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ORIGINAL CONTRIBUTION

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Effect of adding glycols to the micellar properties of Tween: small-angle neutron scattering and turbidity measurements

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Abstract Small-angle neutron scattering (SANS) and turbidity measurements have been carried out on the nonionic surfactants Tween 20 and Tween 80, in the presence of diethyleneglycol (DEG), triethyleneglycol (TEG), ethylene glycol monoethyl ether (EGMEE), and ethyleneglycol mono butyl ether (EGMBE). SANS measurements show that the shapes of the Tween 20 and Tween 80 micelles are oblate ellipsoidal, which do not change predominantly in the presence of DEG and TEG. However, the presence of EGMBE and EGMEE reduces the aggregation number of Tween. This has been attributed to the solubilization of EGMBE and EGMEE in the Tween micelles, providing them with additional hydrophobicity.

Keywords Tween · Glycol oligomers · Small angle neutron scattering · Turbidity

Introduction

Many industrial processes require large quantities of nonionic surfactants [1]. These industrial demands have made nonionic surfactants ubiquitous in the environment. Since all practical applications of surfactants involve the presence of other species [2, 3, 4] such as glycols and alcohols, it is important to establish the effects of these species on micelles in order to explore their fundamental behavior. The aim of the present work is to gain insight into Tween (nonionic surfactant)–glycol interactions with respect to changes in repeating units of glycol oligomers, by using small-angle neutron scattering (SANS) and turbidity measurements. We investigate how glycol oligomers affect the size, shape, and aggregation number of Tween micelles, since both Tween and glycol oligomers are used extensively in the cosmetic industry [5]. In the presence of water, glycols act to break up the large-scale hydrogen-bonded structure of water, which leads to the formation of a new structure involving hydrogen bonding between the water and glycol molecules. This combined-structure phase also provides a complete hydrophobic environment for amphiphilic molecules like surfactants to assemble like they do in pure water.

Conventional techniques cannot provide deep insight into colloidal assemblies, which, in particular, consist of nonionic-nonionic components such as Tween-glycol systems. It is also not an easy task to identify the locus of solubilization of glycol additives in aqueous nonionic micellar solutions, due to an equal probability of finding such additives in the micellar and aqueous environments. In order to quantify such confusing situations, we need to use a technique that can look deep into the aggregated assemblies. SANS is a powerful technique for probing the structure of such colloidal aggregates [6, 7, 8]. The short effective wavelength of neutrons permits the characterization of colloidal assemblies with dimensions of the order 10–1000 Å. Therefore, a change in the micellar parameters of Tween due to the presence of glycols from its properties in pure water will help us to quantitatively identify the preferential solvation of glycol additives.

Experimental

Materials

Tween 20 and 80, diethyleneglycol (DEG), triethyleneglycol (TEG), ethylene glycol monoethyl ether (EGMEE), and ethyleneglycol monobutylether (EGMBE) were products of Central Drug House, Bombay. All reagents were used as received, and were of analytical grade.

Small-angle neutron scattering (SANS) measurements

Small-angle neutron scattering measurements were performed using the SANS instrument at the DHRUVA reactor, Trombay [9]. In all of the measurements, the solutions were prepared in D_2O to enhance the contrast and reduce the incoherent background. A quartz cell of 0.5 cm path length was used to hold the samples. The sample temperature was maintained at 30 °C. The beam size at the sample position was 1.5 cm×1.0 cm. The scattered neutrons from the sample were detected using a 100 cm-long and 3.8 cm-diameter He^3 linear position sensitive detector. The distance between the sample and detector was 1.85 m for all runs. The accessible Q-range of the instrument was 0.018–0.32 $Å^{-1}$. The data were corrected for background, empty-cell contribution, and sample transmission, and normalized to absolute cross-section units.

Turbidity (transmittance) measurements

The turbidity measurements were performed using a Nephelo-Turbidity meter Systronics 132 after allowing sufficient time for equilibration. The instrument works on the basis of light scattering from the colloidal particles. The monochromatic light coming from the light source is focused in the colloidal solution by passing it through a pair of lenses, and the scattered light at right angles to the incident light is detected by a photomultiplier tube which gives the turbidity of the solution in arbitrary nephelo-turbidity units. The titrations were made by adding concentrated stock solutions of aqueous Tween to pure water or water + glycols, keeping the concentration of glycol constant. We should mention here that no cloudiness ever appeared in any of the Tween + glycol systems during the titration, and so turbidity is simply the measure of scattering from the homogeneous and clear colloidal solutions in the form of transmittance.

Results

Turbidity behavior

Figure 1 shows the transmittance plot of Tween 20 with respect to its concentration in pure water. A distinct break where the τ value tends to become constant represents the critical micelle concentration (cmc). Similar plots were observed for other systems in the presence of different glycols. The cmc values for all systems were evaluated from the first derivative curves and are given in Table 1. A perusal of Table 1 suggests that an increase in the amount of each additive leads to an increase in the cmc value of Tween. It is possible to compute the standard free energy of micelle formation ($\Delta G^0_m = RT \ln X_{cmc}$) in all cases, which would explain the stability of Tween micelles in the presence of additives. A transfer of the standard free energy of the micelle,

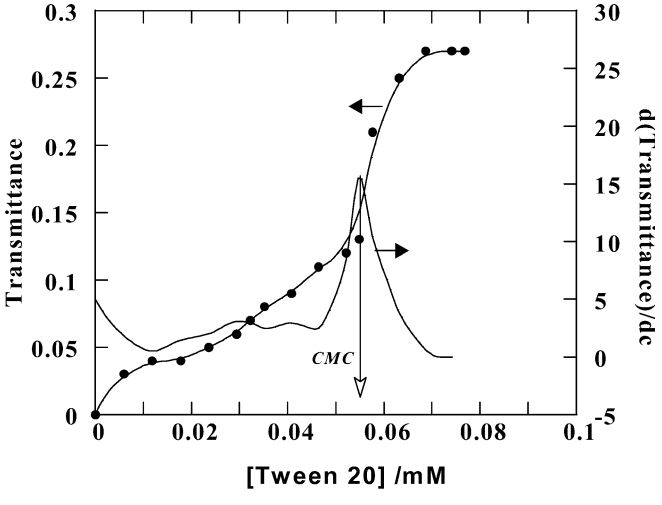

Fig. 1 Plot of transmittance and its first derivative versus concentration of Tween 20. Note that the cmc is given by the maximum of the first derivative of transmittance

Table 1 Cmc/10^{-5} mol dm^{-3} of aqueous solution of Tween in the presence of different glycol oligomers

Additive concentration		0.25 M	0.50 M	1.00 M
Tween 20 = 5.5	DEG	5.5	5.7	6.0
	TEG	5.6	5.6	6.0
	EGMEE	6.0	6.5	7.0
	EGMBE	7.0	7.5	8.0
Tween 80 = 1.2	DEG	1.2	1.6	1.6
	TEG	1.5	1.5	1.8
	EGMEE	1.6	1.8	2.0
	EGMBE	1.8	2.0	2.0

$\Delta G_t^0 = \Delta G_{\text{additive}}^0 - \Delta G_{\text{water}}^0$, from aqueous medium to aqueous additive has been computed and plotted in Fig. 2. $\Delta G_t{}^0$ values in all cases increase with the amount of each additive. This demonstrates that all glycols destabilize the micelles and lead to a delay in the micelle formation process. In fact, several studies that have reported on micelle formation for surfactants in aqueous glycol solutions have reported an increase in the cmc value in the presence of glycol. Nagarajan and Wang [10] discussed the micellization of several surfactants from a theoretical point of view, and concluded that the presence of glycols results in an increase in the cmc, a decrease in the average aggregation number, and an increase in polydispersity. The large values of cmc primarily originate from the smaller magnitude of the surfactant tail transfer of free energy in the mixed solvent. As far as the effect of adding the present glycols is concerned, it is apparent that the presence of EGMEE and EGMBE produces large cmc values for both Tween 20 and 80, and so induces a smaller contribution to the free energy transfer (Fig. 2). Differences in the effects of adding DEG and TEG from the effects of adding EGMEE and EGMBE can be understood quantitatively by determining various micellar parameters from small angle neutron scattering studies.

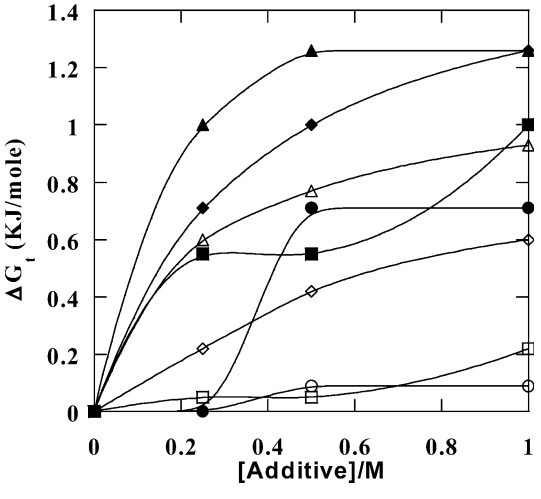

Fig. 2 Plots of ΔG_t for Tween 20 and Tween 80 in the presence of glycol oligomer additives. Open circles: DEG (Tween 20); open squares: TEG (Tween 20); open diamonds: EGMEE (Tween 20); open triangles: EGMBE (Tween 20); filled circles: DEG (Tween 80); filled squares: TEG (Tween 80); filled diamonds: EGMEE (Tween 20); filled triangles: EGMBE (Tween 80)

SANS behavior

The SANS measurements were made on aqueous solutions of 0.024 M Tween 20 and 0.023 M Tween 80 in the presence and absence of various glycol additives. SANS measures the coherent differential scattering cross-section per unit volume ($d\Sigma/d\Omega$) as a function of scattering wave vector transfer Q. For a system of monodisperse interacting micelles, $d\Sigma/d\Omega$ is given by [11, 12],

$$\frac{d\Sigma}{d\Omega} = n_m V_m^2 (\rho_m - \rho_s)^2 \left[\langle F^2(Q) \rangle + \langle F(Q) \rangle^2 (S(Q)) - 1 \right] + B \tag{1}$$

where n_m is the number density of micelles, and ρ_m and ρ_s are the scattering length densities of the micelle and solvent, respectively. $F(Q)$ is the single-particle form factor, $S(Q)$ is the interparticle structure factor, and B is a constant that represents the incoherent scattering background. The measured scattering profiles of all systems bear a close resemblance to each other. SANS distributions for the present systems do not show any indication of peaks. Therefore, the value of $S(Q)$ was assumed to be unity because of negligible intermicellar interference. The SANS data were therefore fitted to the following expression,

$$\frac{d\Sigma}{d\Omega} = n_m V_m^2 (\rho_m - \rho_s)^2 \langle F^2(Q) \rangle + B \tag{2}$$

Different models for the shape of the micelles, such as spherical, prolate and oblate ellipsoidal, and poly-disperse spherical, were used to calculate the scattering intensity. The parameters in the analysis were optimized by means of a nonlinear least-square fitting program. It was found that the oblate ellipsoidal model was the best-fit model for the present Tween + glycol systems, and the parameters extracted look more consistent for this shape. The SANS data for Tween in the presence of various additives at 30 °C are shown in Fig. 3a,b. The solid lines in the figure are curves fitted to the experimental data. The values for the semi-minor axis (a) and semi-major axis (b) of the oblate ellipsoidal micelles were calculated from the analysis. The aggregation number of micelles N_{agg} was calculated using the following expression,

$$N_{agg} = \frac{V_m}{V_h} \tag{3}$$

Here V_m ($=4/3\pi a^2 b$) is the micellar volume, and V_h is the volume of hydrophobic part of the surfactant monomer. Using the calculated value of N_{agg}, the number density of micelles n_m was calculated using the following relation,

$$n_m\ (\mathrm{cm}^{-3}) = (C - \mathrm{cmc})\frac{N_A}{N_{agg}} \times 10^{-3} \quad (4)$$

where C is the concentration in mol dm^{-3} and N_A is Avogadro's number.

The parameters obtained using this method are listed in Table 1.

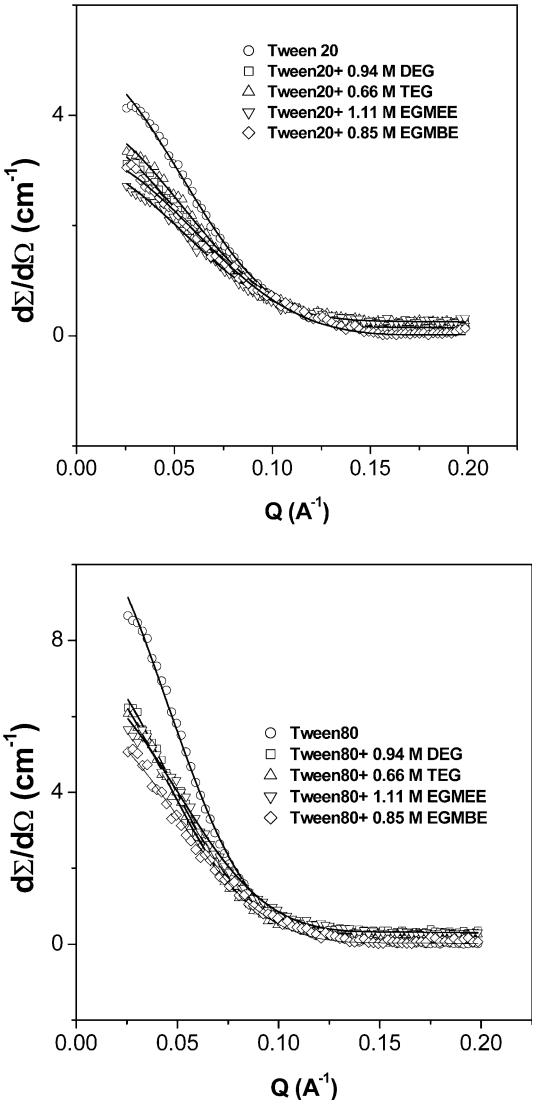

Fig. 3 a SANS distributions for micelles of 0.024 M Tween 20 in D_2O in the presence of different additives at 30 °C. **b** SANS distributions for micelles of 0.023 M Tween 80 in D_2O in the presence of different additives at 30 °C

Discussion

One can observe that there is not much difference between the various micellar parameters of Tween 20 in the presence and absence of DEG, TEG, and EGMEE. However, the addition of EGMBE certainly reduces the values of b/a and N_{agg} for Tween 20. Addition of the glycol additives DEG and TEG does not result in any observable change in the values of the micellar parameters of Tween 80, but addition of EGMEE or EGMBE reduces the values of b/a and N_{agg}. It is clear from these results that neither DEG nor TEG solubilize in the micellar phase, which keeps the micellar paramaters almost invariant.

The addition of an ether glycol additive with a longer tail (EGMBE), rather than EGMEE, reduces the N_{agg} for Tween 20, while the same effect is produced by both on the value of N_{agg} for Tween 80. It shows that both kinds of glycols, DEG and TEG on the one hand, and EGMEE and EGMBE on the other, have different solubilizing sites. This was also discussed by Marangoni et al [13] after comparing the effects of tetra ethylene glycol and tetraethylene glycol dimethyl ether on ionic surfactants. This difference in the solubilizing sites for both kinds of glycols is related to their structures. DEG and TEG are glycols with OH end groups, which have the potential to undergo hydrogen bonding, which in turn dominates their ability to undergo mixed micellization with Tween monomers. On the other hand, EGMEE and EGMBE, with their $-OC_2H_5$ and $-OC_4H_9$ end groups, respectively, introduce significant hydrophobicity and therefore reduce hydrogen bonding potential in the aqueous phase. This hydrophobicity generates an amphiphilic nature for both EGMEE and EGMBE (though much stronger in the case of EGMBE), which facilitates their solubilization in the palisade layer of Tween micelles in order to produce mixed micelles. Therefore, the solubilization of amphiphilic moieties in the palisade layer closer to the head group region will obviously enhance the hydrophilicity by introducing ethylene glycol units at the level of the head groups. This will result in a decrease in the aggregation

Table 2 Values of semimajor axis (b), semiminor axis (a), axial ratio (b/a), aggregation number (N_{agg}), and number density (n_m) of micelles of Tween in the presence of different glycol oligomers

Additive		b (Å)	a (Å)	b/a	N_{agg}	$n_m(\mathrm{cm}^{-3})$
Tween 20	Blank	34.3	21.4	1.6	349	4.14×10^{16}
	DEG	35.2	20.4	1.7	359	4.03×10^{16}
	TEG	34.1	20.7	1.6	340	4.25×10^{16}
	EGMEE	34.1	20.2	1.7	338	4.28×10^{16}
	EGMBE	29.8	20.9	1.4	262	5.50×10^{16}
Tween 80	Blank	40.5	23.3	1.7	350	3.96×10^{16}
	DEG	42.0	23.2	1.8	375	3.69×10^{16}
	TEG	41.9	23.7	1.8	381	3.63×10^{16}
	EGMEE	36.8	23.2	1.6	287	4.83×10^{16}
	EGMBE	36.6	23.3	1.6	284	4.88×10^{16}

number of Tween micelles. A close look at Table 2 shows that the presence of EGMBE is quite effective in reducing the N_{agg} of both Tween 20 and 80 in comparison to EGMEE.

Conclusions

The following conclusions can be made from the study:

- Neither DEG nor TEG solubilize in the Tween micelles; instead they prefer to remain in the aqueous bulk. Therefore, adding DEG and TEG does not influence the micellar parameters of Tween micelles.
- Adding EGMBE followed by EGMEE does however influence the micellar parameters of Tween, by reducing the micellar aggregation number. This has been attributed to the additional hydrophobicity provided by these additives upon solubilization in Tween micelles.

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