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ORIGINAL CONTRIBUTION

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Properties of two polymerisable surfactants aqueous solutions: dodecylethylmethacrylatedimethylammonium bromide and hexadecylethylmethacrylatedimethylammonium bromide. II. Partial molar volume and micelle hydration

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Abstract The partial molar volume and hydration number of two micellised polymerisable surfactants (dodecylethylmethacrylatedimethylammonium bromide ($C_{12}PS$) and hexadecylethylmethacrylatedimethylammonium bromide ($C_{16}PS$)) were determined. Results support marginally the annular conformation of the polar head group ($N^+(CH_3)_2$-CH_2-CH_2-O-CO-$C(CH_3)(=CH_2)$) proposed in the literature.

Keywords Alkylethylmethacrylatedimethylammonium bromides · Partial molar volume · Micelle hydration · Density · Viscosity · Polymerisable surfactants

Introduction

Thermodynamic behaviour of highly dilute aqueous solutions of surfactants is of considerable interest for both theoretical and practical reasons. Infinite dilution partial molar properties and standard hydration number, providing valuable information on water-solute interaction, are highly important for theoretical studies in solution chemistry.

The knowledge of partial molar volume of surfactant is related to the structure of micelles. Moreover, it is of great interest for reactive surfactants such as polymerisable ones, because the pressure dependence of equilibrium constants is closely related to the difference in the partial molar volumes between reactants and products [1].

In Part I of this work the aggregation behaviour of two polymerisable surfactants (dodecylethylmethacrylatedimethylammonium bromide ($C_{12}PS$) and hexadecylethylmethacrylatedimethylammonium bromide ($C_{16}PS$)) was studied. Both amphiphiles showed pre-micellar aggregation at very low concentration, a critical micelle concentration (CMC) and a concentration at which spherical micelles become worm-like.

In this work two properties needed for a better knowledge of micellisation mechanism were studied for the above-mentioned surfactants: these were the partial molar volume and the hydration of the micellised surfactant molecules.

Experimental

Both surfactants were synthesized using the method described by Nika et al. [2].

Samples were prepared in 40-cm^3vials, in concentrations ranging from 10^{-4} to 10^{-3} wt% for the dodecylethylmethacrylatedimethylammonium bromide (C12PS) and from 10^{-3} to 10^{-2} wt% for the hexadecylethylmethacrylatedimethylammonium bromide ($C_{16}PS$). Vials were subsequently sealed and manually stirred. They were then left for 10 days in a thermostatic bath at 25 °C and were periodically gently stirred.

Viscosity measurements were made with a Fenske-Cannon 50 Q977 Ostwald viscometer calibrated with water.

The density measurements were performed with a pyknometer.

The Student t function was employed to compute the error intervals. Confidence level was 0.90.

Results and discussion

Partial molar volume

The dependence of C12PS and C16PS aqueous solutions density on the surfactant concentration may be seen in Fig. 3 of Part I of this work.

The partial molar volume V_{pm} of any solute may be computed from the density (δ) vs concentration (C) curves by the equation [3]

$$V_{pm} = (1/\delta)(M_S - V\partial\delta/\partial C) \tag{1}$$

where M_S is the solute molar weight and V is the solution volume containing 1000 g of water, obtained by

$$V = (1000 + CM_S)/\delta \tag{2}$$

The above equations were applied to the region of the δ vs C curve above the CMC and a series of V_{pm} values were obtained, which depend on the concentration. By extrapolation to the CMC the partial molar volume without inter-micellar interactions ($V°_{pm}$) was obtained.

We used the portion of the δ vs C curve for both surfactants between the CMC and the sphere-to-cylinder transformation to obtain the slopes $\partial\delta/\partial C$ to compute V_{pm} from Eq. (1). Figures 1 and 2 show the representation of V_{pm} as a function of the micellised surfactant concentration (C-CMC) for $C_{12}PS$ and $C_{16}PS$ aqueous solutions. The least squares fitting curves are also included.

The equations of the fitting curves are

$C_{12}PS$:
$\mathrm{VS}(\mathrm{cm}^3.\mathrm{mol}^{-1}) = 386.33 \pm 0.82 - 3.61 \times 104(\mathrm{C} - \mathrm{C}_2)(\mathrm{mol.dm}^{-3}) + 1 \times 107(\mathrm{C} - \mathrm{C}_2)^2(\mathrm{mol.dm}^{-3})$
$r = -0.99999$
$C_{16}PS$:
$\mathrm{VS}\ (\mathrm{cm}^3.\mathrm{mol}^{-1}) = 460.43 \pm 0.31 - (2.0061 \pm 0.00012) \times 106(\mathrm{C} - \mathrm{C}_2)(\mathrm{mol.dm}^{-3})$
$r = -0.99999$

The intercept values are the infinite dilution molar partial volumes of the respective micellised surfactants, i.e. $V°_{C_{12}PS} = 386.33 \pm 0.82\ \mathrm{cm}^3.\mathrm{mol}^{-1}$and $V°_{C_{16}PS} = 460.43 \pm 0.31\ \mathrm{cm}^3.\mathrm{mol}^{-1}$.

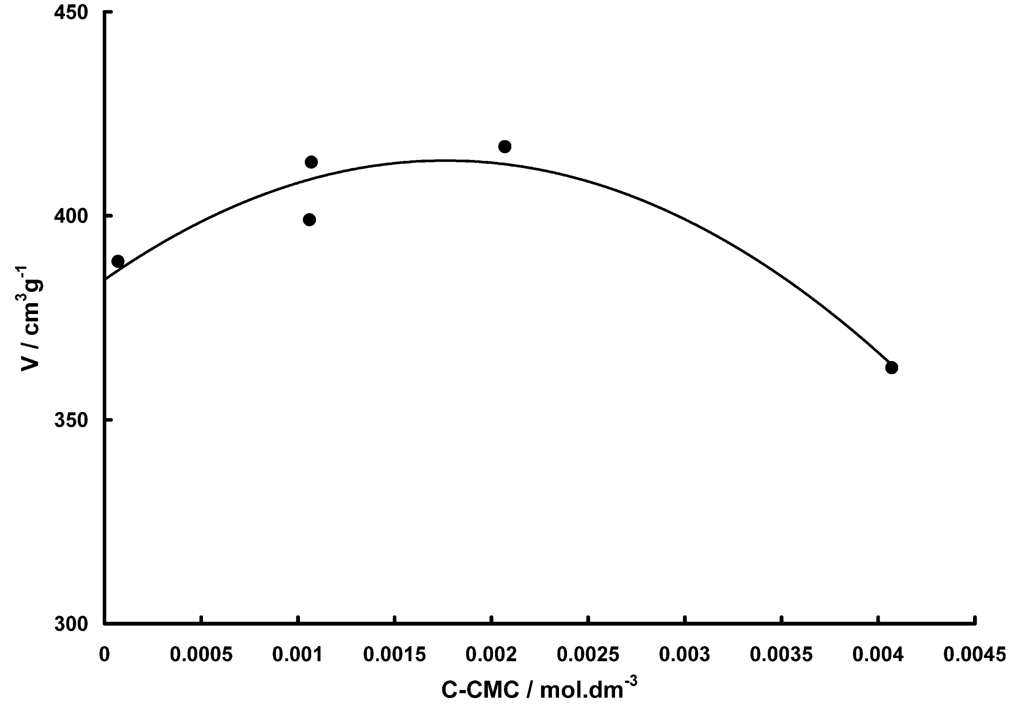


Fig. 1 V_{pm} as a function of the micellised surfactant concentration (C-CMC) for $C_{12}PS$ aqueous solutions and the least squares fitting curve

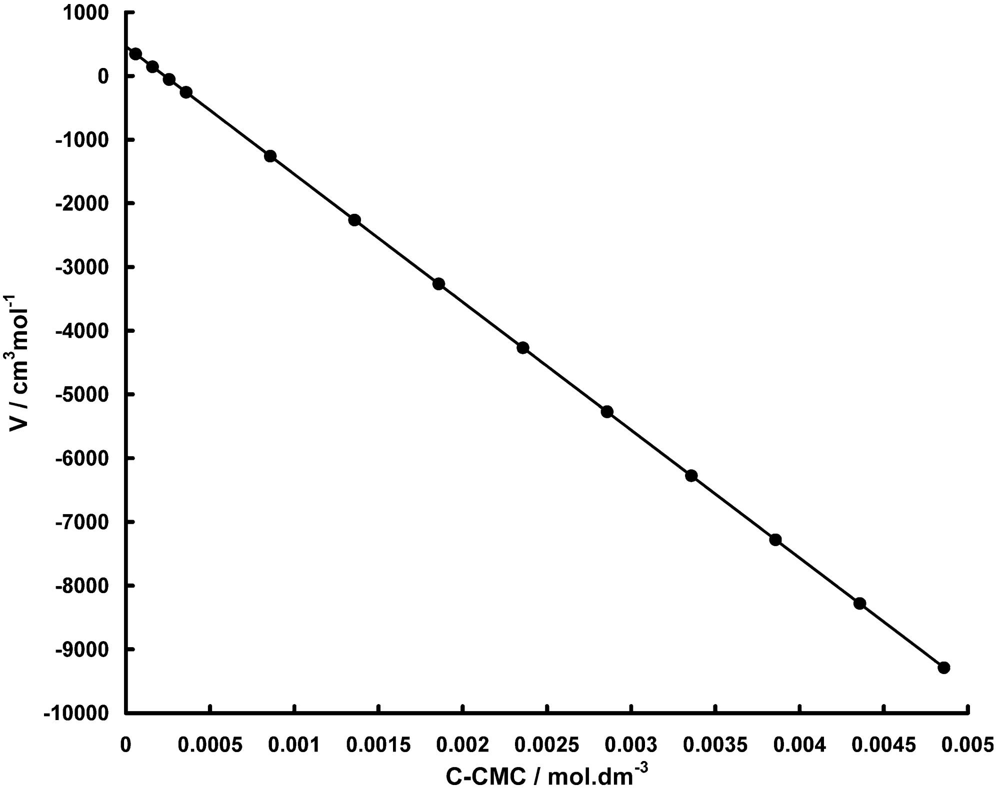


Fig. 2 V_{pm} as a function of the micellised surfactant concentration (C-CMC) for C_{16}PS aqueous solutions and the least squares fitting curve

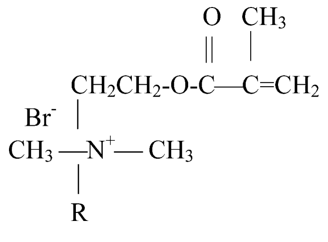
To compare, some literature partial molar volumes of micellised surfactants are: dodecyltrimethylammonium bromide: $V°_{pm} = 295.5$ cm^{3}mol^{-1} [4]–293.5 cm^{3}mol^{-1} [5]; tetradecyltrimethylammonium bromide: $V°_{pm} = 331.2$ [4]–328.0 cm^{3}mol^{-1} [6] and hexadecyltrimethylammonium bromide: $V°_{pm} = 365.4$ [4]–360.8 cm^{3}mol^{-1} [6].

The molar partial volume of surfactants may be separated into the contribution of the different chemical groups of the molecule: that of the polar head group (V_{ph}) and of the hydrocarbon chain (V_{hc}) [5]. In turn, V_{hc} is composed by the contributions of the n_C-1 methylene groups (V_{CH_2}) and that of the methyl group (V_{CH_3}). Here n_C is the number of carbon atoms in the hydrocarbon chain. It was observed that the contribution of the four methylene groups adjacent to the polar head group ($V^*_{CH_2}$) is slightly different to that of the remaining methylene groups of the chain. [7, 8, 9, 10, 11, 12, 13]. The contribution of these methylene groups to the partial molar volume of the micellised surfactant is $V^*_{CH_2} = 15.60 \pm 0.69$ cm^3.mol^{-1}[4]. The contribution of the remaining methylene groups, obtained from the combination of experimental values from several works in the literature, is $V_{CH_2} = 17.28 \pm 0.17$ cm^3.mol^{-1}[14]. The contribution of the methyl group is $V_{CH_3} = 30.10 \pm 0.07$ cm^3.mol^{-1}[15]. The contribution of the polar head group to the partial molar volume of the micellised surfactants may then be computed from the equation

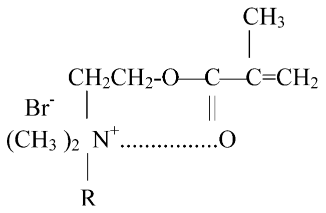
$$V_S = (n_C - 5)V_{CH_2} + 4V^*_{CH_2} + V_{CH_3} + V_{ph} + V_{ci} \qquad (3)$$

where V_{ci} is the partial molar volume of the counterion Br^-, $V_{Br-} = 29.2$ cm^{3}mol^{-1} [16]. The V_{ph} values for both homologous surfactants were $V_{ph} = 143.8 \pm 4.9$ cm^{3}mol^{-1} from C_{12}PS and $V_{ph} = 148.7 \pm 5.1$ cm^{3}mol^{-1} from C_{16}PS. Both values may be considered as an independent estimation of the same property, and then a mean value may be computed by the least variance linear unbiased estimation method [17] giving $V_{ph} = 146.1 \pm 3.5$ cm^{3}mol^{-1}. The value for the trimethylammonium group ($-N(CH_3)_3{}^+$) is 70.6 ± 3.4 cm^3 mol^{-1}[14].

By using the method of group contribution to the partial molar volume proposed by Lepori and Gianni [18], the polar head group volume is $V_{ph} = 148.2 \pm 3.6$ cm^{3}mol^{-1} if it is supposed that the group does not form a ring, and 144.4 ± 4.5 cm^3 mol^{-1} if the formation of an annular conformation of the dimethyl 2-methacrylate ammonium group is supposed, as proposed by Hamid and Sherrinton [19]:



$$CH_3-N^+(CH_2CH_2\text{-}O\text{-}C(=O)\text{-}C(CH_3)=CH_2)(CH_3)(R)\ Br^-$$



Since the value found in this work is intermediate between the two above limits and the confidence intervals are superimposed, our result may not be employed to decide between the two conformations (open or annular). However, it must be remembered that micellisation produces a slight expansion of the surfactant, because of the repulsion among polar head groups which acts as a negative pressure [3]. This situation favours the annular conformation.

Above the sphere-to-cylinder transformation concentration (C_3) the V_{mp} vs C-C_3 dependence may be seen in Figs. 3 and 4. The following curves were fitted to the experimental points:

$C_{12}PS$:
$V_S(\mathrm{cm^3.mol^{-1}}) = 381.18 \pm 0.44 - (12 \pm 94)(\mathrm{C} - \mathrm{C_3})(\mathrm{mol.dm^{-3}})$
$r = -0.9979$
$C_{16}PS$:
$V_S(\mathrm{cm^3.mol^{-1}}) = 462.6 \pm 5.4 - (4.4 \pm 110)(C - C_3)(\mathrm{mol.dm^{-3}})$
$r = -0.9965$

The difference is statistically significant in the case of $C_{12}PS$, whereas the error in the $C_{16}PS$ does not allow conclusions to be drawn. On the basis of the $C_{12}PS$ results, a reduction of 1.3% in the partial molar volume was produced when spherical micelles became rod-like. If it is supposed that all reduction was in the polar head group volume because of the crowding at the micelle surface, $V_{ph} = 138.5 \pm 4.6\ \mathrm{cm^3 mol^{-1}}$. In this case, the V_{ph}value supports the annular conformation of the polar head group. Moreover, this reduction may explain the reduction in absorptivity found in surfactant solutions without added dye. The more crowding at the Stern micelle layer, the larger deformation of the ring and the lower the absorptivity, because the conformation becomes less favourable to the delocalisation, as was said in Part I of this work.

The intrinsic viscosity and hydration

The intrinsic viscosity ($[\eta]$) is obtained by extrapolation to infinite dilution of the specific viscosity ($\eta_{sp} = \eta/\eta_0 - 1$) to the concentration ratio, where η and η_0 are the viscosity of the solution and the solvent, respectively. This ratio is frequently called the reduced viscosity, ($\eta_{red} = \eta_{sp}/C$). When micellar solutions are studied, the

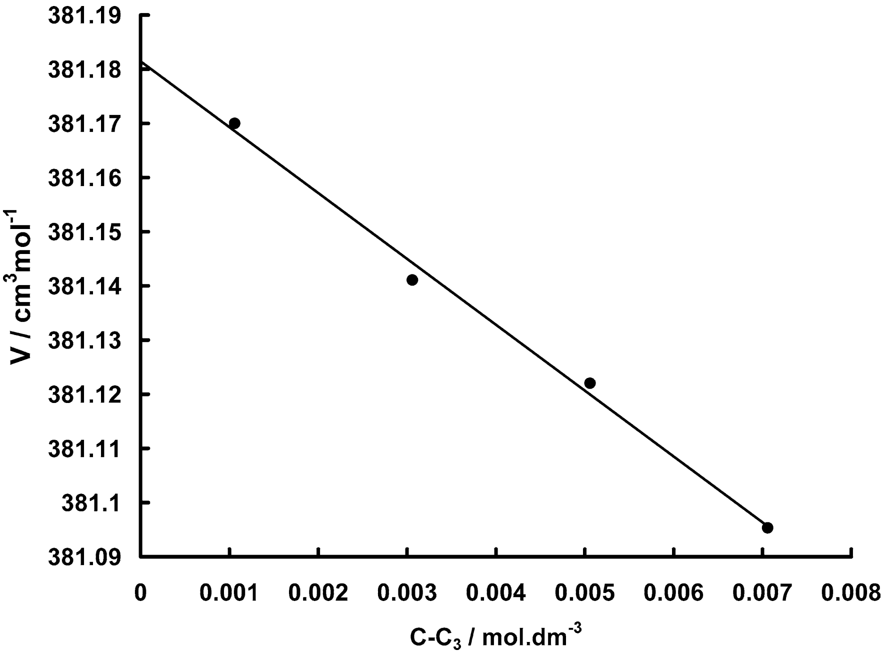


Fig. 3 The V_{mp} vs C-C_3 dependence above the sphere-to-cylinder transformation concentration (C_3) for $C_{12}PS$ aqueous solutions and the least squares fitting curve

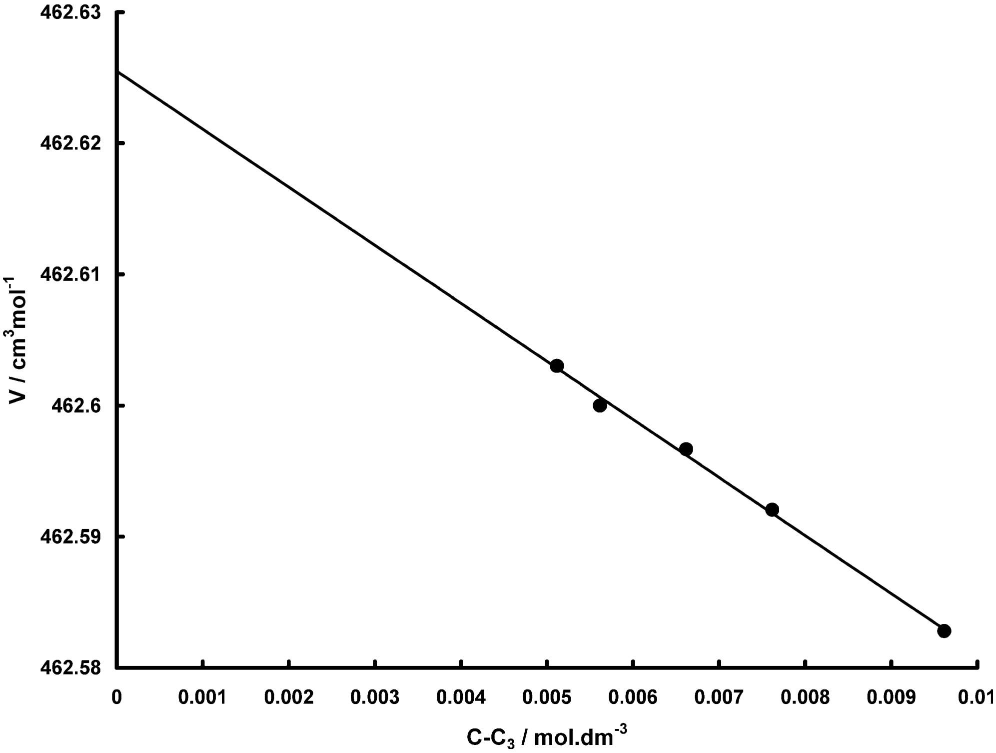


Fig. 4 The V_{mp} vs C-C_3 dependence above the sphere-to-cylinder transformation concentration (C_3) for C_{16}PS aqueous solutions and the least squares fitting curve

concentration (in g cm^{-3}) is the total concentration minus the CMC ($C = C_{tot}$–CMC), and the solvent viscosity η_0 is that of the surfactant solution at the CMC. The intrinsic viscosity is related to the hydration and the surface electric potential of micelles [20]:

$$[\eta] = vE(v_2 + wv_1) \tag{4}$$

where v is the shape factor, v_1 and v_2 are the specific volumes of solvent (water) and the dry surfactant, respectively and w is the weight in grams of water per gram of surfactant. E is the correction for the electroviscous effect, which may be computed with Booth's theory [21]:

$$E = 1 + \frac{\pi\left(\Sigma c_i z_i^2 2u_i^{-1}\right)\left(\Sigma \cdot c_i z_i^2 u_i\right)(\varepsilon\zeta/2\pi)^2(\kappa a)^2(1-\kappa a)^2 Z}{\left(\Sigma c_i z_i^2\right)^2 \kappa_{sp}\eta_0} \tag{5}$$

where c_i and z_i are the concentration and the charge (in e units) of the ion i, whose electrophoretic mobility is u_i. ϵ, κ_{sp} and η_0 are the dielectric constant of the solvent, the specific conductivity and viscosity of the solution at the CMC, ζ is the zeta potential of micelles, whose radius is a, and κ^{-1} is the Debye distance, computed by the Debye-Hückel equation [22]. Z is a function of κa which may be obtained from [23].

The zeta potential of NaDHC micelles was estimated by [24]

$$\zeta = \frac{Q}{4\pi\varepsilon\varepsilon_0 a(1+\kappa a)} \tag{6}$$

where ϵ is the relative dielectric constant of the medium, ϵ_0 the vacuum permittivity, κ the inverse of the Debye distance, and a the micelle radius. The micelle charge $Q = ne\alpha$, n being the aggregation number, e the elementary charge and α the ionisation degree of the micelles.

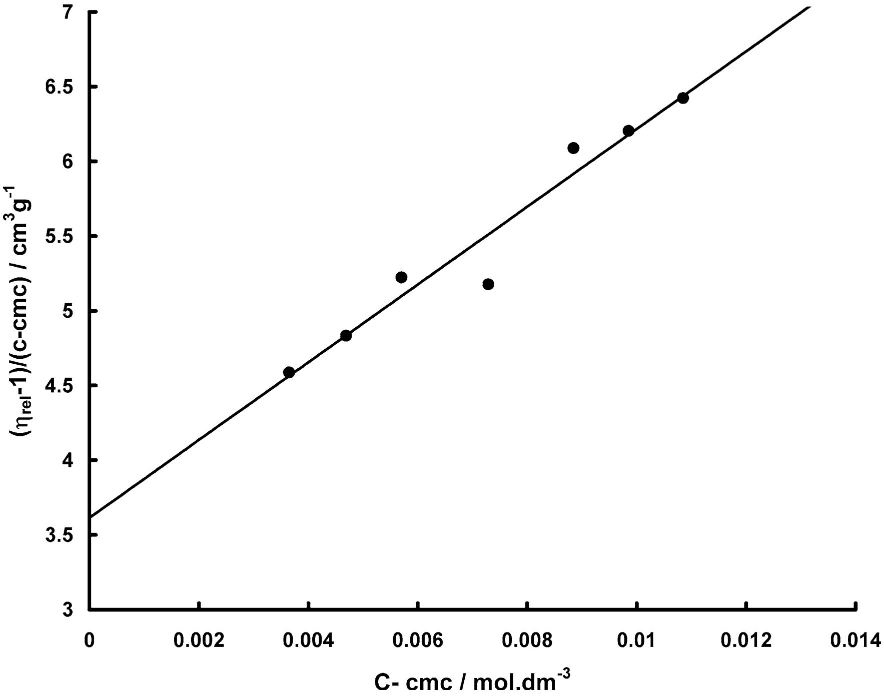
Figure 5 in Part I of this work shows the dependence of the viscosity of C_{12}PS and C_{16}PS aqueous solutions on the surfactant concentration.

Figure 5 shows the η_{red} dependence on C for C_{12}PS and the least squares straight line ($r = 0.9572$), giving $[\eta] = 3.61 \pm 0.19$ cm^3 g^{-1}. The data for C_{16}PS between C_2 and C_3 are too scarce and allowed only to be obtained $[\eta] = 5.97$ cm^3 g^{-1} a value of without error estimation.

Results suggested that micelles of C_{12}PS at the CMC are probably spherical, whereas those of C_{16}PS are elongated.

To compute E, the electrophoretic mobility of the bromide ion was obtained from the literature [25] as $u_{Br-} = 8.093\times10^{-4}$ cm^{2}s^{-1} V^{-1}. The electrophoretic mobility of the surface active ions may be obtained from their equivalent conductivity at infinite dilution, found in the CMC study (Part I of this work): $\lambda^{\circ}_{C_{12}PS} = 23.3$ Scm^{2}eq^{-1}and $\lambda^{\circ}_{C_{16}PS} = 25.7$ Scm^{2}eq^{-1}, then $u_{C_{12}PS} = 2.44 \times 10^{-4}$cm^{2}s^{-1}V^{-1}and $u_{C_{16}PS} = 2.69\times 10^{-4}$ cm^{2}s^{-1}V^{-1}.

Fig. 5 The η_{red} dependence on C for $C_{12}PS$ and the least squares straight line



The specific conductivity of both surfactants at the CMC were $\kappa_{C_{12}PS} = 1.83 \times 10^{-4}$ Scm^{-1}and $\kappa_{C_{16}PS} = 1.68 \times 10^{-5}$ Scm^{-1}. The viscosities of the same solutions were $\eta_{CMC,C_{12}PS} = 9.190 \times 10^{-4}$ Pa.s(0.9190 cp) and $\eta_{CMC,C_{16}PS} = 9.157 \times 10^{-4}$ Pa.s(0.9157 cp).

To obtain the micelle radius we used the aggregation number from the literature, $n_{C_{12}PS} = 11$[2] and $n_{C_{16}PS} = 78.6$[26], together with the partial molar volumes of both surfactants above are given ($V^{\circ}_{C_{12}PS} = 386.33 \pm 0.82$ cm^3.mol^{-1} and $V^{\circ}_{C_{16}PS} = 460.43 \pm 0.31$ cm^3.mol^{-1}). We supposed both micelles to be spherical. Then the micelle radii were $a_{C_{12}PS} = 2.55$ nm and $a_{C_{16}PS} = 5.21$ nm. The micelle ionisation degree was obtained for both surfactants in Part I and were $\alpha_{C_{12}PS} = 0.306$and $\alpha_{C_{16}PS} = 0.373$.

Using Eq. (6) the zeta potential of $C_{12}PS$ micelles at the CMC may be estimated as $\zeta_{C_{12}PS} = 15.5$ mV. With $\kappa a_{C_{12}PS} = 0.377$we obtained $Z_{C_{12}PS} = 0.00411$. Then, $E_{C_{12}PS} = 1.052$.

For $C_{16}PS$ micelles the obtained values were $\zeta_{C_{16}PS} = 93.3$ mV, $\kappa a_{C_{16}PS} = 0.204$, $Z_{C_{16}PS} = 0.00789$and $E_{C_{16}PS} = 1.20$.

The specific volume of water is$v_1 = 0.81659$ cm^{3}g^{-1}, as computed from the literature data [27]. The specific volumes of both surfactants were computed from their partial molar volumes and were $v_{2,C_{12}PS} = 0.9722 \pm 0.0021$ cm^{3}g^{-1}and $v_{2,C_{16}PS} = 1.01531 \pm 0.00068$ cm^{3}g^{-1}.

By application of Eq. (4) to $C_{12}PS$, using $\nu = 2.5$ which corresponds to spherical micelles [28], we obtained $w_{C_{12}PS} = 0.572$ gramsof water per gram of surfactant, i.e. 12.6 water molecules per surfactant molecule. For $C_{16}PS$ micelles $w_{C_{16}PS} = 1.16$ gramsof water per gram of surfactant, i.e. 29 water molecules per surfactant molecule. Because of the poor reliability of the intrinsic viscosity for $C_{16}PS$, the following discussion is based on $C_{12}PS$ results. Two water molecules may be attributed to the bromide ion hydration [29]. In consequence, the ethylmethacrylatedimethylammonium group must have some 10.6 hydration water molecules.

In comparison, dodecyltrimethylammonium hydroxide micelles have 39.2 ± 0.7 water molecules per surfactant molecule [25], alkyltrimethylammonium bromides have 60–70 [30]; sodium soaps have about 10 [31, 32], the non-ionic surfactant triton X-100 has 43 [33], sodium dehydrocholate has 39 [34], and sodium dodecyl sulfate has 6 [35].

The hydration of micellised $C_{12}PS$ is then similar to that of sodium soaps and sodium dodecylsulfate and mainly corresponds to ionic hydration, whilst the high hydration of alkyltrimethylammonium bromides may be related to the hydrophobic hydration. This situation may originate in the antagonism between the hydrophobic hydration of some parts of the head group and the hydrophilic one of the polar regions (oxygen atoms, double bond and charged nitrogen atom), which may cancel each other. The hydrophilic and the hydrophobic hydrations are mutually incompatible.

Concluding remarks

The partial molar volumes at the CMC are 381.18 ± 0.44 cm^3 mol^{-1} for $C_{12}PS$ and $462.6 \pm$

5.4 cm^3mol^{-1} for $C_{16}PS$. The contribution of the polar head group to the partial molar volume is Vph = 146.1 ± 3.5 cm^3mol^{-1}.

At the concentration corresponding to the transformation spherical-to-cylindrical micelles, $V_{C_{12}PS} = 381.18 \pm 0.44$ $cm^3.mol^{-1}$ and $V_{C_{16}PS} = 462.6 \pm 5.4$ $cm^3.mol^{-1}$, giving $V_{ph} = 138.5 \pm 4.6$ cm^3mol^{-1}. The volume reduction may be explained by the crowding of he polar head groups at the Stern micelle layer when spherical micelles become worm-like. The V_{ph} value marginally supports the annular model of the polar head group proposed by Hamid and Sherrington.

Micellised surfactant hydration at the CMC is 12.6 water molecules per surfactant molecule. This value is relatively low in comparison with other cationic surfactants, and may be explained on the basis of the antagonism between the hydrophobic hydration of some parts of the head group and the hydrophilic one of the polar parts, which may cancel each other.

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References

1. Hirata F, Imai T, Irisa M (1988) Rev High Pressure Sci Technol 8(2):96
2. Nika G, Paleos CM, Dais P (1992) Progr Colloid Polym Sci 89:122
3. Schulz, PC (1981) Anales Asoc Quím Argentina 69:185
4. Corkill JM, Goodman JF, Walker T (1964) Trans Faraday Soc 63:768
5. Tanaka M, Kaneshina S, Shin-No K, Okajima T, Tomida T (1974) J Colloid Interface Sci 46:132
6. Bahri H, Bouguerra S, Letellier P (1968) In: Mittal KL, Bothorel P (eds) Surfactants in solution, vol 4. Plenum Press, New York London, pp 91–102
7. Clifford J, Pethica BA (1964) Trans Faraday Soc 60:1483
8. Corkill JM, Goodman JF, Harrold SP, Tate JR (1966) Trans Faraday Soc 62:1
9. Reiss-Husson F, Luzzatti V (1966) J Colloid Interface Sci 21:534
10. Svens B, Rosenholm B (1966) J Colloid Interface Sci 21:53
11. Fendler EJ, Fendler JH (1970) Adv Phys Org Chem 8:271
12. Tanford C (1974) Proc Nat Acad Sci USA 71:1811
13. Courchene WL (1964) J Phys Chem 68:1870
14. Morini MA, Minardi RM, Schulz PC, Puig JE, Rodríguez JL (1998) Colloid Polym Sci 276:738
15. Vikingstad E (1980) J Colloid Interface Sci 73:500
16. Mukerjee P(1961) J Phys Chem 65:740
17. Mandell J (1964) The statistical analysis of experimental data. Interscience, New York
18. Lepori L, Gianni P (2000) J Solut Chem 29:405
19. Hamid S, Sherrington D (1987) Polymer 28:325
20. Oncley LJ (1940) Ann NY Acad Sci 41:121
21. Parker RA, Wasik SP (1958) J Phys Chem 62:967
22. Debye P, Hückel D (1923) Physik Z 24:185
23. Booth F (1950) Proc R Soc (London) A 203:533
24. Alexander AE, Johnson P (1950) Colloid science. University Press, Oxford, p 124
25. Schulz PC, Rodríguez JL, Morini MA, Puig JE (1997) Colloid Polym Sci 275:396
26. Tuin G, Candau F, Zana R (1998) Colloid Surf A 131:303
27. Spernol A(1956) J Phys Chem 60:703
28. Ford TF (1960) J Phys Chem 64:1168
29. Schulz PC, Puig JE, Barreiro G, Torres LA (1994) Thermochim Acta 231:239
30. Ekwall P, Mandell L, Solyom P (1971) J Colloid Interface Sci 35:519
31. Solyom P, Ekwall P (1969) Chim Phys Appl Trat Ag Surface, CR Congr Int Deterg 5th 1968, 2, 1041
32. McBain JW, Kawakami J, Lucz HP (1933) J Am Chem Soc 55:2762, 2763
33. Kushner LM, Hubbard WD (1954) J Phys Chem 58:1163
34. Messina p, Morini ma, Schulz pc (2004) Colloid Polym Sci (submitted)
35. Mukerjee P (1964) J Colloid Sci 19:722