Colloid Polym Sci (2005) 283: 646–652
DOI 10.1007/s00396-004-1195-z

ORIGINAL CONTRIBUTION

M. A. Sanz
N. Granizo
M. Gradzielski
M. M. Rodrigo
M. Valiente

Mixed micellar systems of octyl β,D-glucopyranoside with a nonionic surfactant and a water-soluble polymer

Received: 13 January 2004
Accepted: 14 July 2004

M. A. Sanz · N. Granizo
M. M. Rodrigo · M. Valiente (✉)
Dpto. Química Física,
Universidad de Alcalá, 28871 Madrid,
Spain
E-mail: mercedes.valiente@uah.es

M. Gradzielski
Lehrstuhl für Physikalische Chemie I,
Universität Bayreuth, 95440 Bayreuth,
Germany

Abstract We have made a comparative study between the micellar regions of the octyl β-D-glucoside (OG)–tetraethylene glycol monododecyl ether and the OG–poly(ethylene glycol) 20,000 systems by means of surface tension and viscosimetric measurements. The incorporation of the tetraethylene glycol monododecyl ether nonionic surfactant in the OG micelles decreases the critical micelle concentration, whereas the presence of polymer increases it. The nonionic surfactant mixture exhibits nonideal mixing behaviour. The data fit to Rubingh's treatment with a β value of -5.1, which implies a modest attraction between both surfactants. The surfactant–poly(ethylene glycol) 20,000 system does not form mixed micelles. The incorporation of polymer increases the critical micelle concentration of the surfactant. The viscosity for the surfactant–polymer system is higher than that for the pure polymer, demonstrating a surfactant-induced structuring.

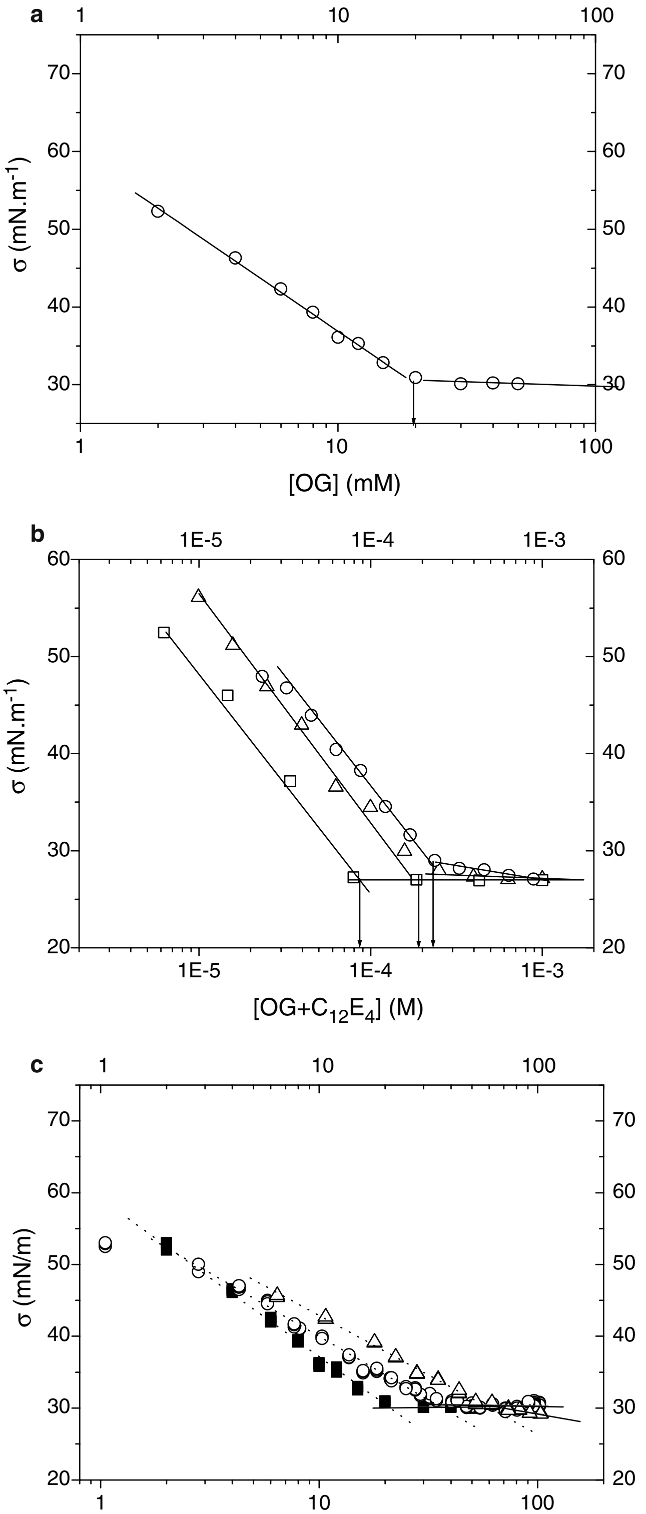
Keywords Octyl β,D-glucopyranoside · Poly(ethylene glycol) · Dodecyl tetraethylene glycol · Micelles · Critical micelle concentration

Introduction

Surfactant mixtures and mixtures of surfactants and water-soluble polymers have very broad ranges of applications [1]. There are many technical applications of polymer–surfactant systems. This is a way to control the rheological properties, emulsification behaviour, etc. Accordingly the interactions between polymers and surfactants in aqueous solution are currently attracting much interest. Several types of binding have been identified in surfactant–hydrophobic polymers and polymer–ionic surfactant. The modification of water-soluble homopolymers by grafting a low number of hydrophobic groups leads to hydrophobically modified water-soluble polymers. Such polymers can be viewed as modified surfactants and they form mixed micelles with ionic surfactants [2].

A well-chosen mixture of surfactants often offers synergetic effects. It produces a larger decrease of the surface tension and lower critical micelle concentration (cmc) values than each of the pure surfactants would do. There are many studies of nonionic surfactant mixtures in aqueous solution [3, 4, 5]. Only a few pairs of surfactants behave like an ideal mixture of its components, while most mixtures show deviations from ideality.

In this contribution we report a comparative study for the micellar regions of two octyl β-D-glucoside (OG) systems, one with a nonionic surfactant (tetraethylene glycol monododecyl ether, $C_{12}E_4$) and another with a water-soluble polymer [poly(ethylene glycol) 20,000, PEG]. Surface tension and viscosity measurements have been carried out to determine the cmc, the surface activity of the surfactant and thermodynamic properties of these aggregates.



►

Fig. 1 **a** Variation of the surface tension with the octyl β-D-glucoside (*OG*) concentration at 30.0 ± 0.1 °C. **b** Variation of the surface tension with the total surfactant concentration (OG and tetraethylene glycol monododecyl ether, *$C_{12}E_4$*) at 30.0 ± 0.1 °C for different OG molar ratios (α_1): 0.6 (*squares*), 0.8 (*triangles*), 0.9 (*circles*). **c** Variation of the surface tension with the OG concentration at 30.0 ± 0.1 °C for different poly(ethylene glycol) 20,000 (*PEG*) concentrations: 0 mM (*squares*), 5 mM (*circles*), 15 mM (*triangles*)

Experimental

Materials

n-Octyl-β,D-glucopyranoside (Sigma, more than 98% purity, gas chromatography grade), $C_{12}E_4$ (Fluka, more than 98% purity, gas chromatography grade), and PEG (Aldrich) were used as received.

Surface tension

The surface tension of aqueous mixed-surfactant solutions and aqueous surfactant–polymer solutions were determined as a function of the concentration using the ring method with a LAUDA TE-1C tensiometer. All measurements were carried out at 30.0 ± 0.1 °C. The surface tension measurements were made with a standard deviation lower than 0.1 mN m^{-1}. The surface tension data below and above the cmc were fitted to straight lines by a least-squares method. The cmc values were determined from the sharp breakpoint in the curves of the surface tension against the logarithm of the concentration.

Viscosity

The viscosimetric study was performed using a Carri-Med CSL^2 100 rheometer in stress-controlled mode. A cone–plate sensor was used, with a diameter of 40 mm and a cone angle of 1°. Steady flow experiments were carried out at 30.0 ± 0.1 °C.

Results and discussion

The OG surfactant forms micelles up to high surfactant concentration (higher than 50% in weight). The cmc value of OG was determined from surface tension measurements (Fig. 1a). This surfactant shows a relatively high cmc (19.5 mM) owing to the short alkyl chain and the large and highly hydrophilic head group.

In contrast, $C_{12}E_4$ has a very low cmc (4.6×10^{-2} mM) and it tends to form a lamellar phase at low surfactant contents. The surface activity of $C_{12}E_4$ has been widely studied [6].

At low surfactant concentration, mixtures of $C_{12}E_4$ and OG form micelles at high OG mole fraction and a lamellar phase at low OG mole fraction [7]. The extension of the mixed micellar phase depends on temperature and on the total surfactant concentration. At 0.1 M surfactant concentration and 30.0 ± 0.1 °C, the micellar phase extends from an OG mole fraction of 0.45 to 1. Two isotropic phases appear at a lower mole fraction than 0.45. The cmc for the mixed systems was determined by surface tension measurements for different OG mole fractions (Fig. 1b).

The micellar phase of the mixed surfactant–polymer system was studied in the same range of OG concentrations by varying the polymer content. Surface tension isotherms for the surfactant–polymer systems at fixed polymer concentration are given in Fig. 1c. The surface tension of the pure aqueous polymer solutions at room temperature was measured in the range 0.66–8 mM and showed a value of 55.0 ± 0.9 mN m^{-1}. No significant changes in surface tension as a function of polymer concentration were found for the binary aqueous polymer solution.

The surface activity of a surfactant molecule is characterized by the cmc, the required area per head group of the molecule, and the surface tension at the cmc. The required area per head group, A, at the interface may be calculated using the Gibbs equation:

$$\Gamma = \frac{1}{2.303RT}\left(-\frac{\partial\sigma}{\partial\log c}\right)_T, \tag{1}$$

where Γ is the maximum interfacial excess concentration in moles per square metre and $\partial\sigma/\partial\log c$ is the slope of the surface tension. The maximum interfacial excess concentration is obtained from the slope of the plot of the surface tension versus the logarithm of the concentration. The minimum area per molecule, A (in square angstroms), is given by Eq. (2):

$$A = \frac{10^{20}}{N\Gamma}, \tag{2}$$

where N is Avogadro's number. The Values of the cmc, Γ, A, and the surface tension above the cmc are listed in Table 1 for both systems.

The first difference between both systems is that the addition of the nonionic $C_{12}E_4$ decreases the cmc, whereas the presence of polymer increases it. It should be pointed out that for the calculation of the parameters for the surfactant mixtures we have taken into account the total surfactant concentration, while for the data of the surfactant–polymer mixtures, we only considered the surfactant. The surfactant mixtures have lower surface tension values at high concentration, i.e. above the cmc, than the corresponding surfactant–polymer mixtures. Moreover the area per head group of the surfactant decreases when $C_{12}E_4$ surfactant is replacing OG surfactant. This is an interesting effect as the pure $C_{12}E_4$ has a head group area of 46 Å^2 [6], i.e. the decrease in the mixture should be the result of synergetic interactions as confirmed by the interaction parameter β (see later). Contrary to that, the presence of the polymer increases the area per head group of OG surfactant.

If we consider an ideal mixed-micelle formation, the cmc of the mixture is given by Lange's treatment, which treats the micelles as a separate phase from that of the dissolved surfactant monomers [8]:

$$\frac{1}{\mathrm{cmc}} = \frac{\alpha_1}{\mathrm{cmc}_1} + \frac{1-\alpha_1}{\mathrm{cmc}_2}, \tag{3}$$

where cmc is the cmc of the mixture, cmc_1 is the cmc of pure OG, cmc_2 is the cmc of pure $C_{12}E_4$ and α_1 is the mole fraction of OG. The experimental cmc values at different mole fraction of OG and the calculated cmc values for ideal behaviour are plotted in Fig. 2. A negative deviation from ideality is observed owing to attractive interactions between both surfactants.

In order to explain the nonideal behaviour of the mixed micelles we use Rubingh's treatment [9] based on the phase-separation model in the same way as Lange's treatment using the regular solution theory in order to obtain the activity coefficient. Accordingly the surfactant concentrations in the solution are given by

$$C_1 = x_1 \mathrm{cmc}_1 f_1 = \alpha_1 \mathrm{cmc}, \tag{4}$$

Table 1 Values of the critical micelle concentration (*cmc*), the maximum interfacial excess concentration, Γ, the minimum area per molecule, A, and the surface tension above the cmc for mixed micelles of surfactants and for the mixed system of surfactant and polymer. Octylβ-D-glucoside (*OG*), tetraethylene glycol monododecyl ether (*$C_{12}E_4$*), poly(ethylene glycol) 20,000 (*PEG*)

	cmc (M)	Γ (mol m^{-2})	A (Å^2)	σ (mN m^{-1})
OG + $C_{12}E_4$				
$\alpha_1 = 0.6$	8.8×10^{-5}	4.7×10^{-6}	35.3	27.0
$\alpha_1 = 0.8$	1.8×10^{-4}	4.0×10^{-6}	41.5	28.0
$\alpha_1 = 0.9$	2.2×10^{-4}	3.8×10^{-6}	43.6	28.4
OG + polymer				
OG	2×10^{-2}	3.9×10^{-6}	42.6	30.1
OG + PEG (5 mM)	3.7×10^{-2}	3.1×10^{-6}	53.6	30.4
OG + PEG (15 mM)	6.1×10^{-2}	2.8×10^{-6}	58.3	29.2

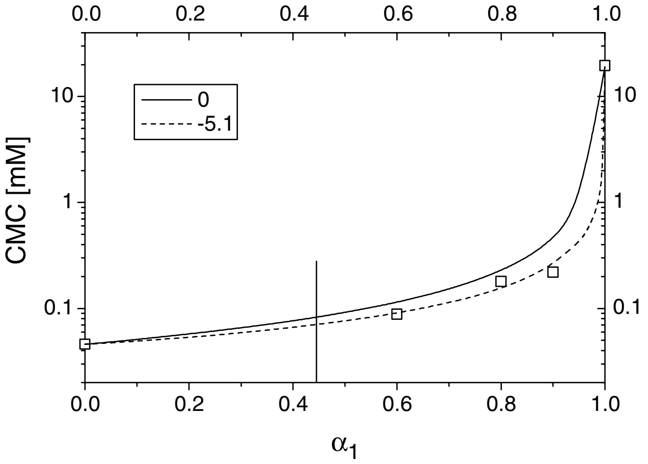


Fig. 2 Variation of the critical micelle concentration (*cmc*) with the molar ratio of OG: ideal model (*solid line*), Rubingh's model (*dashed line*)

Table 2 Mole fraction of OG in the mixed micelles, activity coefficient and β values

α_1	x_1	f_1	β	x_1 (ideal)
0.6	0.144	0.019	−5.4	0.0034
0.8	0.146	0.051	–4.1	0.0091
0.9	0.266	0.038	–6.0	0.020

where x_1 is the mole fraction of component 1 (OG) in the mixed micelles and f_1 is the activity coefficient given by the regular solution theory as

$$\ln f_1 = \beta(1 - x_1)^2, \tag{5}$$

where β is a nonideality parameter that accounts for the interaction energy between the surfactant molecules in a mixed aggregate.

Taking into account the same kind of equations for surfactant 2 and a simple mass-balance equation, we can easily deduce the following equation:

$$x_1^2 \ln\left(\frac{\alpha_1 \mathrm{cmc}}{x_1 \mathrm{cmc}_1}\right) = (1 - x_1)^2 \ln\left(\frac{(1 - \alpha_1)\mathrm{cmc}}{(1 - x_1)\mathrm{cmc}_2}\right). \tag{6}$$

This equation can be solved by an iterative calculation method that gives x_1 from the experimental values of the cmc. From the x_1 value, it is possible to obtain the activity coefficients and the β value (Table 2).

The value of β varies between −4.1 and −6.0 for the samples investigated and an average value of β=–5.1 fits the results as can be seen in Fig. 2. This parameter takes into account the interaction energy between the monomers of surfactant 1, surfactant 2, and the monomers of surfactants 1 and 2 in the mixed micelle, respectively ($\beta = E_{11} + E_{22} – 2E_{12})/RT$). For mixtures of surfactants with ionic charges, β may depend on the mole fraction of the surfactants [10, 11, 12, 13]. The negative β value implies a modest attraction between the components. Strong attractive interaction in mixed micelles has been described for mixed micelles of anionic and cationic surfactants (decyl sulfate/decyltrimethyl ammonium bromide) with a β value of –18.5 [14] or for anionic and zwitterionic surfactants with β values from –10.6 to –15.5 [15]. The average value of –5.1 is close to that observed for mixtures of nonionic surfactants of the C_iE_j type with anionic surfactants with sulfate or sulfonate head groups, e.g. for $C_{12}E_8$–sodium dodecyl sulfate a value of –3.9 has been observed, while mixtures with cationic trimethylalkylammonium surfactants yield smaller β values [14]. Apparently the sugar head group behaves similarly in that respect as an anionic sulfate head group and one possible explanation for that would be a similarly large polarizability of the head group.

The composition of the mixed micelles is given by the x_1 values. According to the data in Table 2 the mixed micelles are built up mainly of $C_{12}E_4$ but are significantly enriched with OG compared with what would be expected for ideal mixing. For example when the OG-to-$C_{12}E_4$ ratio in solution is 9:1, the molar ratio in the mixed micelles at the cmc is 1:3. As expected the molar ratio of OG in the mixed micelles decreases as the molar ratio of OG in the solutions decreases. Once the molar ratio of OG in the mixed micelles reaches a certain lower threshold, the composition would be so rich in $C_{12}E_4$ that the formation of mixed micelles no longer takes place. Instead the solution separates in two phases, one phase rich in OG and the other phase rich in $C_{12}E_4$. The almost pure $C_{12}E_4$ phase follows its natural tendency to form bilayers [7] in the form of vesicles that phase-separate form the micellar solution. The formation of vesicles at low concentration of $C_{12}E_4$ has been described in detail before [16, 17]. Accordingly one now has a system where vesicles rich in $C_{12}E_4$ are in equilibrium with a micelle phase rich in OG. The viscosimetric study of these phases clarifies the nature of these phases as we will see later.

For the surfactant–polymer mixture, the polymer cannot form micelles and is very soluble in water. Addition of PEG to the OG leads to a pronounced increase of the cmc which cannot be explained by solvent effects. For a comparison we measured the cmc of OG in water–ethylene glycol mixtures (3:1 and 3:2 in volume) and here the cmc is almost constant. The considerable increase in the cmc of OG indicates some kind of interaction between surfactant and polymer. The formation of mixed micelles is not feasible but other possibilities have been described in the literature, e.g. by an interaction in terms of an association or binding of the surfactant to the polymer or in terms of a micellization of surfactant on or in the vicinity of the polymer chain. The formation of complexes between the surfactant and

Table 3 Packing parameters for OG surfactant at different amounts of polymer

PEG concentration (mM)	0	5	15
P	0.49	0.39	0.36

the polymer has already been described for ionic surfactants and polymers, e.g. for the case of sodium dodecyl sulfate and PEG [18]. The micelle should be surrounded by polymer, thereby forming a pear-necklace structure with the surfactant forming discrete micelle-like clusters along the polymer chain. From the shift of the cmc induced by the presence of the polymer one may estimate the amount of OG bound to PEG according to (cmc_{OG+PEG}–cmc_{OG})/[PEG], which yields 3.4 and 3.1 molecules of OG per PEG molecule for 5 and 15 mM PEG, respectively, i.e. a relatively small number of surfactant molecules per polymer molecule.

For ionic surfactants, the polymer–surfactant self-assembly always starts at a lower concentration (critical aggregation concentration) [19] than that required for surfactant–surfactant self-assembly (cmc). We have not found any abrupt change in the surface tension below the cmc, but our uncharged system should be a more weakly interacting system.

An apparent packing parameter $v/a_0 l_C$ can be calculated from simple geometry by approximating the optimal head group area (a_0) by the minimum area obtained from the surface tension, using 242.6 Å^3 and 16.6 Å for the molar surfactant volume v and the chain length l_C, respectively. a_0 corresponds to the effective area of OG and it does not account for the area occupied by PEG. The packing parameters are in Table 3.

As already known, $P < 1/3$ corresponds to spherical micelles and $1/3 < P < 1/2$ corresponds to nonspherical micelles. The OG micelles in water are rod micelles [15, 20 , 21] but there is controversy in the literature. The polymer incorporation decreases the apparent packing parameter. That means the polymer favours spherical curvatures. Fluorescence measurements of OG micelles with polyoxyethylene carried out by Aoudia and Zana [22] have shown the invariance of the aggregation number with this polymer, but the polymer content was much lower (1.97 wt %) than the polymer content used in this work (10 and 30 wt %). With the pear-necklace model similar micellar sizes have been found with and without homopolymer being present and the aggregation numbers are typically similar to or slightly lower than those micelles forming in the absence of polymer. Lower aggregation numbers agree with spherical curvatures.

A viscosimetric study of both systems has also been carried out. The viscosity for the mixed-surfactant system at 50 mM OG with vary concentration of $C_{12}E_4$ is plotted in Fig. 3. The straight lines Fig. 3 show only the tendency of the points and the abrupt change in viscosity produced with concentration. The viscosity of the micelles increases with the $C_{12}E_4$ content. If worded differently, upon increasing the mole fraction of OG the viscosity decreases. So, at a mole fraction higher than 0.5 or a $C_{12}E_4$ concentration lower than 70 mM, the viscosity is constant. It should be pointed out that the phase boundary between the single and the two-phase regions depends on the total surfactant content. The formation of mixed micelles in these conditions occurs therefore at a lower OG mole fraction than in the preceding investigations.

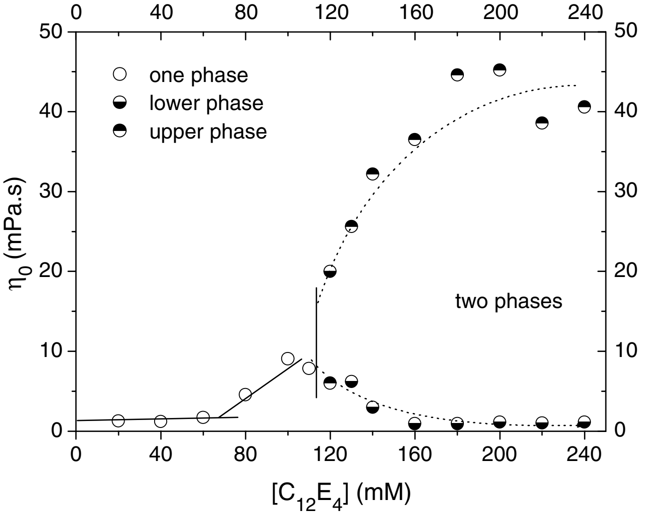


Fig. 3 Variation of zero shear rate viscosity of the mixed micelles with $C_{12}E_4$ concentration ([OG] = 50 mM)

The viscosity data for the lower and upper phases are given in Fig. 3. One observes that solutions near the phase boundary ([$C_{12}E_4$] = 110 and 120 mM) show anomalous behaviour in the viscosity. Excepting these solutions, the data reveal that the lower phase with the viscosity of water has to be a micellar phase while the upper phase ought to be a vesicular phase.

On the other hand, the viscosity of the surfactant–polymer system at low polymer content allows us to obtain the cmc (Fig. 4a). This value is in agreement with the cmc value obtained from surface tension isotherms. But it was not possible to obtain the cmc at a polymer concentration of 15 mM owing to the high viscosity of the polymer solution that is the dominating contribution to the viscosity.

The zero shear rate viscosity η_0 for a polymer and a surfactant–polymer solution with a constant amount of surfactant (50 mM) is plotted in Fig. 4b. The viscosity of the simple micelles of OG is near the viscosity of water.

Polymer and surfactant have to interact to some degree as the viscosity of the mixed system is higher than

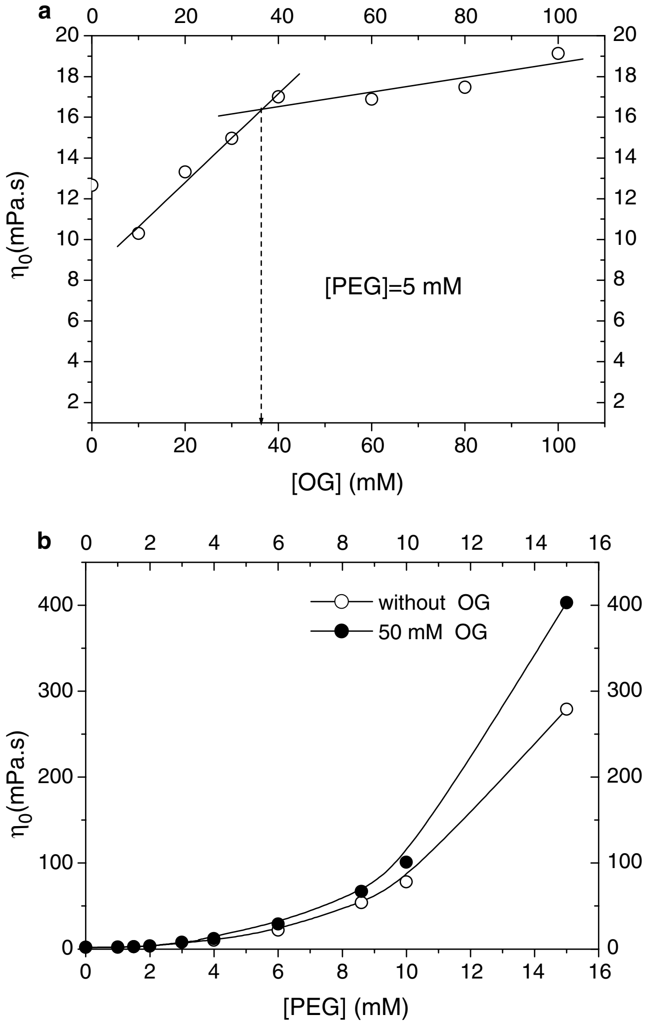


Fig. 4 **a** Variation of the viscosity with OG surfactant at a fixed PEG content of 5 mM. **b** Variation of zero shear rate viscosity with PEG concentration without OG and for [OG] = 50 mM

that of the pure polymer solution. The surfactant content was kept constant but the cmc increases with polymer concentration, accordingly the micellized surfactant concentration decreases with polymer concentration. For [PEG] = 5 mM, the micellized surfactant content is $[OG]_m = 50-37 = 13$ mM and for the highest amount of polymer $[OG]_m = 0$. Moreover, if we consider an aggregation number around 100 for OG micelles [22], the micelle concentration should be $[OG]_m/100$. That means the polymer-to-micelle molar ratio is 40 to 1 for [PEG] = 5 mM. Consequently at low PEG content the presence of micelles should not change the viscosity of the polymer solution and the increase in viscosity is due to the adsorption or the anchorage of monomers of surfactant on PEG molecules. It should be pointed out that for the most viscous samples, the viscosity decreases with shear rate at high shear rate values. The anchorage of monomer in the polymer can swell the polymer and increase the viscosity. These conditions are below the cmc, so the same fact can explain the increase in the cmc with polymer content as the monomer surfactant is anchored on a polymer molecule and it is not free in water solution and a larger amount of surfactant is required to form micelles.

Conclusions

Surfactant mixtures of $C_{12}E_4$ and OG form mixed micelles that are described by nonideal mixing. The data fit to Rubingh's treatment with a β value of –5.1. This negative β value implies a modest attraction between both surfactants, where the attractive interactions between the surfactants are presumably due to the large polarizability of the OG head groups that can interact strongly with the ethylene oxide head groups of the $C_{12}E_4$ surfactant.

The surfactant–PEG system does not form mixed micelles but the presence of the PEG polymer shifts the cmc values to significantly higher values. Monomers of surfactant seem to be bound to the polymer molecules. The viscosity of the polymer increases even at OG concentrations well below the cmc. The binding could also explain the increase in the cmc with increasing polymer concentration. Accordingly, the formation of OG micelles requires larger amounts of surfactant as first a substantial part of the surfactant becomes bound to the polymer.

Acknowledgements This work was supported by the research project MAT2001-1188-C02-01 from the Ministry of Science and Technology of Spain and for the "Acción integrada HA2001-0037" between Spain and Germany.

References

1. Lindman J, Kronberg K (eds) (1999) Surfactants and polymers in aqueous solution. Wiley, Chichester
2. Carlsson A, Karsltröm G, Lindmann B (1990) Colloids Surf 47:147
3. Nilsson PG, Lindman B (1984) J Phys Chem 88:5391
4. Guering P, Nilsson PG, Lindmann B (1985) J Colloid Interface Sci 105:41
5. Garamus VM (1997) Langmuir 13:6388
6. Rosen MJ, Cohen AW, Dahanayake M, Hua X-Y (1982) J Phys Chem 86:541
7. Granizo N, Thunig C, Valiente M (2004) J Colloid Interface Sci 273:638

8. (a) Lange H (1953) Kolloid Z 131:96; (b) Lange H, Beck KH (1973) Kolloid Z Z Polym 251:424
9. Rubingh DN (1979) In: Mittal KL (ed) Solution chemistry surfactants, vol 1. Plenum, New York, p 337
10. Rosen MJ, Zhu ZH, Gao T (1993) J Colloid Interface Sci 157:254
11. Motomura K, Yamanaka M, Aratono M (1984) Colloid Polym Sci 262:948
12. Ghosh S, Moulik SP (1998) J Colloid Interface Sci 208:357
13. Rodenas E, Valiente M, Villafruela MS (1999) J Phys Chem B 103:4549
14. Holland PM, Rubingh DN (eds) (1992) Mixed surfactant systems. ACS symposium series 501. American Chemical Society, Washington, DC, p 31
15. Zhang R, Marone PA., Thiyagarajan P, Tiede DM, (1999) Langmuir 15:7510
16. Jonströmer M, Strey R, (1992) J Phys Chem 96:5993
17. Olsson U, Nakamura K, Kunieda H, Strey R (1996) Langmuir 12:3045
18. Cabane B, Duplessic R (1982) J Phys 43:1529
19. Jönsson B, Lindmann B, Holmberg K, Kronberg B (1998) Surfactant and polymers in aqueous solution. Wiley, New York
20. D'Aprano A, Giordano R, Jannelli MP, Magazu S, Maisano G, Sesta B (1996) J Mol Struct 383:177
21. He LZ, Garamus VM, Niemyere B, Helmholz H, Willumeit R (2000) J Mol Liq 89:239
22. Aoudia M, Zana R (1998) J Colloid Interface Sci 206:158