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SHORT COMMUNICATION

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Depression in the cloud point of Tween in the presence of glycol additives and triblock polymers

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Abstract Cloud point (C_P) measurements of Tween 20 and Tween 80 were carried out in the presence of various glycol oligomers and triblock polymers (TBP). The cloud points of both Tween 20 and 80 decrease in the presence of both types of additives. Among the glycol oligomeric additives, ethylene glycol monobutyl ether was found to reduce the C_P maximum. An increase in the repeating units of polymeric glycol additives leads to a decrease in C_P. Reduction in the C_P in the presence of TBP depends upon the increase in hydrophobic/hydrophilic ratio among the polypropylene to polyethylene units.

Keywords Tween · Glycol oligomers · Triblock polymers · Cloud point

Introduction

Surfactants find a multitude of uses in household detergents, personal care products, industrial cleaners and industrial processing. One particular type, the non-ionic surfactants, have diverse uses in various fields. Like most of the ethylene oxide (EO) derivatives, they exhibit inverse solubility characteristics and precipitate with increase in temperature of their solutions. The temperature at which precipitation occurs is called the cloud point (C_P) of the surfactant [1]. At this temperature a transition occurs from a single-phase micellar solution to surfactant-rich and surfactant-poor phases. The phase separation presumably occurs due to decrease in hydration of the head group because of attainment of less polar conformation at higher temperature. The aggregates in the cloudy dispersion are much larger than micelles. This sometimes precludes their use in high-temperature applications, e.g. when designing detergents for use in hot water, and separation of organic compounds and proteins [2, 3, 4]. Knowing the C_P is also important for determining storage stability, since formulations at temperatures significantly higher than the C_P may result in phase separation and instability. Generally, non-ionic surfactants show optimal effectiveness when used near or below their C_P and, hence, the C_P of surfactant solutions can be strongly influenced in the presence of other materials.

The additive effect of glycols on micelle formation of non-ionic surfactants is still not clear in comparison to that on micelle formation of ionic surfactants, since the former is considered to have very weak interactions in comparison to the latter. The ethoxylated sorbitan esters are a large class of non-ionic surfactants. They are water soluble and frequently used as industrial emulsifiers, antistatic agents, fibre lubricants and solubilisers. Apart from this, recently the use of triblock polymers, which also constitute polymeric repeating units of different glycols, has become of considerable importance in many industrial applications [5]. The aim of the present work is to understand the solubility behaviour of ethoxylated sorbitan ester non-ionic surfactants such as Tween in the presence of glycols and triblock polymers. An effort has been made to understand the interaction between solvent and additives leading to a change in solubility of Tween.

Experimental

Tween 20, Tween 80, ethylene glycol (EG), diethylene glycol (DEG), triethylene glycol (TEG), ethylene glycol monomethyl ether (EGMME), ethylene glycol monoethyl ether (EGMEE), ethyleneglycol monobutyl ether (EGMBE) and polyethylene glycols (PEG) with average molecular weight 200, 400, 600, 4,000 and 6,000 were products of CDH Bombay. Triblock polymers were received from Sigma and their characteristic features are listed in Table 1. All the chemicals were of analytical grade and used as received.

The C_P measurements were made visually [6] for the onset of turbidity by controlled heating (ca. 1 °C/min) of the well-stirred samples and then cooling of the solutions until they cleared. The temperatures were measured with a precision of 0.1 °C. The values determined are the mean of three separate determinations. The method has a reproducibility of better than ± 0.5 °C. The concentrations of Tween 20 and Tween 80 used for measurements were 0.5 and 0.1 mM, respectively.

Results and discussion

The C_P of Tween in the absence and presence of additives were determined. The results show that the C_P of Tween 20 (0.5 mM) = 75.6 °C and that of Tween 80 (0.1 mM) = 95.1 °C decrease in the presence of glycols and glycol ethers. A change in the C_P (ΔC_P) of Tween in the presence of monomeric and oligomeric glycols is represented in Fig. 1, whereas that in the presence of polymeric glycols is shown in Fig. 2. Figure 1 shows that ΔC_P is very small in the presence of EG, DEG, TEG, EGMME and EGMEE, but significantly large in the presence of EGMBE. A decrease in C_P is related to the solvation capacity of micelles by the aqueous environment in the presence of additive. The lesser the solvation of Tween micelles, the lower would be the C_P. In other words, a decrease in the hydration of Tween micelles would lead to a decrease in the C_P. A more water-structure-breaking additive would render fewer water molecules available for the hydration of Tween micelles. Glycol ethers have been found to be stronger structure breakers than glycols; thus, EGMBE is considered to be the most effective among all glycols in reducing the C_P of Tween micelles, in agreement with the fact that polar organic compounds depress the C_P [7, 8, 9]. A comparison of the relative decrease in the magnitudes of C_P of Tween 20 and Tween 80 suggests (Fig. 1) that ΔT is higher for Tween 80 micelles than Tween 20. It means Tween 80 micelles get less hydrated than Tween 20 micelles, which is expected to be due to the stronger hydrophobicity of the former.

Table 1 Composition of various triblock polymers (PEO—PPO—PEO)

Polymers	Molecular weight	Total no. of EO units (1/2 in equal no.).	No. of PO units	Hydrophobic/ hydrophilic ratio
TBP_1	1,100	4	15.5	3.9
TBP_2	3,400	36	31	0.9

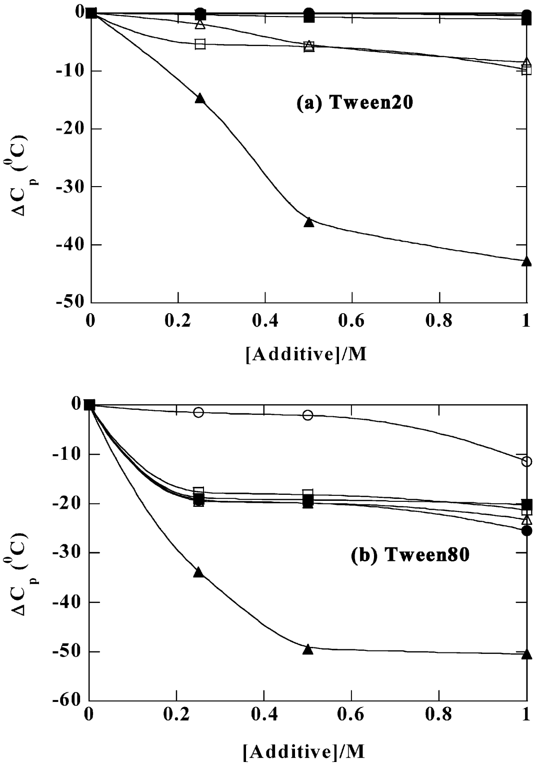

Fig. 1 **a** Plot of change in C_P of Tween 20 (0.5 mM) in the presence of glycol oligomer additives: EG (○), DEG (●), TEG (□), EGMME (■), EGMEE (△), EGMBE (▲). **b** Plot of change in C_P of Tween 80 (0.1 mM) in the presence of glycol oligomer additives: EG (○), DEG (●), TEG (□), EGMME (■), EGMEE (△), EGMBE (▲)

Figure 2 shows a systematic decrease in ΔC_P with an increase in the amount of each PEG. The decrease in magnitude further increases with an increase in the number of repeating units or average molecular weight. That is why PEG 6,000 induces a maximum negative ΔC_P value. Although there are several reports regarding the presence of interactions between ionic surfactants and PEG [10, 11, 12, 13], little is known about such interactions between non-ionic surfactants and PEG. A regular decrease in C_P with an increase in number of PEG units, therefore, can be related to the favourable Tween–PEG interactions, which would be predominantly hydrophobic in nature. To explore such interactions further, we carried out C_P measurements of Tween + TBP systems.

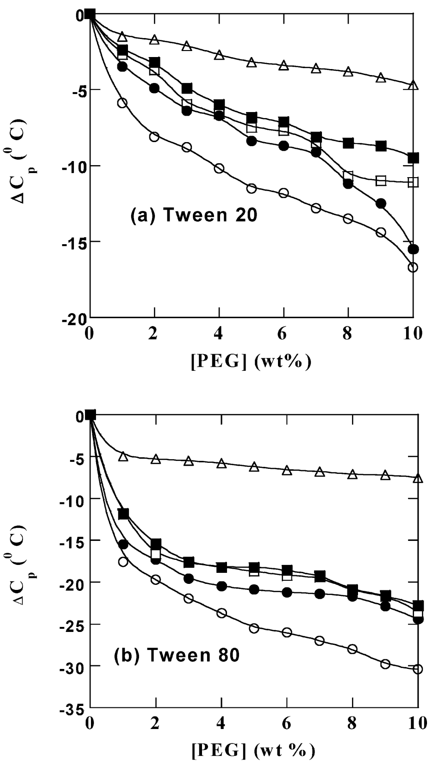

Fig. 2 **a** Plot of change in C_P of Tween 20 (0.5 mM) in the presence of polyethylene glycols: PEG 6,000 (○), PEG 4,000 (●), PEG 600 (□), PEG 400 (■), PEG 200 (△). **b** Plot of change in C_P of Tween 80 (0.1 mM) in the presence of polyethylene glycols: PEG 6,000 (○), PEG 4,000 (●), PEG 600 (□), PEG 400 (■), PEG 200 (△)

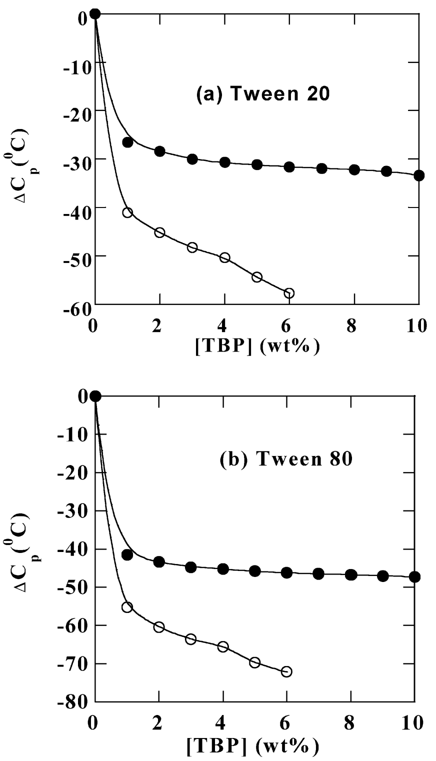

Fig. 3 **a** Plot of change in C_P of Tween 20 (0.5 mM) in the presence of triblock polymers: TBP_1 (○), TBP_2 (●). **b** Plot of change in C_P of Tween 80 (0.1 mM) in the presence of triblock polymers: TBP_1 (○), TBP_2 (●)

Figure 3 demonstrates a variation in ΔC_P of Tween in the presence of TBP_1 and TBP_2. The C_P decreases with an increase in the amount of both TBP initially, while it tends to become constant in the former case. A decrease in C_P is related to dehydration of non-ionic micelles or, in other words, an increase in its hydrophobicity. Table 1 suggests that TBP_1 has a higher hydrophobic/hydrophilic ratio, i.e. 3.9, than that of TBP_2, i.e. 0.9, hence it is expected to produce mixed micelles with Tween of higher hydrophobicity. The micelles of higher hydrophobic environment would get dehydrated at relatively lower temperatures, hence the C_P regularly decreases in the presence of TBP_1 rather than TBP_2.

Conclusions

The following conclusions can be drawn from this study:

1. The C_P of aqueous Tween 20 and 80 decreases in the presence of glycol oligomers, with a stronger additive effect from ethylene glycol monobutyl ether.
2. The C_P of aqueous Tween 20 and 80 decreases in the presence of polyethylene glycols, with a stronger additive effect from PEG having a higher average molecular weight.
3. The C_P of Tween 20 and 80 also decreases in the presence of triblock polymers, with a stronger additive effect from triblock polymer with a higher hydrophobic/hydrophilic ratio.
4. These studies demonstrate that different kinds of glycols, whether in the monomeric or polymeric form, do interact with non-ionic Tween surfactants.

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References

1. Myers D (1992) Surfactant science and technology, 2nd edn. VCH, New York
2. Frieberg SE, Chiu M (1988) J Disper Sci Technol 9:443
3. Cordero BM, Pavon JLP, Pinto CG, Laespada MEF (1993) Talanta 40:1703
4. Saitoh T, Hinze WL (1995) Talanta 42:119
5. Alexandridis P, Hatton TA (1995) Colloid Surface A 96:1
6. Da Silva RC, Loh W (1998) J Colloid Interface Sci 202:385
7. Goto A, Nihei M, Endo F (1998) J Phys Chem 84:2268
8. Goto A, Endo F, Higashida S (1985) Bull Chem Soc Jpn 58:773
9. Donbrow M, Azaz E (1976) J Colloid Interface Sci 57:20
10. Bakshi MS, Kaur G (2000) J Surfactants Deterg 3(2):159
11. Bakshi MS (2001) Tenside Surfact Det 38(2):103
12. Marinov G, Michels B, Zana R (1998) Langmuir 14:2639
13. Thurn T, Couderc S, Sidhu J, Bloor DM, Penfold J, Holzwarth JF, Wyn-jones E (2002) Langmuir 18:9267