

## **EFFECTIVE HYDROPHILE–LIPOPHILE BALANCE AND MICELLE FORMATION OF NON-IONIC SURFACTANTS IN THE PRESENCE OF SHORT-CHAIN GLYCOL ETHERS**

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### **SUMMARY**

The effect of short-chain glycol ethers on the cloud point and the critical micelle concentration (cmc) was investigated. It was found that all these additives increase the cloud point and cmc, increasing in this manner the hydrophile–lipophile balance (HLB) of polyoxyethylated non-ionic surfactant. The increase was in the following order: carbitol > cellosolve > diethylene glycol monomethyl ether > ethylene glycol monomethyl ether > diethylene glycol > ethylene glycol. The solvent effect of glycol ethers was divided into two groups: primary on the hydrocarbon part of surfactant molecule, weakening of hydrophobic bond and increasing cmc, and secondary on the polyoxyethylene part, decreasing cmc. The secondary effect was related to the hydrogen bonding tendency exhibited by investigated glycol ethers.

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### **INTRODUCTION**

Short-chain glycol ethers are good solvents as they contain alkyl, ether, and alcohol group in a single molecule. An investigation of the effect of these solvents on the surfactant solutions would be desirable from a formulation point of view since short-chain glycol ethers can be employed along with surfactants in pharmaceutical formulations.

The micellization process in aqueous solutions of surfactants is regulated by the balance between two opposite forces: the cohesive forces between the hydrophobic groups which favour micelle formation and the affinity of the hydrophilic group to water molecules, which aids in keeping non-ionic surfactants in solution. Factors, which normally affect the balance between hydration and cohesion (or hydrophile–lipophile balance) such as temperature or additives, would also be expected to affect the formation of micelles. The additives which affect the micellization of surfactants may be divided into

those which penetrate the micelles and change their structure, and those which do not (Becher, 1967). Penetrative additives might be expected to be molecules which have a certain hydrophobic content although they may be miscible or partially miscible with water. Non-penetrative additives affect the micellar properties by changing the environment of the micelle.

On the other hand, the HLB (hydrophile–lipophile balance) value of non-ionic surfactants is one of the important factors which not only condition the stability of emulsion and predict the performance of non-ionic substances as emulsifiers but also, as a measure of the balance between hydration and cohesion, condition the formation of micelles and their structure (Marszall and Van Valkenburg, 1979).

We maintained that at least 4 basic factors affect the hydrophile–lipophile balance of non-ionic surfactants and they must be taken into account to correct determination of HLB value. They include: presence of additives, temperature, structural modifications of molecules and decomposition of surfactants. Therefore, the so-called effective HLB value, which is the equivalent HLB of the reference surfactant which yields the same physical results as the one under investigation, is of greater practical relevance than the actual HLB value (Marszall, 1978a).

The present work was undertaken in order to ascertain the effect of short-chain glycol ethers on the micelle formation and the change of actual HLB of non-ionic surfactants.

## MATERIALS AND METHODS

### *Materials*

The surfactants used (Rewo, Steinau, Germany) were polyoxyethylene nonyl phenols nominally containing 8, 14 and 25 moles of ethylene oxide per mole of surfactant (abbreviated  $NPE_x$ ). The average chain lengths of the  $NPE_x$  and the mean molecular weights were determined from their hydroxyl values. These polyoxyethylene derivatives fall into the polydisperse category (Becher, 1967) and their properties will be close to that of the homogeneous compounds having the composition of the mean.

The additives investigated in this work were reagent grade materials (BASF, Ludwigshafen) and include: ethylene glycol (EG), ethylene glycol monomethyl ether (MEG), diethylene glycol monomethyl ether (MdiEG), diethylene glycol (diEG), ethylene glycol monoethyl ether (EEG – cellosolve), and diethylene glycol monoethyl ether (EdiEG – carbitol).

### *Methods*

The critical micelle concentrations were determined from the sharp breaks in the surface tension vs logarithm of concentration plots. The surface tensions were determined by the method of maximum bubble pressure at  $293 \pm 0.2^\circ\text{K}$  using doubly distilled water. This method is applicable to the determination of cmc of the surfactants whose cmcs range within  $1 \times 10^{-2} - 1 \times 10^{-4}$  mol/dm<sup>3</sup>, if their molecules are not too extended and if the time of the bubble generation is relatively long (there above 300 s) (Kucharski, 1978). The investigated solutions prepared by dilution of the stock surfactant solution were equilibrated at  $293 \pm 0.5^\circ\text{K}$  for several hours before surface tensions were determined. The cmc values for investigated  $NPE_x$  are in good agreement with those described in litera-

ture – e.g. for polydisperse  $\text{NPE}_x$  the cmc values using the surface tension method at  $298^\circ\text{K}$  are (Becher, 1967):  $\text{NPE}_{9,5}$  85;  $\text{NPE}_{15}$  120; and  $\text{NPE}_{30}$   $275 \mu\text{mol}/\text{dm}^3$ . In our work, for investigated  $\text{NPE}_x$  we obtained at  $293^\circ\text{K}$ :  $\text{NPE}_8$  95;  $\text{NPE}_{14}$  125; and  $\text{NPE}_{25}$   $250 \mu\text{mol}/\text{dm}^3$ .

Since investigated glycol ethers are also surface active (see below), sharp breaks in surface tension vs surfactant concentration plots become uncertain with an increase in the concentration of additive. Therefore, the surface tension method was used only with 2 M of additive, and within this range well defined cmc values were obtained.

Cloud points of 0.025 M  $\text{NPE}_8$  solutions in the presence and the absence of additives were determined following the usual procedure, by heating a solution until it clouds and then measuring the temperature at which clearing occurs on cooling.

## RESULTS AND DISCUSSION

Fig. 1 shows the effect of short-chain glycol ethers on the cloud point of  $\text{NPE}_8$  (0.025 M).

The phase separation which occurs at the cloud point is the result of a change in the HLB of the non-ionic surfactants as affected by temperature. The cloud points increase in value with an increasing number of ethylene oxide groups (or HLB) in the non-ionic surfactants. A substance which changes the cloud point value of a given surfactant can therefore be considered to change its actual HLB (Florence et al., 1975; Marszall, 1977a, 1977b).

Investigated short-chain glycol ethers have a cloud point increasing effect only and increase the actual HLB value of  $\text{NPE}_8$  to a varying degree. A similar result, as in the case of formamide derivatives (Marszall, 1979b), the effective HLB value of non-ionics is higher than the actual ones. The effectiveness of the glycol ethers in causing an apparent increase in the actual HLB for  $\text{NPE}_8$  is:



The cloud point is functionally related to the formation of micelles and their structure. This relation between the cloud point and the micellar properties of non-ionic surfactant was investigated by Arai (1967) and Kuriyama (1962). With a decrease in the cloud point, the cmc decreased and the micellar weight increased (this increase of the micellar weight is one of the most important factors in the cloud point formation and the phase separation). These relationships were found to hold even in the presence of added salts and ethyl alcohol. To gain further insight into the effect of glycol ethers on the HLB values of surfactants, an investigation of their effect on the cmc is in order.

There have been a number of investigations regarding the effect of various organic solvents on micellar properties of non-ionic surfactant solutions (Becher, 1965; Vogt and Dillmann, 1966; McDonald, 1970; Ray and Nemethy, 1971; Deguchi et al., 1974; Nishikido et al., 1974), but none of them treats the effect of glycol ethers.

Fig. 2 shows the effect of glycol ethers on the cmc value of  $\text{NPE}_8$ .

In the experimental part we showed that at constant temperature the cmc increases with polyoxyethylene chain-length agreeing with previous studies (Becher, 1967). This

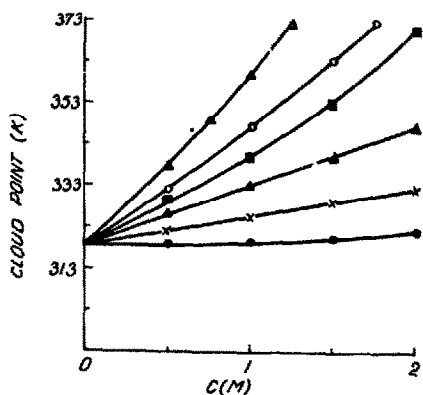


Fig. 1. Cloud point of NPE<sub>8</sub> solutions (0.025 M) as a function of additive concentration. Key: ●, EG; ×, diEG; ▲, MEG; ■, MdiEG; ○, EEG; △, EdiEG.

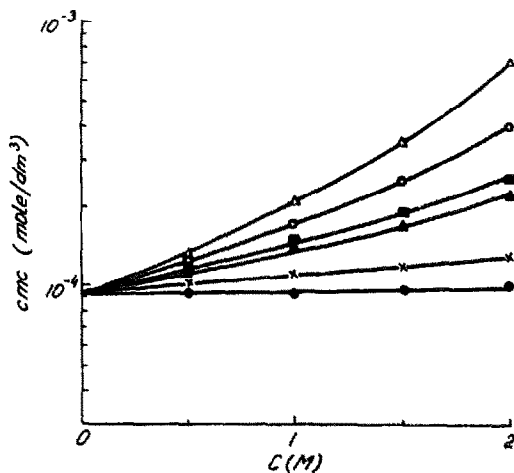


Fig. 2. Effects of a series of glycol ethers on the cmc of NPE<sub>8</sub>. Key: ●, EG; ×, diEG; ▲, MEG; ■, MdiEG; ○, EEG, △, EdiEG.

effect may be also achieved by using additives, which tend to make the effective HLB of the surfactant higher than its assigned value. The short-chain glycol ethers increase the cmcs of non-ionic surfactants with increasing concentration of additive. The successive-ness is the same as in the case of cloud point measurements. Since both measurements are a function of hydrophile-lipophile balance, their agreement is not fortuitous. Quantitative comparisons are, however, impossible, because under the influence of the same additive, the change of the investigated property (e.g. cloud point, phenol index) depends strongly on the surfactant concentration (Marszall, 1979a). As the surfactant concentration increases so the effect of additives is markedly reduced. Thus, a quantitative comparison of the HLB change of the same surfactant under the influence of an additive should only be made when equimolecular concentrations of surfactant are used.

Further quantitative differences may arise from the fact that, in the case of cmc measurements, a hydrophobic group of a surfactant molecule determines to a greater extent the size of cmc changes than a hydrophilic group. In the case of cloud point measurements, the situation is reversed. On the other hand, in the HLB system, in which the function of hydrophilicity in a molecule changes asymptotically, a hydrophilic group contributed more to change an overall HLB value than a hydrophobic group. Although the cloud point is functionally related to the formation of micelles, both parameters are also governed by factors other than HLB, and therefore the comparisons from the hydrophile-lipophile balance point of view are only made for better explanation of the mechanism of glycol ether action on the surfactant solutions.

Glycol ethers are also surface active and depress the surface tension, but none of those investigated showed a sharp break in the surface tension vs concentration plot as is shown in Fig. 3.

Only butylcarbitol and butylcellosolve, not investigated here, are highly associated in

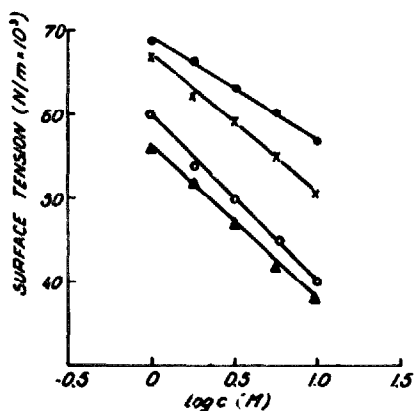


Fig. 3. Surface tension of aqueous solutions of ethylene glycol and glycol ethers against concentration at 293° K. Key: ●, EG; ×, diEG; ○, EEG; ▲, EdiEG.

solution and they showed a clear break point also for other physical properties (Donbrow and Jacobs, 1966; Kato and Sato, 1970).

Investigated glycol ethers may undergo association, but since the aggregation numbers of these substances are probably quite small, it would be expected that the transition from monomer to aggregated state would be less sharp than in the case of butylcarbitol, butylcellosolve or typical surface active agents. The continuing decrease in surface tension of these solutions with increasing solute concentration even after beginning a hypothetical aggregation, appear to indicate that the concentration (activity) of the monomers of glycol ethers continues to increase in this region according to the mass action treatment of micelle formation. The increase is more pronounced at lower aggregation numbers than at higher ones (Elworthy and Macfarlane, 1965).

Since there is no evidence that investigated short-chain glycol ethers form micelle-like structures, but probably only undergo association with small aggregation number, we will consider their effect on the surfactant solutions further. The solvent effect of glycol ethers will be divided into two groups: on a non-polar group and that on a polar group of a surfactant molecule.

The measure of the stability of the micelle is the free energy of micelle formation ( $\Delta G_m^0$ ) which could be calculated from the cmc. The thermodynamic equations for determining the standard free energy of micelle formation may be based on the phase separation and mass action models of micelle formation. Since the aggregation numbers of the surfactants were not known, we take the pseudo-phase separation approach to calculate  $\Delta G_m^0$ :

$$\Delta G_m^0 = 2.303 \times RT \times \log C$$

where  $C$  is the cmc expressed as mole fraction, i.e.  $C = \text{cmc}/55.34$ . Differences between free energies calculated from these models are close to experimental error for determination of the cmc (Barry and El Eini, 1976).

In all cases,  $\Delta G_m^0$  becomes less negative, as is shown in Table 1, indicating that micellization was less spontaneous in the presence of glycol ethers.

TABLE 1

THE FREE ENERGY OF MICELLIZATION OF NPE<sub>8</sub> IN GLYCOL ETHERS-WATER MIXTURES AT 293°K

Additive	G <sub>m</sub> <sup>0</sup> (kcal/mol)	Additive	G <sub>m</sub> <sup>0</sup> (kcal/mol)
in water	-7.72	1 M MdiEG	-7.45
1 M EG	-7.72	2 M MdiEG	-7.15
2 M EG	-7.68	1 M EEG	-7.38
1 M diEG	-7.63	2 M EEG	-6.88
2 M diEG	-7.53	1 M EdiEG	-7.22
1 M MEG	-7.49	2 M EdiEG	-6.55
2 M MEG	-7.22		

The main effect of the investigated glycol ethers is directed at the solubility behavior of the non-polar part of the surfactant. They weaken the hydrophobic interaction, which is the main thermodynamic driving force for the formation of micelles. A characteristic feature of the hydrophobic interaction is that it is dominated by entropy effects, and therefore weakening the hydrophobic interaction will be related presumably to the reduction in entropy after addition of glycol ethers to the surfactant solutions. The effectiveness of reducing entropy changes from ethylene glycol to carbitol and this difference is reflected in the changes of  $\Delta G_m^0$ , which becomes less negative with increase of content of glycol ethers as is shown in Table 1.

The water molecules close to the hydrophobic group form a stronger hydrogen-bonded network than in bulk water and this effect may be interpreted in terms of a hydrophobic hydration of the non-polar part. The hydrophobic interaction is primarily due to the property of the solvent water and not to the chemical properties of the solute and therefore a change in the thermodynamic parameters of micelle formation after addition of glycol ethers results presumably from their ability to produce strong structural changes of the solvent medium, changing in this manner the hydrophobic hydration.

This primary effect on the hydrocarbon part leads to an increase in cmc, and the order of glycol ethers causing this increase, corresponds to their ability to act as hydrophobic bond breakers.

The interaction of the polyoxyethylene chain with the glycol ethers is complex, but this effect seems to be secondary. In aqueous solutions the ether oxygen atoms in the polyoxyethylene chain are involved in hydrogen bonding with water. In glycol ether aqueous solutions it is also possible that the existence of hydrogen bonds is between the -OH of the glycol and the ether oxygens of the surfactant. Reduced hydration of the polyoxyethylene portion of the surfactant caused by the hydrogen-bonded additive results in the cmc decreasing effect and in the greater negative free energy of micelle formation, but these effects are less significant in comparison to the contribution of free energy change of the hydrocarbon chain. It seems that the magnitude of the cmc decreasing effect may depend on the strength of the hydrogen bonding tendency exhibited by investigated glycol ethers. For example, ethylene glycol and diethylene glycol are classi-

fied as strongly hydrogen-bonding solvents and other investigated glycol ethers are only moderately hydrogen bonding (Barton, 1975). The so-called hydrogen-bonding component in the solubility parameter value of investigated glycol ethers decreases in the order of their tendency to overall increase of cmc. Ethylene glycol and diethylene glycol have two terminal -OH groups, capable of hydrogen bonding, and the remaining glycol ethers have one -OH group blocked by -CH<sub>3</sub> or -CH<sub>2</sub>CH<sub>3</sub> groups and therefore their tendency to hydrogen bond is distinctly reduced. At the same time, in the case of the glycol ether molecules (with the exception of ethylene glycol), which are hydrogen bonded with a polyoxyethylene chain, there are additional ether oxygens in comparison to EG, which may be involved in hydrogen bonding with water, increasing indirectly the hydration of glycol ether-polyoxyethylene chain complex.

Hydrogen bonding energy is highly directional and depends on the relative orientation and distance between atoms and molecules. Since the molecules of EG are smaller than those other glycol ethers, it seems that the contact with ethoxy group is sterically more favorable in the case of EG. E.g., studies on the molecular models indicate that when EG is hydrogen-bonded to a polyoxyethylene chain, van der Waals interactions between the -CH<sub>2</sub>CH<sub>2</sub>- groups from EG and polyoxyethylene chain can be formed simultaneously (Ray and Nemethy, 1971).

In summary, taking into account the two opposite factors, primary on the hydrocarbon part increasing cmc, and secondary on the polyoxyethylene part decreasing cmc, the overall effect of glycol ethers is inclined towards raising the cmc.

As the cmc is the characteristic parameter of the single monomer-micelle equilibrium, a solvent effect on the micelle must also be taken into account. The interior of the micelles is not penetrated by glycol ethers to any significant extent. Contact with solvent seems to begin in the region of the first ethoxy group followed by the phenyl group and gradually increasing towards the other end of the polyoxyethylene chain (Podo et al., 1973).

McDonald (1970) found a general relation between cmc and the solubility parameter value which provides a useful measure of the polarity of solvent. Therefore, another possible explanation for the observed changes in the cmc of non-ionic surfactants may be based on the changes in solubility parameter values of the solvent-water mixtures. Thus, our cmc results suggest that in mixed aqueous solution containing glycol ethers with a lower solubility parameter value (e.g. EdiEG, EEG; according to Barton, 1975), NPE<sub>8</sub> has a higher cmc than that with glycol ethers with a higher solubility parameter value (e.g. diEG, EG) at the same concentration of organic solvent. In a similar manner, using the concept of solubility, parameter was interpreted as the solvent effect on the micellar destruction of non-ionic surfactant (Deguchi et al., 1974).

Although a different explanation of mechanisms for the observed phenomena may be presented, the result due to the additive activity will be the change in the hydrophile-lipophile balance of non-ionic surfactant in relation to that exhibited in pure water, as indicated by the cloud point, phenol index, critical micelle concentration and other measurements. In this fashion the effective HLB, which is true measure of the HLB, is of greater practical significance than calculated ones.

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