

# Triggered aggregation of nonionic surfactants in glycol mixtures

Using mixtures of two mutually miscible hydrogen-bonding solvents has led to a surprising finding: it is possible to switch 'on' and 'off' aggregation of a nonionic surfactant. This unexpected behaviour may find uses in triggered release, targeted delivery and critical non-aqueous cleaning applications (1).

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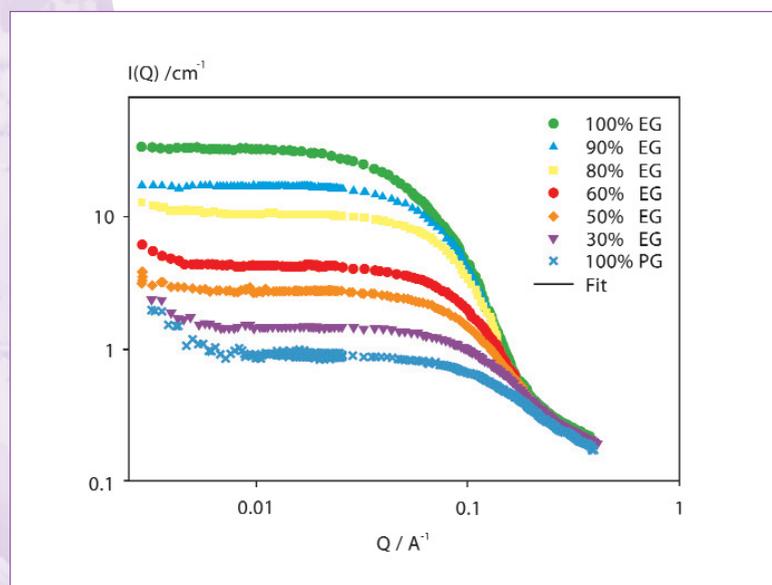
The solvents are ethylene glycol (EG, normal 'anti-freeze') and propylene glycol (PG), and the surfactant is  $C_{12}E_8$  (octaethylene monododecyl ether). Small-angle neutron scattering (SANS) was used to follow the solvent-induced changes, by employing contrast variation to highlight the surfactant molecules in the background sea of deuterated solvents. The 'on' state is achieved in pure EG, whereas if the solvent is pure PG then aggregation is strongly inhibited. For blends of EG and PG the extent of aggregation can be readily controlled by the EG:PG mixture ratio. These findings are made all the more surprising when it is realised that the solvents have very similar chemical structures, differing merely by an additional  $-CH_2-$  group for PG.

Small-angle neutron scattering (SANS) was used to characterise micellar aggregates of  $C_{12}E_8$ . SANS experiments were carried out at the D22 diffractometer at the ILL. Fully deuterated solvents provided contrast against the *h*-surfactant aggregates.

**Figure 1** shows SANS curves of  $C_{12}E_8$  surfactant in different solvents which are either pure deuterated d-EG, or d-PG, or their mixtures.  $C_{12}E_8$  was from Fluka BioChemika,

$\geq 98.0\%$  GC) and used without further purification. Fully deuterated ethylene and propylene glycol were obtained from Q<sub>max</sub> laboratory (CDN isotopes). Obviously, the nature of the solvent, and its composition in terms of the EG:PG ratio, has a strong effect on the measured intensity. Even without quantitative analysis (described below), it is clear that the strong aggregation seen in pure EG (•) is suppressed as the mixed solvent composi-

tion is made richer in PG (x). Detailed analyses of the SANS curves were performed using two related models describing anisotropic cylindrical, or ellipsoidal particles. For the EG-rich systems, the micelles appeared to be cylindrical in shape (described by a cross-sectional radius and a length). However, as the PG content is increased there is evidence for a subtle shape change to ellipsoidal micelles (described by principal radii  $r_1$  and  $r_2$ , and



**Figure 1:** SANS curves for 10 wt % solutions of  $C_{12}E_8$  in solvents at different mole % of d-PG in d-EG, at 25°C. The solid lines are model fits, and the parameters are discussed in the article.

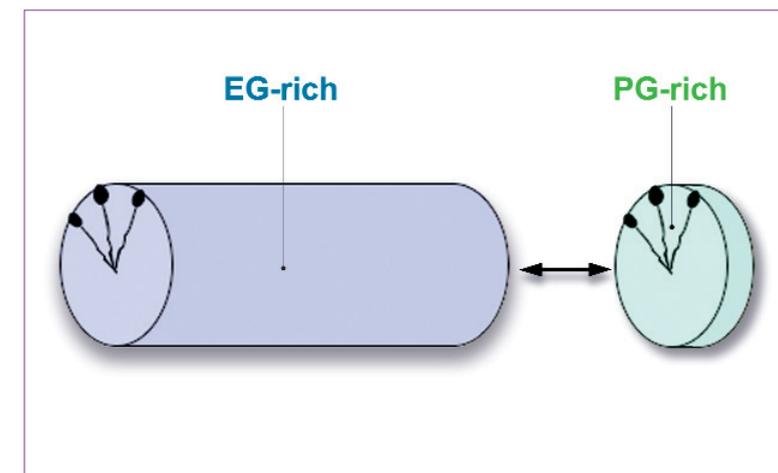
Solvent	R / Å	L / Å	V / (x10 <sup>4</sup> Å <sup>3</sup> )
100% d-EG	19	143	17
90% d-EG	19	84	9
80% d-EG	18	58	6

Solvent	$r_1$ / (Å) (core radius)	$r_2$ / (Å) (core radius)	t / (Å) (thickness)	V / (x10 <sup>4</sup> Å <sup>3</sup> )
60% d-EG	16	8	8	4
50% d-EG	16	5	5	2
30% d-EG	16	3	5	1
100% d-PG	16	1	3	1

**Table 1:** Parameters obtained by analysis SANS data from 10 wt% surfactant solutions of  $C_{12}E_8$  in different deuterated glycol solvents at 25°C. Uncertainties:  $r_1, r_2, t \pm 2\text{Å}$ ; Overall radius  $\pm 2\text{Å}$ , Length  $L \pm 10\text{Å}$ .

a shell thickness  $t$  to account for some weak solvent penetration into the outer surface of the micelles). These fitted functions are shown in **figure 1**. The values of internal micellar dimensions are consistent with those found in literature, by Lu *et al.* [2]. Using these parameters it has been possible to estimate the effective volume of each individual micelle  $V$ , which decreases dramatically as EG is systematically replaced by PG. It appears that changing the solvent from pure EG to PG causes a dramatic shift in surfactant properties, effectively switching 'off' aggregation. The tendency to cylinder formation in pure EG may be a result of a lower effective solvation of the EO head-groups compared to PG. This finding is also consistent with work of others [3], which suggested that EG can penetrate in the micelle and alter the micellar surface.

Aggregation of common nonionic  $C_{12}E_8$  surfactant was determined using SANS. When mixed EG/PG solvents are employed, aggregation and nature of the micelles were affected by the solvent composition. Therefore, ethylene glycol may be considered as a 'structure-making' solvent, whereas propylene glycol behaves as a 'structure-breaker'. The micelles tend to change from elongated rod-like aggregates in EG into ellipsoidal aggregates at higher PG content. This unusual behaviour



**Figure 2:** Switching from ethylene glycol (EG) to propylene glycol (PG) induces a massive change in the clustering and aggregation.

demonstrates potential for expanding the uses and applications of these two industrial solvents. Amongst others, this may have benefits for protein studies or conservation fluids. Furthermore, owing to special "anti-freeze" properties, EG also finds many commercial applications: now it is possible to consider high-performance cooling fluids containing surfactant micelles for added lubrication and cleaning functions.

### References

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- (2) J. R. Lu, Z. X. Li, and R. K. Thomas, *J. Phys. Chem.* 98 (1994) 6559
- (3) C. Carnero Ruiz, *J. Colloid Interface Sci.* 221 (2000) 262