of the present work, as the appearance of the minimum is not remarkable and analytical results show sufficient purity. The surfactant used in this study might fall in the category of polydisperse materials. Becher (8) has argued that a great deal of useful information can be obtained from the study of such polydisperse compounds because their properties will be close to those of the homogenous compounds having the composition of the mean (8). Additionally, we stress that we do not intend to draw more than qualitative conclusions from these results. Note that Ray and Nemethy (20) also used polydisperse Tritons in determining several thermodynamic parameters relating to micelle formation by nonionics in water/ethylene glycol mixtures. These authors suggest that their results may be expected to correlate with results which would be obtained with monodisperse materials.

The additives investigated in this work were reagent-grade materials (BASF, Ludwigshafen, Germany), including ethylene glycol, diethylene glycol, 1,2-propylene glycol, dipropylene glycol and butylene 1,4-glycol.

Methods

The cmc were determined from the sharp breaks in the plots of surface tension vs logarithm of concentration. Surface tensions were determined at 293 ± 0.2 K by the maximum bubble pressure method using double-distilled water. This method is applicable to the determination of cmc of surfactants for which the cmc range between 1×10^{-4} to 1×10^{-2} mol/dm^3, providing the molecules have a moderate hydrocarbon chain length and the time of the bubble generation is relatively long (i.e., above 300 sec) (24). As many glycols are also surface-active (see below), sharp breaks in the plots of surface tension vs surfactant concentration become uncertain as the concentration of additive increases. Therefore, the surface tension method was used only to an additive concentration of 2 M, which constitutes a concentration range where well defined cmc values could still be obtained.

Cloud point and phenol indices were determined as previously reported (1).

RESULTS AND DISCUSSION

Figure 1 shows the effect of glycols and diglycols on the cloud point of NPE_8 (0.025 M).

The relationship between HLB value and cloud point of nonionic surfactants has been described by several authors (9,25,26). The cloud point of a nonionic surfactant is sensitive to additives, which may raise or lower it. A substance which changes the cloud point of a given surfactant therefore can be considered to change its HLB value (25-27). The glycol additives reported here increase the cloud point and hence increase the HLB value of NPE_8. Thus, the "effective HLB value" of nonionics in the presence of glycols is higher than the normal, calculated HLB. The effectiveness of glycols and diglycols in causing this apparent increase in the actual HLB for NPE_8 is: dipropylene glycol > butylene glycol > propylene glycol > diethylene glycol > ethylene glycol.

The effect of glycols and diglycols on the phenol index of NPE_8 (0.02 M) is shown in Figure 2.

The effect of glycols on the phenol indices of NPE_8 (which is also a simple measure of the effective HLB value) is analogous to the effect of glycols on the cloud point measurements of NPE_8. This agreement is not fortuitous. There is a close relationship between phenol index and cloud point (22), because the phenol index is basically related to the amount of phenol required to lower a cloud

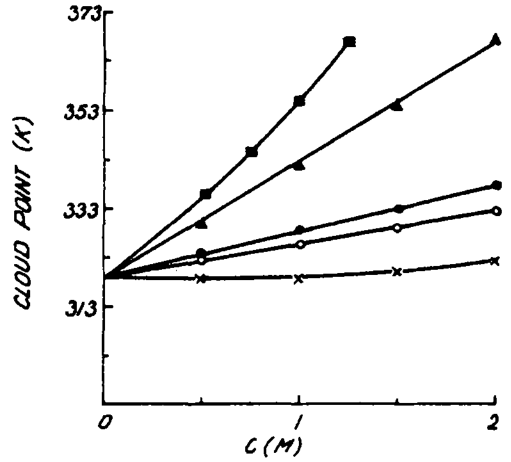

FIG. 1. Effects of glycols and diglycols on the cloud point of NPE_8 (0.25 M). X, Ethylene glycol; ●, propylene glycol; ▲, butylene glycol; ○, diethylene glycol; ■, dipropylene glycol.

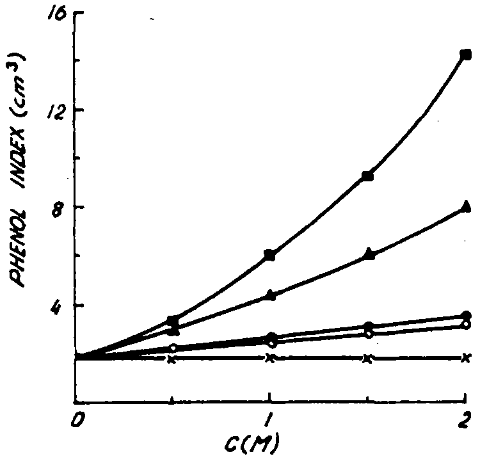

FIG. 2. Effects of glycols and diglycols on the phenol index of NPE_8 (0.025 M). See legend to Fig. 1 for explanation of symbols.

point to the temperature of the measurements, i.e., 298 K (28). We postulate that the mechanism of action of the phenol may be a reduction in the hydrophilicity of the polyoxyethylene chain due to the binding of the phenol. Thus, the addition of phenol to a dilute surfactant solution can have the same effect as an increase in temperature.

Figure 3 shows the effect of glycols and diglycols on the cmc value of NPE_8.

All glycols used in this investigation tended to increase the cmc of the nonionic surfactant. The relative effectiveness of the glycols in altering the cmc corresponds to their effectiveness in altering the cloud point and phenol index. Recall that, as a surfactant molecule becomes more hydrophilic (higher HLB) due to extending the polyoxyethylene chain or shortening the hydrocarbon chain, the cmc and cloud point increase. Thus, adding glycols to a single surfactant has the effect of making the surfactant behave as if it were more hydrophilic.

In the cmc measurements, the magnitude of the shifts in cmc is primarily determined by the hydrophobic group of the surfactant. However, cloud point measurements are more dependent on the hydrophilic portion of the molecule. Additionally, the change of any physical property of a surfactant under the influence of the same additive is strongly dependent on the surfactant concentration (22). Thus, a quantitative determination of an HLB shift cannot be measured by independent cmc or cloud point measurements.

Glycols are surface-active and depress the surface tension of aqueous solutions. Propylene glycol, butylene glycol and dipropylene glycol are highly associated, forming micelle-like structures in solution, as indicated by a break point in surface tension and other physical properties (29). The transition from a monomer to aggregated state, however, is less sharp than in the case of a typical surface-active agent. This indicates that the aggregation numbers of these substances are probably quite small. The continuing decrease in surface tension of these solutions with increasing solute concentrations, even after the beginning of aggregation, indicates that the concentration (activity) of the glycol monomers continues to increase in compliance with the mass action treatment of micelle formation. A measure of the stability of the micelle is the free energy of micelle formation (ΔG_m^o) which may be calculated from the cmc. Because the aggregation numbers of the surfactants were unknown, we took the pseudo-phase separation approach in the calculation of ΔG_m^o:

$$\Delta G_m^o = RT \ln C,$$

where C is cmc expressed as mol fraction.

In all cases, ΔG_m^o becomes less negative, as is shown in Table I, indicating that micellization was less spontaneous in the presence of glycols.

The cmc is a characteristic parameter relating to the equilibrium between the micelle and the single monomer. If a solvent affects the monomer and/or the micelle, the cmc and the associated equilibria will be shifted. In the following paragraphs, we will discuss the solvent effects on a nonpolar group and on a polar group of a surfactant molecule.

The primary effect of the glycols investigated here is on the solubility behavior of the nonpolar part of the surfactant. The glycols weaken the hydrophobic interaction, which is the main thermodynamic driving force for the formation of micelles. In an aqueous solution, the water molecules form "icebergs" around nonpolar groups. This type of solute-solvent interaction has been called "hydrophobic hydration" (30) or "hydration of the second kind." Glycols affect the micellization through a possible change in the hydrophobic hydration, but the mechanism is unclear. This may depend on the disruption of the iceberg structure around the hydrophobic chain, on preferential solvation of the hydrophobic chain by the glycols or on a more appropriate solubility parameter of the mixed solvents, e.g., a characteristic of a hydrophobic interaction is that the energetics are dominated by entropy effects. Thus, the weakening of the hydrophobic interaction will be connected with a reduction in the entropy after addition of glycols to the surfactant solutions. The effectiveness in reducing entropy changes from ethylene glycol to butylene glycol and this difference is reflected in the changes of ΔG_m^o, which becomes less negative with an increase of glycol content (Table I). This primary effect of the glycols on the hydrocarbon chain leads to an increase in cmc associated with an increase in the free energy of the hydrophobic group in the surfactant molecule.

In the micellization process, the effect of glycols on the polyoxyethylene portion of the surfactant molecule is more complex. The major contribution to the negative free energy of micelle formation is contributed primarily by the hydrophobic portion of the molecule. In the absence of glycols, the first few ethylene oxide groups, next to the hydrophobe, tend to act more like a hydrophobe, as the ether linkages are easily dehydrated. This means that these first ether linkages are weaker bases (electron donors) than ethers farther out on the chain. Because these ethers are weak bases, they associate with other molecules, function-

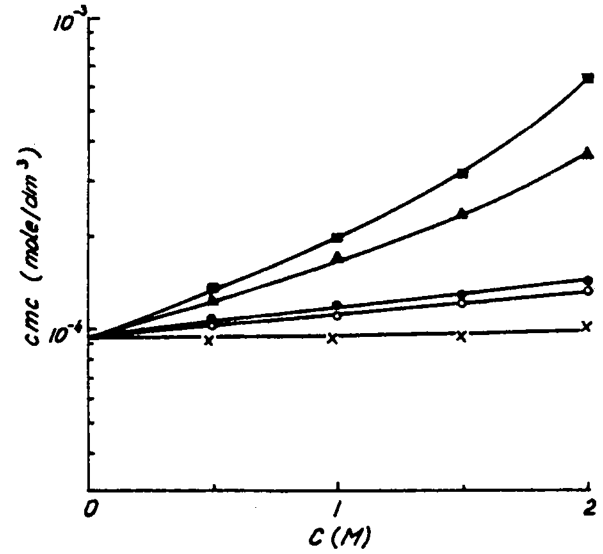

FIG. 3. CMC of NPE_8 solutions as a function of additive concentration. See legend to Fig. 1 for explanation of symbols.

TABLE I

Free Energy of Micellization of NPE_8 in Glycol/Water Mixtures at 293 K

Additive	ΔG_m^o (Kcal/mol)
None (water alone)	-7.72
1 M ethylene glycol	-7.72
2 M ethylene glycol	-7.68
1 M diethylene glycol	-7.63
2 M diethylene glycol	-7.53
1 M propylene glycol	-7.58
2 M propylene glycol	-7.49
1 M butylene glycol	-7.38
2 M butylene glycol	-6.94
1 M dipropylene glycol	-7.28
2 M dipropylene glycol	-6.62

ing as weak acids (electron acceptors or proton donors). Hence, when the ethers associate with water, water is functioning as a proton donor or weak acid.

When glycols are present, there is competition between water and glycol for the weakly basic ether site (31). The glycol is a weaker acid (stronger base) than water. According to the Pearson theory (32), weak acids prefer weak bases. Thus, because the glycol represents a weaker acid than water, the ethers early in the chain tend to prefer to associate with glycols as opposed to interacting with water. Farther out on the ethoxylate chain, the ethers become stronger bases and increasingly prefer to associate with water.

In glycol/aqueous solutions, it is possible to have hydrogen bonds between -OH of the glycol and the ether oxygens of the surfactant. If hydration is reduced on the far polyoxyethylene portion of the surfactant by hydrogen-bonded glycols, the cmc is decreased. The magnitude of the cmc decreasing effect depends on the strength of the hydrogen bonding tendency (or acid-base interaction) exhibited by the glycols in relation to the water bonding strength to the ether groups far removed from the hydrophobe. This interpretation is consistent with the fact that the hydrogen bond component of the solubility parameter (33) decreases with increasing molecular weight. With this decrease in hydrogen bonding, the glycol has a tendency to increase the cmc of the surfactant.

Diglycols behave slightly differently than glycols. In the case of these additives, which also hydrogen-bond with the polyoxyethylene chain, there is an additional ether oxygen compared to the parent glycol. This extra ether linkage may be involved in hydrogen bonding with water, thus indirectly increasing the hydration of the diglycol-polyoxyethylene chain complex.

Thus, there are 2 effects of glycols on surfactants: the first on the hydrophobic hydrocarbon part causing an increase in the cmc, and the second on the hydrophilic polyoxyethylene part decreasing the cmc if the water of hydration is replaced by glycol, but increasing the cmc if unhydrated ether linkages hydrogen-bond to the glycol. The overall effect of glycols and diglycols is inclined toward raising the cmc.

The increase in cmc in the presence of additives basically indicates that the nonionic surfactant molecule becomes more hydrophilic. In other words, the effective HLB of the nonionic molecule is higher than that calculated or exhibited under standard conditions, i.e., in pure water. Similar indications are obtained from the cloud point, phenol index and other measurements.

Although alternate explanations may be advanced for the aforementioned phenomena, the net result of the combination of a surfactant and additives is an apparent change of the HLB of the nonionic surfactant in comparison to the value exhibited in water under standard conditions. No matter what the correct mechanism is for the interaction between the glycols and nonionic surfactants, the interaction results in an increase in the hydrophilicity of the nonionics which is equivalent to a hypothetical increase in the effective polyoxyethylene chain length (cloud point and phenol index measurements), or alternatively equivalent to a hypothetical shortening of the effective hydrocarbon chain (cmc measurements). Thus, the effective HLB, which is a true measure of the HLB under experimental conditions, is of greater practical significance than a calculated HLB.

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