

Marcela A. Morini
Paula V. Messina
Pablo C. Schulz

The interaction of electrolytes with non-ionic surfactant micelles

Received: 16 September 2004
Accepted: 3 December 2004
Published online: 11 May 2005
© Springer-Verlag 2005

Abstract The effect of NaCl and HCl on two non-ionic surfactant micelles was studied using several techniques, including conductivity and ion-selective electrodes. Both surfactants exhibit opposite behaviour. When Tween 20 is titrated with HCl the conductivity notably increases in comparison with water, whereas that of Triton X-100 solutions do not change with respect to water until a certain HCl concentration is reached, when it increases. The hydrogen ion activity is lower in Triton X-100 solutions and higher in Tween 20 solutions than in pure water. Chloride ion activity is higher in Tween 20 solutions than in water, whereas in Triton X-100 the activity does not significantly differ from that in water. The activity of sodium ion is lower in Tween 20 solutions than in water, whereas that in Triton X-100 solutions does not differ from the titration of water. These phenomena are explained by the chan-

ges in conformation of the non-ionic headgroups, which capture water, and in some cases ions, modifying the activity of ions in the intermicellar solution.

Keywords Electrolytes · Triton X-100 · Tween 20 · Non ionic surfactants · Micelles

M. A. Morini · P. V. Messina
P. C. Schulz (✉)
Departamento de Química, Universidad
Nacional del Sur, 8000 Bahía Blanca,
Argentina
E-mail: pschulz@criba.edu.ar

Introduction

Non-ionic surfactants are widely used to stabilize suspensions and emulsions, among other important applications. Some dispersion systems used in pharmaceutical and industrial applications also contain electrolytes, occasionally at high concentrations, which may adversely affect their stability.

Understanding the nature of non-ionic surfactant-electrolyte interactions is relevant to the manufacture of

many products including detergents, cosmetics, paints and coatings, adhesives and glues, lubricants, photographic films, and pharmaceutical products. Usually, the simultaneous presence of surfactants and salts is required to achieve optimal dispersion effects in which surfactants provide emulsification capacity, interfacial tension control and colloidal stability.

A large number of studies have been made on the effects of additives like electrolytes on the micellar properties of polyoxyethylene non-ionic surfactants, e.g.

the critical micelle concentration (CMC) [1–8] and cloud point [3, 6, 9–14].

Many electrolytes salt in polyoxyethylated non-ionic surfactants by complexation between the cations and the ether oxygen atoms (e.g. $\text{Mg}(\text{NO}_3)_2$ and $\text{Al}(\text{NO}_3)_3$), or because the anions break the structure of water (e.g. NaSCN , NaI). Other electrolytes salt out the surfactants by enhancing the structure of water or by dehydration (e.g. NaCl , Na_2SO_4) [15].

In general, the studies in the literature were focused on the effect of electrolytes on the non-ionic surfactant aggregation structures and solubility. Here we have focused the study on how the activity of ions is affected by the presence of non-ionic micelles, to put light on the complex interaction between polyoxyethylene chains and inorganic ions. We studied the interaction of three electrolytes (HCl , NaCl and NaOH) with two non-ionic, polyoxyethylenic surfactants having very different hydrophilic groups: Tween 20 and Triton X-100, whose structure is shown in Fig. 1. Triton X-100 was extensively studied in the literature, whereas Tween 20 is less known. The electrolytes were selected because they included both salting in and salting out ions, and because with only three ion-selective electrodes all solutions may be studied.

Theoretical background

In aqueous non-ionic surfactant–electrolyte systems there are complex interactions among the components: water, surfactant and ions. To understand the effect of the presence of surfactant on the properties of electrolytes in solution, the interaction between water and surfactant, and the effect of electrolytes on this interaction must be taken into account.

The interaction of water with oxyethylene type surfactants and polymers is not yet fully understood, but from the theoretical and experimental standpoint three different models have been proposed to interpret the mechanism [16–21].

The first mechanistic model is based on the assumption that the rotational conformation around the C–C bond of the oxyethylene groups is of importance for interaction with water [16, 17]. The gauche conformer has a larger dipole moment and is more soluble in water, while the trans conformer has a smaller dipole moment and is less soluble in water. The second model is a hydrogen-bond mechanism where the solubility is explained as a consequence of hydrogen bonding between the oxyethylene group and water [18, 19]. Finally, a third water-structure model [20, 21] was proposed based on the similarity between the O...O distances in water (0.274 nm in the hexagonal water structure of ice I_h) and in poly (ethylene oxide) molecules (0.276 nm), suggesting that water sites are replaced by the oxygen atoms of the oxyethylene group.

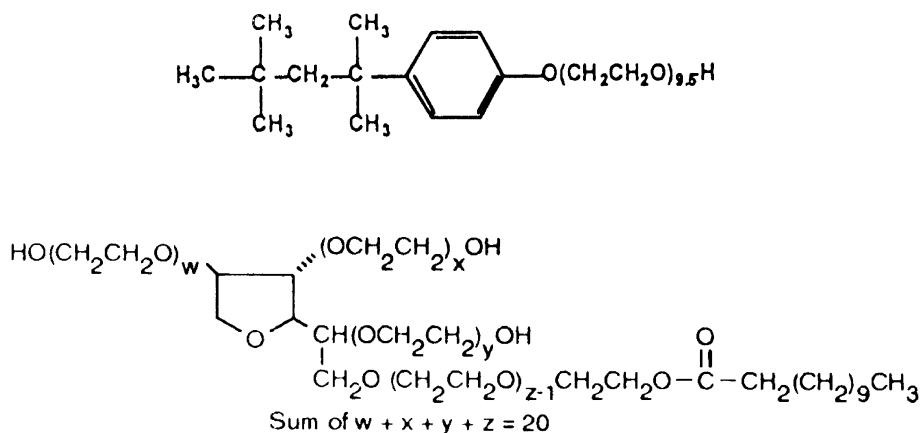
The stability of aqueous solutions of non-ionic amphiphiles of the polyoxyethylene type is determined by a rather special oxyethylene–water interaction. In this interaction the ether groups form highly directional hydrogen bonds with the water molecules while the ethylene parts are accommodated in the overall water structure [21]. The interaction between ether oxygen atoms and water is affected by the presence of ions.

Some studies on polyethyleneglycol [22–29] have shown that between two and three water molecules are bound per oxyethylene repeating unit, and have led to the development of structure models to account for the bound water [21].

In general, hydration of non-ionic micelles appears to be insensitive to changes in surfactant concentration and to decrease gradually with increasing temperature [30–32], although results for Triton X-100 suggest that, at least for this surfactant, hydration increases with temperature [33].

Non-ionic surfactants based on poly (oxyethylene) form a number of aggregate structures and phases that depends on surfactant structure and on the hydration of the ethylene oxide chain [34–36].

Fig. 1 The structure of Triton X-100 (above) and Tween 20 (below)



In solid poly (ethylene oxide) the helical conformation contains seven OE chemical units $[(-O-CH_2-CH_2-)_7]$, and two turns in a fibre period of 1.93 nm (7_2 helix) [37–39]. In dilute aqueous solution the polyoxyethylene chain retains the helical conformation [40]. At low n_{OE} , the polymer chain is not long enough to fold into a hydrated coil; once it has done so, high-molecular weight solutes are excluded from the poly (ethylene oxide) coil [41, 42]. Accordingly Marszall [43] from the correlation between the HLB and the Israelachvili–Mitchell–Ninham packing number, for $n_{OE} \leq 4$, the polyoxyethylene chain is not long enough to form an helix conformation.

The change in hydrate structure is consistent with the hypothesis that, as the polymer molecular weight rises and the polymer chains are more able to fold upon themselves (adopt a “secondary” structure), loosely-bound water molecules can be more easily shared between adjacent segments of a single chain, e.g. as in a helix. This accounts for the small rise with molecular weight in the amount of water contained in the polymer hydrate [26].

Jonstromer et al. [44] concluded that water is not distributed uniformly in the interfacial region but that the fraction of the interfacial region of $C_{12}OE_5$ and $C_{12}OE_8$ micelles filled by water increases radially from the hydrocarbon core to the outer edge of the aggregate. This is compatible with a helical conformation of the poly (oxyethylene) chain. The hydration of polyoxyethylene surfactants is generally expressed as n_w/n_{OE} , where n_w and n_{OE} are the number of hydration water molecules and oxyethylene units in the surfactant molecule. For long-chain polyoxyethylene non-ionic surfactants, n_w/n_{OE} increases from 5.2 to 10.5 as the hydrophilic chain length increases. Most of the water is mechanically trapped in the polyoxyethylene chains [45].

There is detailed information on hydration for some specific surfactants. The oxyethylene region of hexaoxyethylene monododecylther ($C_{12}OE_6$) micelles has a hydration that depends on both the surfactant concentration and temperature. The n_w/n_{OE} number was found to gradually decrease with increasing $C_{12}OE_6$ concentration at 40°C from 3.5 at 0.01 mol dm⁻³ to 2.5 at 1.2 mol dm⁻³, and to 0.84 at 1.83 mol dm⁻³, above the lamellar phase region. The n_w/n_{OE} number for 0.01 mol dm⁻³ $C_{12}OE_6$ ranges from 4.2 at 20°C to 2.9 at 60°C, passing through the cloud point at 50°C [46]. A two-state model would define the hydration of Triton X-100: a bulk water zone and a hydration water zone that is occupied by 5–7 water molecules per oxyethylene unit [40].

For long-chain polyoxyethylene non-ionic surfactants, n_w/n_{OE} increases from 5.2 to 10.5 as the hydrophilic chain length increases. Most of the water is mechanically trapped in the polyoxyethylene chains [45]. For polyoxyethylene, the “bond” water varies from 2.3 to 3.8 water molecules per repeat unit, with a change at the molecular weight of 750–1,000 ($n_{OE} = 17–23$). Over a

wide range of n_{OE} , the amount of tightly bond water is constant and between 2 or 3 water molecules per repeat unit. At high n_{OE} , some free water is loosely trapped within the secondary structure. [47].

The properties of hydration water molecules were also determined in several cases. For small ethylene oxide oligomers and polymers the hydration water relaxation time increases with n_{OE} . Above $n_{OE} = 6$, however, the relaxation time is independent of the degree of polymerisation ($\tau_h/\tau_w = 2.2 \pm 0.1$), where τ_h and τ_w are the relaxation times of hydration and free water molecules [48, 49]. In highly concentrated mixtures, the relaxation time of water may be unusually high. While for solutions at low or moderate solute concentration $\tau_h/\tau_w \leq 3$ has been found throughout, the relaxation time ratio may be substantially higher if the water content remains below a certain value, and may reach values as high as $100\tau_w \approx 0.8$ ns. These high relaxation-time values seem to be due to an entropy effect rather than an unusual energy of interaction [50]. Measurements on polyethylene oxide [48, 51] show that this effect starts at a volume fraction of solute of about 0.3. In general, with polyoxyethylene groups, interfacial water is less structured than bulk water. Neutron diffraction measurements in the lamellar phase of $C_{12}OE_4$ in water showed that the hydration water has enhanced hydrogen-bonded structure and modification of the inter-molecular structure over the intermediate range (0.25–0.8 nm). [52]. The same conclusion was reached about the hydration layer of non-ionic and zwitterionic micelles by NMR spectroscopy measurements [53]. However, the water of hydration of Triton X-100 is less structured than bulk water [54–56]. In aqueous Triton X-100 systems, the OH stretching frequency of water increases with increasing water content up to about $n_w/n_{OE} = 0.4$ and decreases suddenly up to about $n_w/n_{OE} = 2$, after which it stays constant. The initial increment in OH stretching frequency is due to the progression of the hydrogen bonding between water and the ether oxygen in the oxyethylene groups of Triton X-100, and the subsequent reduction is the result of the linkages among the water molecules. Above $n_w/n_{surf} = 5$, the water added in excess interrupts the linkage among adjacent oxyethylene chains of the $n_w/n_{OE} = 2$ complex and destroys the liquid crystalline phase. The polyoxyethylene chain is completely surrounded by a second nearest neighbour water layer. This layer can be considered as bulk water. [40].

Accordingly Florin et al. [57, 58], in the presence of many salts, the above-mentioned hydration shell around the poly-OE chain with enhanced water structure also corresponds to a zone with decreased salt concentration (i.e. with an excess of water molecules), as compared with the bulk. This must increase the activity of ions in the bulk, which might be detected with ion-selective electrodes. The addition of electrolytes affects both the hydration amount and the properties of hydration water.

The salting in and salting out effects of electrolytes on aqueous non-ionic surfactant solutions are commonly disclosed by their effects on the cloud point. Cloud points are independent of surfactant concentrations between relatively wide limits [59] but are markedly affected by additives [2, 9, 13].

Other properties of non-ionic surfactants are also affected by the presence of electrolytes. Some authors [4, 60] have reported that the aggregation number of polyoxyethylene glycol alkyl ethers decreases in the presence of NaCl. The existence domains of mesophases are also affected by the presence of lyotropic salts like NaCl [61].

The influence of electrolytes can be separated into the effects of cations and that of anions [62–65].

Electrolytes that raise the cloud point extend the temperature range in which the surfactant is soluble in water (salting in), while electrolytes that lower the cloud point reduce the solubility range (salting out). Among the cations, only Na^+ , K^+ , Cs^+ (and presumably Rb^+), NH_4^+ and tetramethylammonium salt out non-ionic surfactants, lowering their cloud point. H^+ , (which form oxonium salts) Ag^+ , Li^+ , and di- and tri-valent cations salt in polyoxyethylated surfactants by complexation with their ether groups. The polyoxyethylene moiety of the amphiphiles acts as a polydentate ligand [13, 66, 67]. Weak cation binding imparts a slightly cationic character to the non-ionic surfactants micelles, which accounts for the salting in [68].

Anions which enhance the structure of water, promoting association among water molecules, and anions that compete with the surfactant for water of hydration, salt it out and reduce the cloud point. These anions include SO_4^{2-} , F^- , PO_4^{3-} , OH^- and Cl^- . [64, 69, 70].

The large polarizable anions I^- , SCN^- , and ClO_4^- break the structure of water. This action increases the amount of unassociated water molecules which, not being hydrogen-bonded to other water molecules, can form hydrogen bonds with the ether groups of the non-ionic surfactants, thereby increasing their cloud point and solubility [3, 13, 66, 67]. NO_3^- and Br^- , which occupy intermediate positions in the Hoffmeister series, leave cloud point and solubility unaffected [72].

The polarity in the hydrated outer layer of Triton X-114 (which has 8 OE units as an average) micelles with NaCl added in the temperature range of 5–13°C was higher than in the solution without any additives. Since NaCl is a strong electrolyte, it increases the polarity of this region, which implies that the electrolyte is distributed in the polyoxyethylene zone [72].

In *n*-octyl polyoxyethylene glycol micelles the addition of NaCl modifies the hydrodynamic radius of micelles and changes the intermicellar interactions [73]. The effect of added strong salting-out agents such as NaCl and NaF was explained in terms of a reduced interaction

of the oxyethylene chains with the aqueous solvent [74]. The effect was explained by the presence of salt-deficient regions around the micellar hydrophilic layer. If the interaction of the oxyethylene chains with the solvent is observed at a specific temperature, then added NaCl reduces the absolute apparent hydration, whereas the temperature dependence of the interaction remains unchanged.

Deguchi and Meguro [75] found that in aqueous C_{12}OE_7 , the addition of salting-out salts increases the compactness of micelles, whereas the addition of salting-in salts increases their looseness.

The effect of the adding electrolytes is not absolute, and may change with concentration. HCl and H_2SO_4 increase the cloud point of non-ionic surfactants. However, at low concentration they caused a slight reduction in the cloud point. The minimum cloud point in Triton X-100 solutions was 63°C in 0.031–0.125 mol dm^{-3} of HCl. Other salting-in salts also show this phenomenon [13]. The salting-in effect of KSCN on oxyethylated methyl dodecanoates increases with concentrations up to 2 mol dm^{-3} , and then decreases at higher KSCM concentrations, so this salt can even act as salting-out at high concentration [76].

The non-ionic surfactant itself may affect the structure of water. As an example, Brij 35 below the CMC is a strong water structure breaker [77]. This situation affects the properties of added electrolytes and must be taken into account when the properties of electrolytes in aqueous non-ionic systems are studied.

Experimental

Triton X-100 (SigmaUltra having $\text{Cl}^- < 0.5\%$, $\text{Na}^+ < 0.1\%$ and $\text{K}^+ < 0.005\%$, total content of ionic impurities $< 0.66\%$) and Tween 20 (SigmaUltra having $\text{Cl}^- < 0.05\%$, $\text{Na}^+ < 0.01\%$ and $\text{K}^+ < 0.005\%$, total content of ionic impurities $< 0.26\%$) were used as purchased. All measurements were performed by titration of 50 mL of solution 0.015 mol dm^{-1} of each surfactant with 0.1000 mol dm^{-1} HCl, 0.1000 mol dm^{-1} NaCl or 0.1000 mol dm^{-1} NaOH solution at 25°C. HCl was 37% A.C.S. reagent from Aldrich, having ≤ 5.2 ppm total ionic impurities, NaCl was 99+ % A.C.S. reagent from Aldrich, having ≤ 12 ppm total ionic impurities, and NaOH was semiconductor grade 99.99% from Aldrich. Only double-distilled water was used.

Conductivity measurements were made with an immersion cell and an automatic conductimeter, namely an Antares II of Instrumentalia.

The pH determinations were made with a millivoltmeter and pH-meter CRIBABB and a Broade and James glass electrode. The same millivoltmeter was used with an Orion 8411 Ross Na^+ -ion-selective electrode and a combined Cl^- -ion-selective electrode (Oakton).

The Na⁺-ion-selective electrode was used against a saturated calomel electrode. All electrodes were calibrated by titration of 50 mL of double-distilled water with the appropriate electrolyte.

Details about the treatment of potentiometric data may be found in the literature [78, 79]. The electrode potential may be written:

$$E = E^\circ + S_e \log a_m \quad (1)$$

where a_m is the true monomer activity and S_e the experimental slope, which may or may not be Nernstian [80].

Results

Figure 2 shows the specific conductivity of Tween 20, Triton X-100 and water when titrated with HCl. Figures 3 and 4 show the variation of pH on HCl and NaOH addition. Figure 5 shows the response of the Cl⁻ ion-selective electrode to the titration of water, Tween 20 and Triton X-100 with HCl.

Figure 6 shows the Na⁺ ion-selective electrode response to the titration of water and Tween 20 solution with NaOH.

Discussion

Interaction with HCl

Figure 7 shows the conductivity increase $\Delta \kappa = \kappa_{\text{surf}} - \kappa_{\text{water}}$ for Tween 20 and Figure 8 that of Triton X-100

solutions as a function of the concentration of the added HCl. Here κ_{surf} and κ_{water} are the specific conductivity of surfactant and water at the same HCl concentration. Tween 20 shows an increase of the specific conductivity with respect to the same HCl concentration in pure water. Except for low concentrations in which $\Delta \kappa$ is negative, Triton X-100 shows the same behaviour. Concentrations at which changes in the dependence of $\Delta \kappa$ on added HCl occur are indicated in both figures. This is a surprising result, because one may expect that the presence of the non-ionic surfactant does not influence the conductivity, or, if the polyoxyethylene chain captures the electrolyte as suggested in the literature, that the conductivity should be reduced. The contribution of the charged micelles cannot compensate the loss of highly mobile H⁺ ions. The reduction in the volume fraction of the conducting phase, i.e. the aqueous intermicellar phase, by the inclusion of the non-ionic surfactant micelles should be negligible. In case that it was not negligible, the effect should be the opposite, i.e. a reduction in the specific conductivity.

The pH dependence on HCl concentration is different for both surfactants (Fig. 3). For the most diluted samples, Triton X-100 solutions show pH below that is water but for $[\text{HCl}] \geq 0.0074 \text{ mol dm}^{-3}$ the pH is above that of water with the same HCl total concentration, whilst Tween 20 solutions show pH monotonically lower than water. Figure 9 shows the difference $\Delta[\text{H}^+] = [\text{H}^+]_{\text{surf}} - [\text{H}^+]_{\text{water}}$ for the titration of both surfactants with HCl, $[\text{H}^+]_{\text{surf}}$ and $[\text{H}^+]_{\text{water}}$ being the concentration of hydrogen ions in the surfactant solution and in water, having the same HCl concentration.

Fig. 2 Specific conductivity of Tween 20 (diamonds), Triton X-100 (open circles) aqueous solutions and water (solid line) as a function of the concentration of added HCl

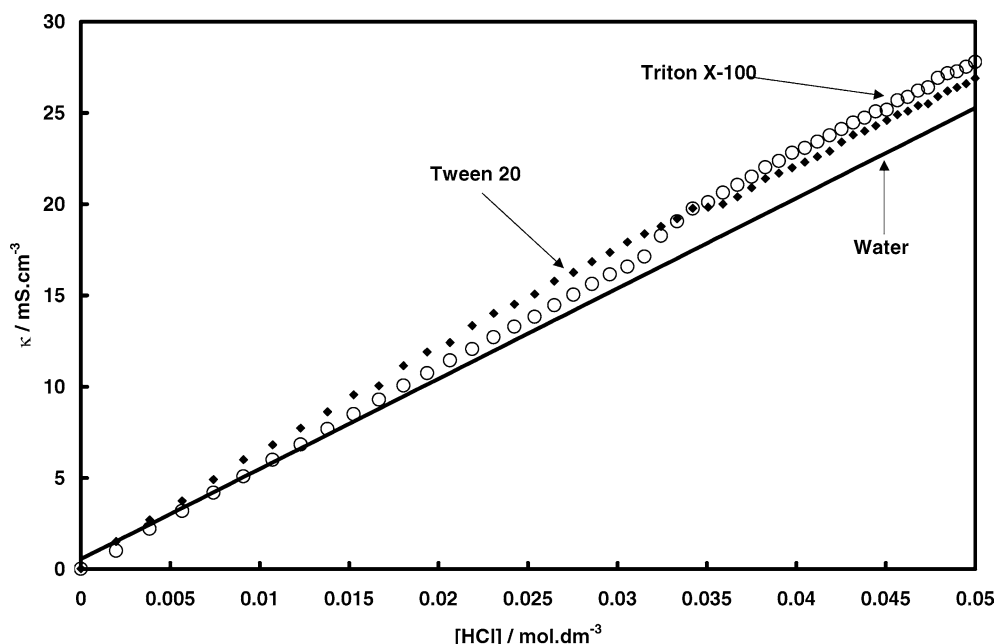
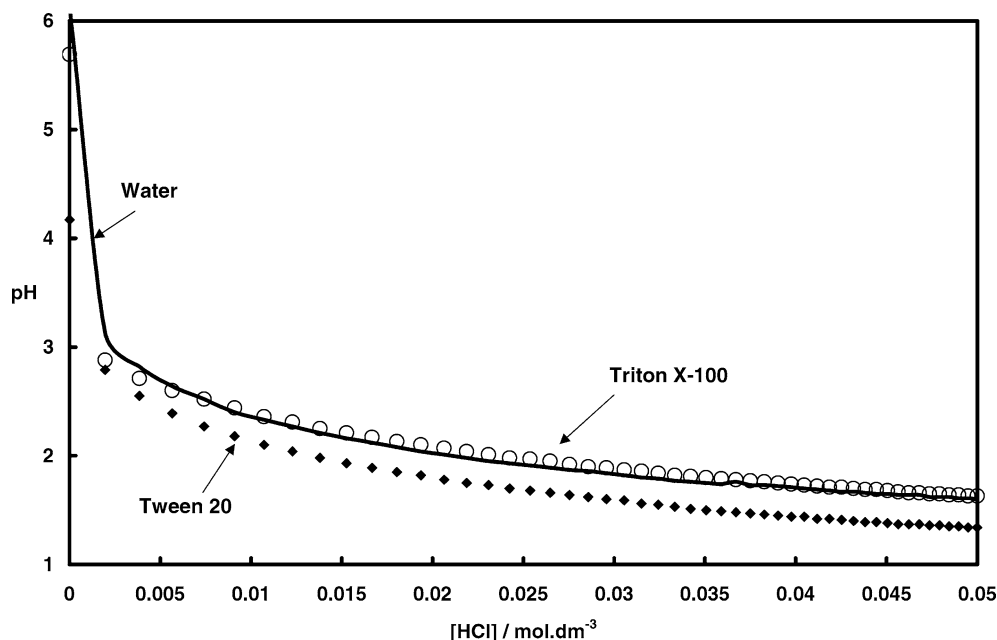


Fig. 3 pH of Tween 20 (*diamonds*), Triton X-100 (*open circles*) aqueous solutions and water (*solid line*) as a function of the concentration of added HCl



Except for $[\text{HCl}] < 0.0074 \text{ mol dm}^{-3}$, Triton X-100 shows negative values with a reduction of the concentration of hydrogen ions with increasing HCl concentration, with a slight step increase at $[\text{HCl}] = 0.0375 \text{ mol dm}^{-3}$. This means that above $[\text{HCl}] = 0.0074 \text{ mol dm}^{-3}$ the hydrophilic moiety of Triton X-100 micelles captures H^+ ions, thus reducing the proton activity in the intermicellar solution. This is in agreement with assertions in the literature [13, 51, 66]. The behaviour below this concentration was detected pre-

viously for HCl with some surfactants, including Triton X-100 [13]. Figure 10 shows the $n_{\text{H}^+}/n_{\text{OE}}$ ratio as a function of the HCl concentration, n_{H^+} and n_{OE} being the moles of hydrogen ions and oxyethylene groups in solution. It is easily seen that the retention increases with HCl concentrations, but the increase is not linear.

The capture of H^+ by the hydrophilic groups of non-ionic surfactants may be explained by their nature. All groups are weak Brønsted acids with the following pK_a

Fig. 4 pH of Tween 20 (*diamonds*), Triton X-100 (*open circles*) aqueous solutions and water (*solid line*) as a function of the concentration of added NaOH

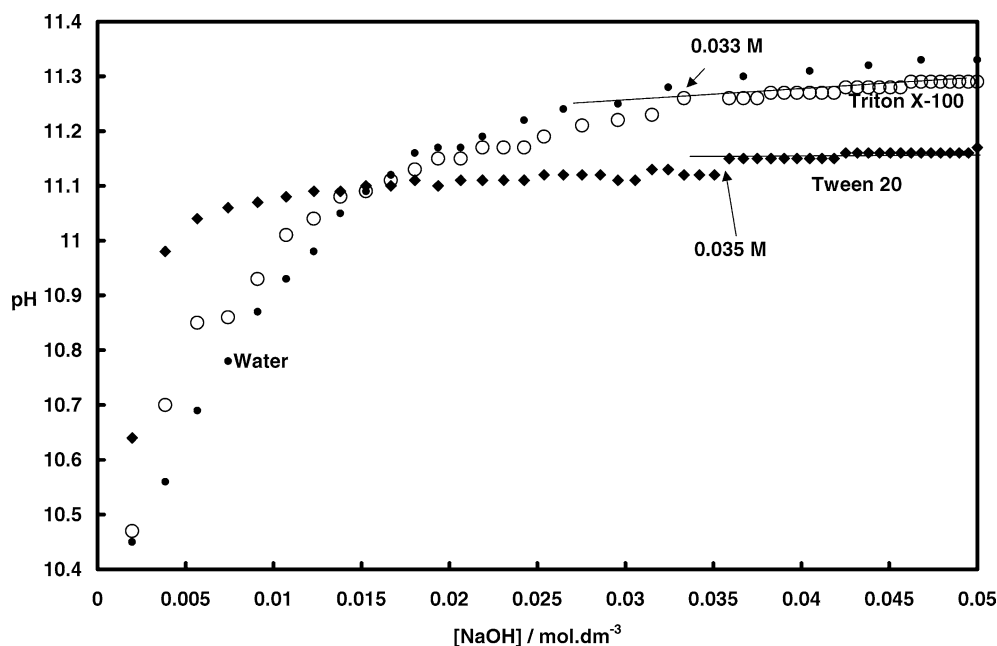


Fig. 5 Response of the Cl^- ion-selective electrode to the titration of water (solid line), Tween 20 (diamonds) and Triton X-100 (open circles) with HCl

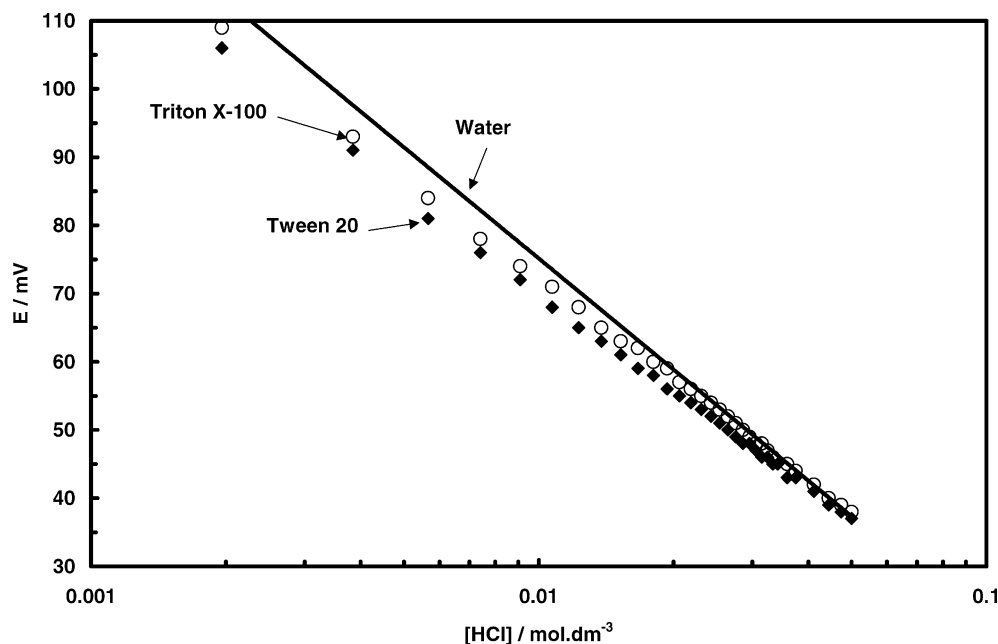
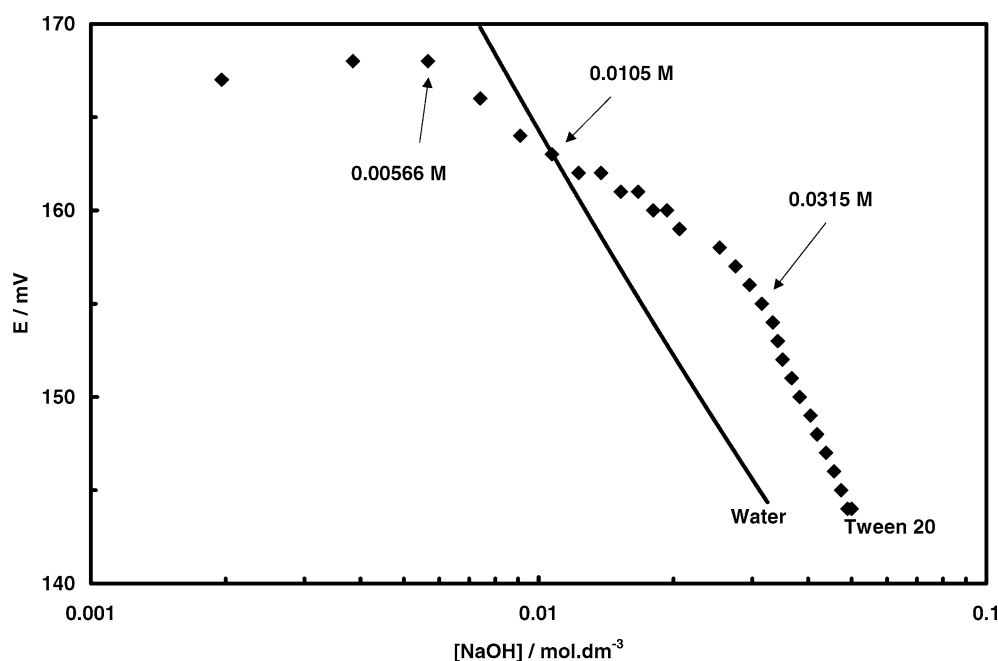


Fig. 6 Response of the Na^+ ion-selective electrode to the titration of water (solid line) and Tween 20 (diamonds) with NaOH



values (for the reaction $\text{HX}^+ \leftrightarrow \text{X}$, relative to water): aliphatic alcohol $p K_a = -2$; aliphatic ether $p K_a = -3.5$, and aliphatic carbonyl group $p K_a = -7$ [81]. Since $p K_a = -1.74$ for water, all the preceding groups are stronger Brønsted acids than water but weaker than HCl.

Figure 11 shows the difference $\Delta[\text{Cl}^-] = [\text{Cl}^-]_{\text{surf}} - [\text{Cl}^-]_{\text{water}}$ for the titration of both surfactants with HCl, $[\text{Cl}^-]_{\text{surf}}$ and $[\text{Cl}^-]_{\text{water}}$ being the concentrations of chloride ions in the surfactant solution and in water having

the same HCl total concentration. The behaviour of both surfactants is similar, but the chloride excess for Tween 20 is higher than that of Triton X-100. Concentrations at which changes appear in the dependence of $\Delta[\text{Cl}^-]$ on $[\text{HCl}]$ are marked in the figure.

It may be concluded that the low-concentration region where HCl causes a slight reduction of the cloud point of Triton X-100, is associated with the exclusion of H^+ and Cl^- ions from the hydrophilic layer of micelles.

Fig. 7 Difference $\Delta \kappa = \kappa_{\text{surf}} - \kappa_{\text{water}}$ for Tween 20 aqueous solutions when titrated with HCl

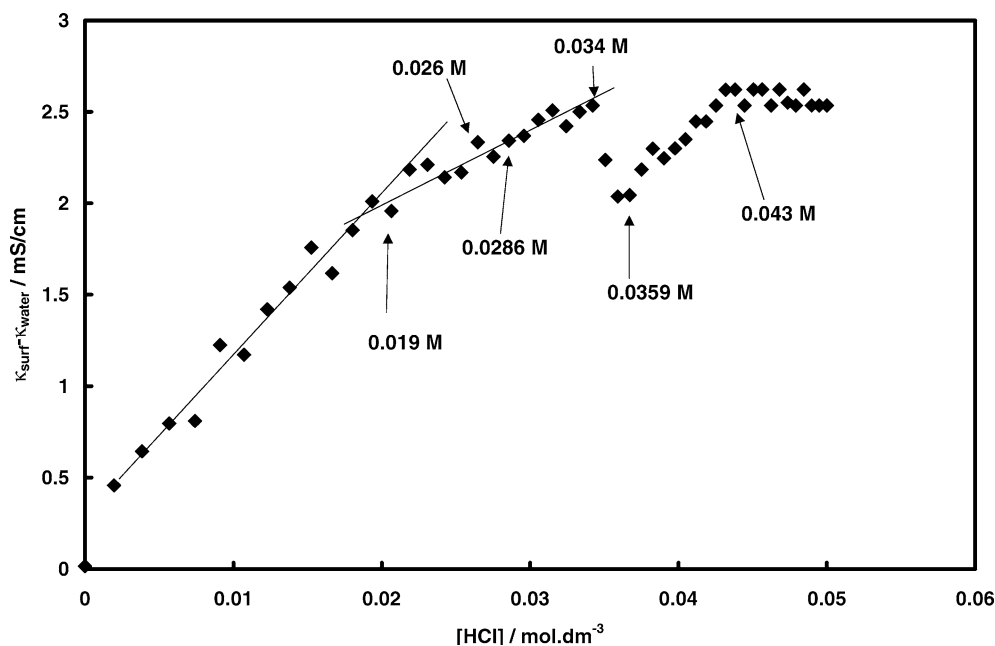
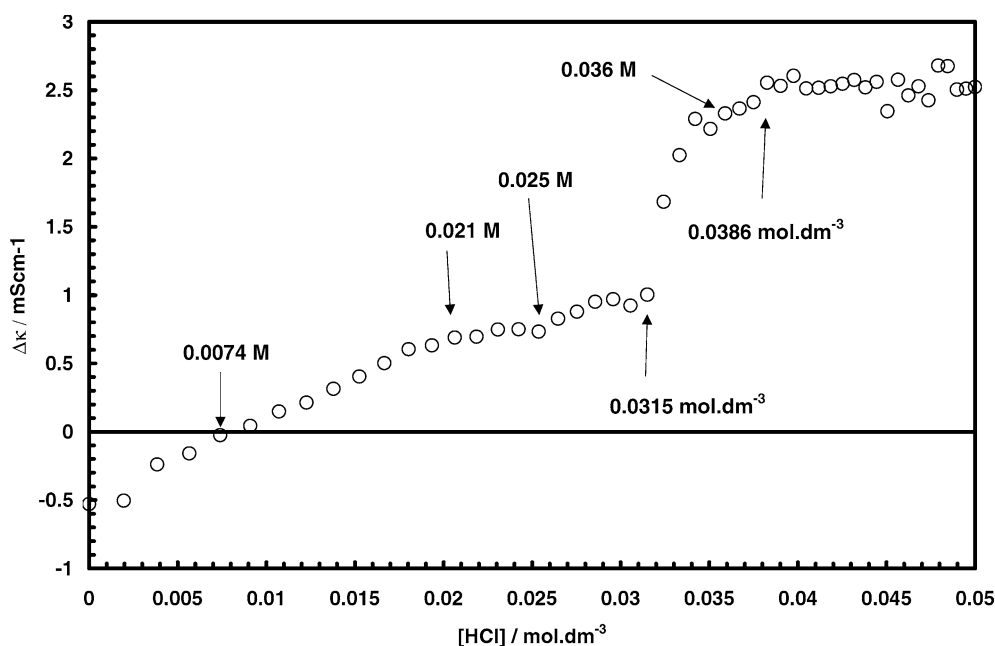


Fig. 8 Difference $\Delta \kappa = \kappa_{\text{surf}} - \kappa_{\text{water}}$ for Triton X-100 aqueous solutions when titrated with HCl



Increasing HCl concentrations above 0.0074 mol dm⁻³, protons are captured by the polyoxyethylene layer and the excess of chloride ions is reduced, until it become negative at $[\text{HCl}] > 0.036$ mol dm⁻³. A glance at Fig. 8 indicates that all the concentrations showing changes with the ion-selective electrodes are represented in the $\Delta \kappa$ curve by changes in behaviour. In particular, the inclusion of Cl⁻ ions in micelles is marked by a sudden increase in $\Delta \kappa$. This is rather surprising, because the

reduction of H⁺ and Cl⁻ ions activity and the reduction of the neat charge of micelles by partial neutralization of the trapped protons by the inclusion of chlorine, should decrease the specific conductivity. A possible explanation is that the non-micellised surfactant molecules reduce the viscosity of the inter-micellar solution by water structure breaking as Brij 35 below the CMC [77].

Tween 20 shows only positive values of $\Delta[\text{H}^+]$ in Fig. 9 and a monotonic increase up to $[\text{HCl}] = 0.046$

mol dm⁻³, where the hydrogen excess is stabilised. Thus there is an increase in the proton activity in the intermicellar solution.

For Tween 20 $\Delta[\text{Cl}^-]$ (Fig. 11) is always positive and almost parallel to that of Triton X-100. Then, both ions are excluded from the hydrophilic layer of Tween 20 micelles. The behaviour of the $\Delta\kappa$ curve roughly reflects the above points (Fig. 7). Since both H⁺ and Cl⁻ ions activities in the intermicellar solution are higher than in water, the positive excess conductivity may be easily explained.

The hydrophilic group of Tween 20 is very different from that of Triton X-100. It is much more hydrophilic and bulky, as it can be seen in Fig. 1. Thus, at equal surfactant and acid concentration, Tween 20 must retain much more water than Triton X-100, not only by primary hydration but by mechanically trapping in the secondary conformation of the hydrophilic group, as stated in the theoretical background section.

It is noteworthy that both surfactants behave differently when HCl is added to the micellar solution. Some differences in behaviour have been previously found between Triton X-100 and other surfactants [33].

Interaction with NaCl

Figure 12 shows the difference $\Delta[\text{Na}^+] = [\text{Na}^+]_{\text{surf}} - [\text{Na}^+]_{\text{water}}$ for the titration of Tween 20 with NaCl, $[\text{Na}^+]_{\text{surf}}$ and $[\text{Na}^+]_{\text{water}}$ being the concentration of

sodium ion in the surfactant solution and in water having the same NaCl concentration. There is a slight excess of sodium ions at low NaCl concentration, corroborating that the interaction between non-ionic micelles and electrolytes may depend on concentration. $\Delta[\text{Na}^+]$ decreases as NaCl concentration increases, becoming negative at $[\text{NaCl}] = 0.01 \text{ mol dm}^{-3}$ and constant at $[\text{NaCl}] = 0.033 \text{ mol dm}^{-3}$ with $\Delta[\text{Na}^+] = -0.01456 \pm 0.00023$. Triton X-100 does not show any noticeable effect. Above 0.01 mol dm^{-3} the behaviour is the inverse of the H⁺ ion, as expected by the different general effect of Na⁺ and H⁺ ions on polyoxyethylene surfactants. Na⁺ ions are captured by the hydrophilic moiety of Tween 20 micelles, thus reducing the intermicellar activity and increasing the polarity, as found by Komaromy-Hiller et al. [72] in Triton X-114 micelles. This is in opposition to the suggestion of Weckström and Zulauf [74] that NaCl generates salt-deficient regions around the micellar hydrophilic layer in n-octyl polyoxyethylene glycol micelles. However, as the present work corroborates, different non-ionic surfactants may interact in different ways with the same electrolyte.

As mentioned above, the polarity in the hydrated outer layer of Triton X-114 (which has 8 OE units as an average) micelles with NaCl added was higher than in the solution without any additives [73]. Since NaCl is a strong electrolyte it increases the polarity of this region, which implies that the electrolyte is distributed in the polyoxyethylene zone [72]. Since $\Delta[\text{Cl}^-]$ was positive, this increase of polarity must be

Fig. 9 $\Delta[\text{H}^+] = [\text{H}^+]_{\text{surf}} - [\text{H}^+]_{\text{water}}$ for the titration of Tween 20 (diamonds) and Triton X-100 (open circles) aqueous solutions with HCl

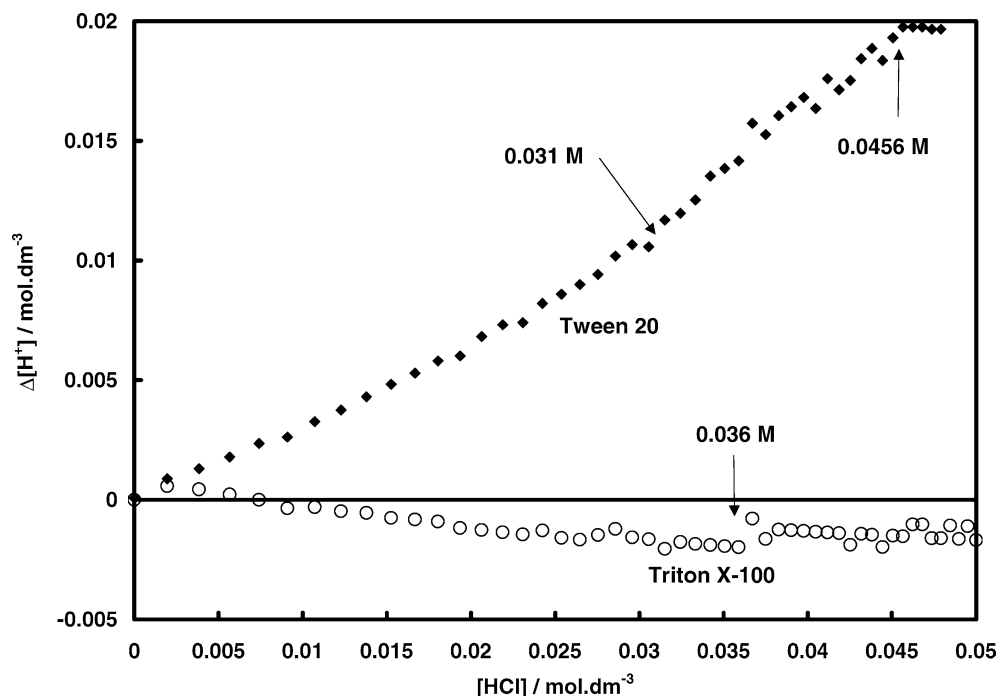


Fig. 10 The ratio of moles of protons captured by Triton X-100 micelles to moles of oxyethylene units, n_{H^+}/n_{OE} , as a function of the concentration of added HCl

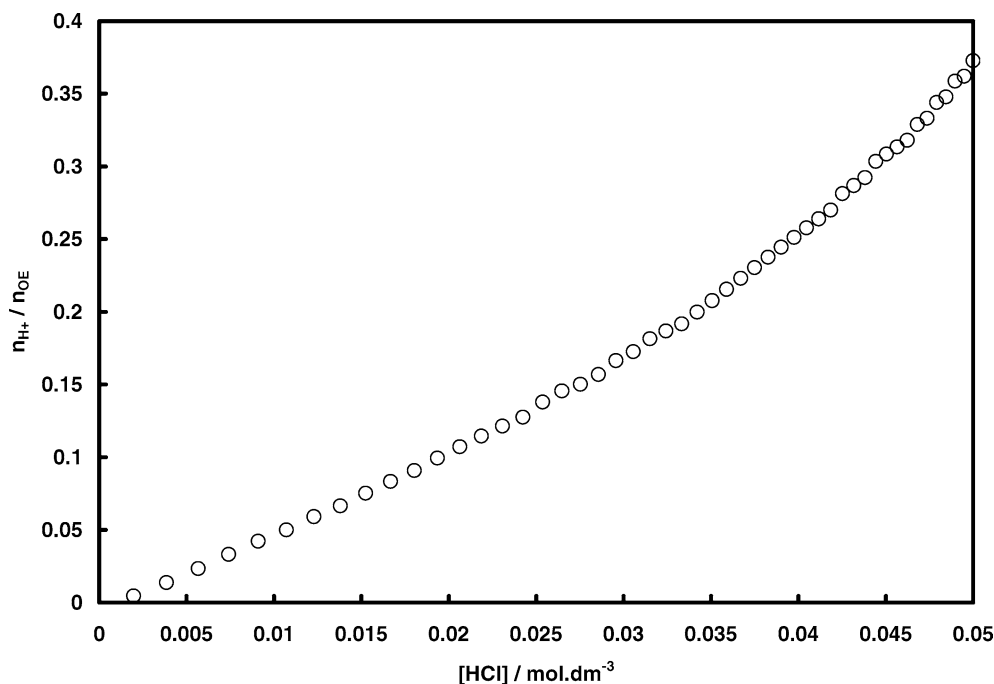
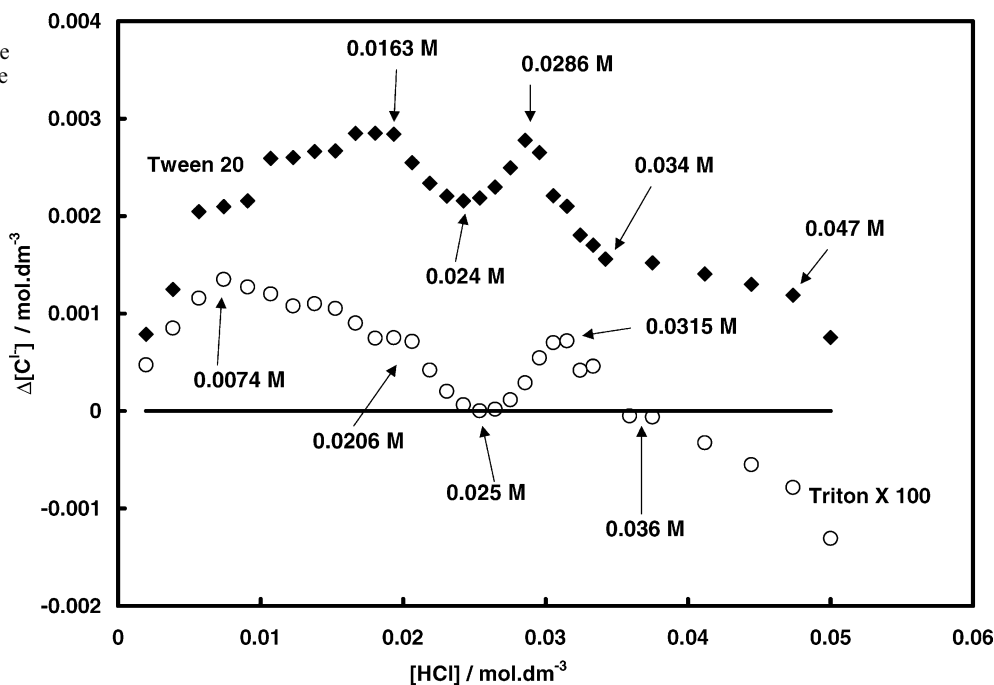


Fig. 11 The difference $\Delta[Cl^-] = [Cl^-]_{surf} - [Cl^-]_{water}$ for the titration of Tween 20 (diamonds) and Triton X-100 (open circles) aqueous solutions with HCl



caused by the capture of Na^+ ions by the hydrophilic layer.

Crown ethers have the property of forming complexes with positive ions, generally metallic ions or ammonium and substituted ammonium. In most cases the guest ions are held tightly in the centre of the cavity. Each crown ether binds different ions, e.g. a six oxygen atoms ring binds K^+ but not Li^+ [82]. Since

the polyoxyethylene chains adopt a helix conformation, each step seems a crown ether structure and can capture ions in its inner space.

Interaction with NaOH

Figure 13 shows $\Delta[OH^-] = [OH^-]_{surf} - [OH^-]_{water}$ when NaOH is added to the solutions of each surfactant.

Fig. 12 The difference $\Delta[\text{Na}^+] = [\text{Na}^+]_{\text{surf}} - [\text{Na}^+]_{\text{water}}$ for the titration of Tween 20 aqueous solution with NaCl

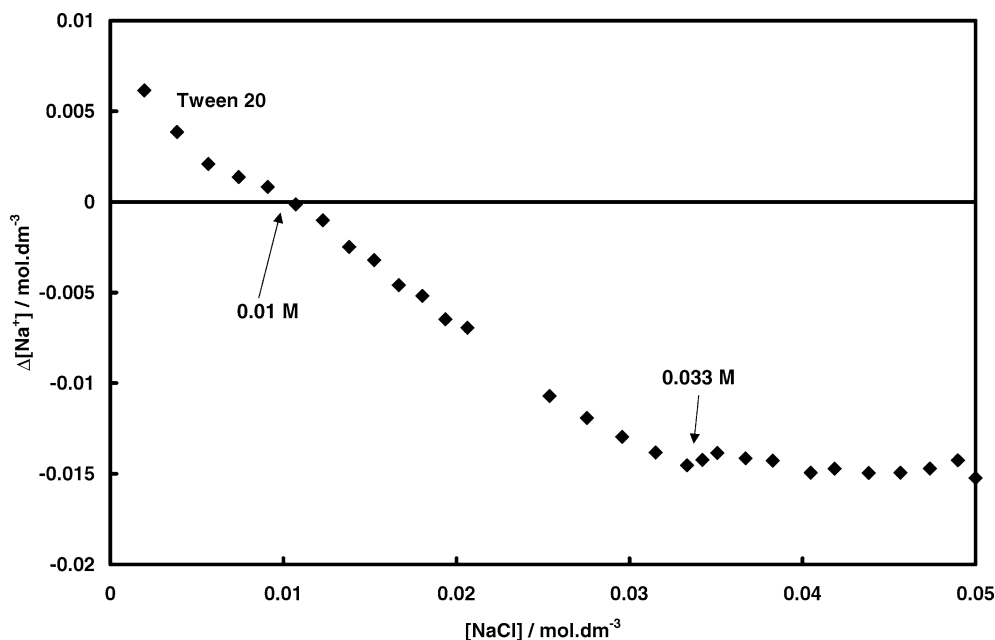
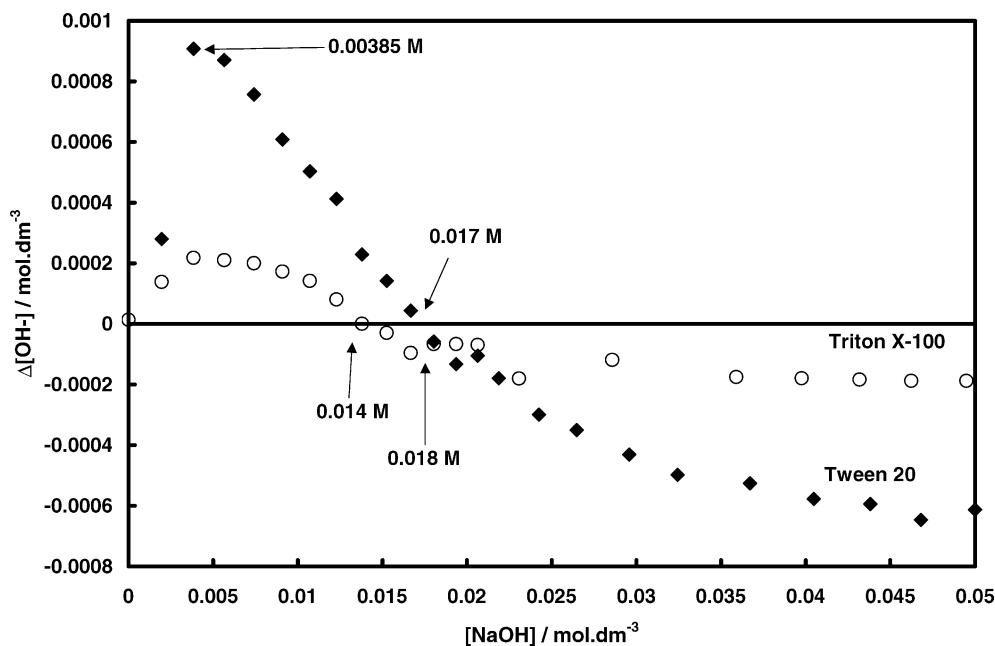


Fig. 13 The difference $\Delta[\text{OH}^-] = [\text{OH}^-]_{\text{surf}} - [\text{OH}^-]_{\text{water}}$ for the titration of Tween 20 (diamonds) and Triton X-100 (open circles) aqueous solutions with NaOH



Results for both surfactants are similar. At very low NaOH concentrations the excess is positive for both surfactants and has a maximum at $0.00385 \text{ mol dm}^{-3}$. Then, $\Delta[\text{OH}^-]$ decreases and becomes negative at $[\text{NaOH}] = 0.014 \text{ mol dm}^{-3}$ (Triton X-100) and $0.017 \text{ mol dm}^{-3}$ (Tween 20) seeming to approach asymptotically to a value of $\Delta[\text{OH}^-] \approx -0.00019 \text{ mol dm}^{-3}$ (Triton X 100) and $-0.00006 \text{ mol dm}^{-3}$ (Tween 20). Notice that the behaviour of OH^- and Na^+

ions is similar. Since both ions are salting out, this coincidence is not surprising.

Concentration effects

It is evident that there is an interaction between electrolytes and micelles of Triton X-100 and Tween 20. This interaction changes in nature at three concentrations:

$C_1 = 0.015 \pm 0.014 \text{ mol dm}^{-3}$ (Triton X-100) and $0.0098 \pm 0.0067 \text{ mol dm}^{-3}$ (Tween 20); $C_2 = 0.0300 \pm 0.0048 \text{ mol dm}^{-3}$ (Triton X-100) and $0.0321 \pm 0.0013 \text{ mol dm}^{-3}$ (Tween 20); and $C_3 = 0.0368 \pm 0.0017 \text{ mol dm}^{-3}$ (Triton X-100) and $0.049 \pm 0.012 \text{ mol dm}^{-3}$ (Tween 20). The main change occurs at C_2 .

Since the interaction of electrolytes with non-ionic surfactants affects the hydration of the OE units, and this change in hydration affects the structure and conformation of the hydrate, it may be concluded that the above concentrations are possibly associated with changes in hydration, structure and conformation of the polyoxyethylene chains.

Conclusions

By studying of the ion activity of the electrolytes added to two different non-ionic surfactants we found that:

- Both surfactant solutions show higher specific conductivity than water when titrated with HCl.

- While Tween 20 excludes protons from its micelles hydrophilic moiety, Triton X-100 reject H^+ at low concentrations but captures it at high [HCl].
- Chlorine ion is rejected from the hydrophilic groups of both surfactants micelles.
- Sodium ion is rejected at low concentrations and captured by the hydrophilic group of Tween 20 micelles at high [NaCl].
- OH^- ions are rejected from both surfactant micelles at low concentrations, and captured at high [NaOH].
- The above results confirm in general the behaviour of salting out and salting in ions described in the literature, including the change in effect when ion concentration is increased, and the fact that Triton X-100 sometimes has a different behaviour than other non-ionic surfactants.

Acknowledgements MAM is an adjunct researcher of the Consejo Nacional de Investigaciones Científicas y Técnicas de la República Argentina (CONICET). PM has a fellowship of the CONICET. This work was financed by a grant of the Universidad Nacional del Sur and the grant PIP no. 2739 of CONICET.

References

- Hsiao L, Dunning HN, Lorenz PB (1956) *J Phys Chem* 60:657
- Becher P (1956) *J Colloid Sci* 17:325
- Schick MJ (1962) *J Colloid Sci* 17:801
- Schick MJ, Atlas SM, Eirich FR (1962) *J Phys Chem* 66:1326
- Schick MJ (1964) *J Phys Chem* 68:3585
- Arai H (1967) *J Colloid Sci* 23:348
- Malik WU, Saleem SM (1968) *J Am Oil Chem Soc* 45:670
- Malik WU, Jhamb OP (1970) *Kolloid Z u Z Polym* 242:1209
- Maclay WN (1956) *J Colloid Sci* 11:272
- Saito H, Shinoda K (1967) *J Colloid Interface Sci* 24:10
- Doren A, Goldfarb J (1970) *J Colloid Interface Sci* 32:67
- Shinoda K, Takeda H (1970) *J Colloid Interface Sci* 32:642
- Schott H (1973) *J Colloid Interface Sci* 43:150
- Schott H (1998) *J Colloid Interface Sci* 205:496
- Schott H, Royce A (1986) *Colloids Surf* 19:399
- Karlström G (1985) *J Phys Chem* 89:4962
- Karlström G, Lindman B (1992) In: Friberg SE, Lindman B (eds) *Organized solutions*. Marcel Dekker, New York, p 49
- Goldstein RE (1984) *J Chem Phys* 80:5340
- Wartewig S, Alig I, Hergeth W-D, Lange J, Lochmann I, Scherzed T (1990) *J Mol Struct* 219:365
- Blandamer MJ, Powell MF, Fox A, Stafford JL (1969) *Makromol Chem* 124:222
- Kjellander R, Florin E (1981) *J Chem Soc Faraday Trans I* 77:2053
- Breen J, Huis D, de Bleijser J, Leyte JC (1988) *J Chem Soc Faraday Trans I* 84:293
- Ling JN, Murphy RC (1982) *Pysiol Chem Phys* 14:209
- Zinchenko VD, Mank VV, Moiseev VA, Ovcharenko FD (1976) *Kolloidn Zh* 38:44
- Hager SL, MacRury TB (1980) *J Appl Polym Sci* 25:1559
- Bogdanov B, Mihailov M (1985) *J Polym Sci Polym Phys Ed* 23:2149
- Graham NB, Zulfiqar M, Nwachuku NE, Rashid A (1989) *Polymer* 30:528
- de Vringer T, Joosten JGH, Junginger HE (1986) *Colloid Polym Sci* 264:623
- Tilcock CPS, Fisher D (1982) *Biochim Biophys Acta* 688:645
- Carlstrom G, Halle B (1989) *J Chem Soc Faraday Trans I* 85:1049
- Nilsson PG, Lindman B (1983) *J Phys Chem* 87:4756
- Alami E, Kamenka N, Raharimihamina A, Zana R (1993) *J Colloid Interface Sci* 158:342
- Streletzky K, Phillies GDJ (1995) *Langmuir* 11:42
- Mitchell DJ, Tiddy GJT, Waring L, Bostock T, McDonald MP (1983) *J Chem Soc Faraday Trans I* 79:975
- Nilsson P-G, Wennerström H, Lindman B (1985) *Chem Sci* 25:67
- Lindman B, Carlsson A, Karlstrom G, Malmsten M (1990) *Adv Colloid Interface Sci* 32:183
- Miyazawa T, Fukushima K, Ideguchi Y (1962) *J Chem Phys* 37:2764
- Tadokoro H, Chatani Y, Yoshihara T, Tahara S, Murahashi S (1964) *Makromol Chem* 73:109
- Yoshihara T, Tadokoro H, Murahashi S (1964) *J Chem Phys* 41:2902
- Kimura N, Umemura J, Hayashi S (1996) *J Colloid Interface Sci* 182:356
- Mori Y, Nagaoka S, Takiuchi H, Kikuchi T, Noguchi N, Tanzawa H, Noishiki Y (1982) *Trans Am Soc Artif Intern Organs* 28:459
- Hlady V, van Wagenen RA, Andrade JD (1985) In: Andrade JD (ed) *Surface and interfacial aspects of biomedical polymers*, vol 2. Plenum, New York, p 81
- Marszall L (1973) *Pol J Pharmacol Pharm* 25:481
- Jonstromer M, Jonsson B, Lindman B (1991) *J Phys Chem* 95:3293
- El Eini, DID, Barry BW, Rhodes CT (1976) *J Colloid Interface Sci* 54:348
- Romsted LS, Yao J (1996) *Langmuir* 12:2425

47. Antonsem KP, Hoffman AS (1992) In: Harris MJ (ed) Poly(ethylene glycol) chemistry: biochemical and biomedical applications, Plenum, New York, pp 14–28
48. Kaatze U, Göttmann O, Podbielski D (1978) Theory of dielectric polarization, vol 2. Elsevier, Amsterdam, p 124
49. Kaatze U (1978) Ber Bunsenges Phys Chem 82:690
50. Kaatze U (1997) J Solution Chem 26(11):1049
51. Kaatze U, Wei D, Patey GN (1994) J Chem Phys 98:4959
52. Baker JM, Dore JC, Seddon JM, Soper AK (1996) Chem Phys Lett 256:649
53. Walker T (1973) J Colloid Interface Sci 45(2):372
54. El Seoul OA, Farah JPS, Vieira PC, El Seoul MI (1987) J Phys Chem 91:1950
55. El Seoul MI, Farah JPS, El Seoul OA (1989) Ber Bunsenges Phys Chem 93:180
56. El Seoul OA, Blaskó A, Bunton CA (1994) Langmuir 10:653
57. Kjellander R, Florin E (1981) J Chem Soc Faraday Soc 177:374
58. Florin E, Kjellander R, Eriksson JC (1984) J Chem Soc Faraday Trans 180:2889
59. Schott H (1969) J Pharm Sci 58:1443
60. Corkill JM, Goodman JF, Ottewill RH (1961) Trans Faraday Soc 57:1627
61. Jonströmer M, Strey R (1992) J Phys Chem 96:5993
62. Huibers P, Shah D, Katrizky A (1997) J Colloid Interface Sci 193:132
63. Materna K, Szymanowsky (2002) J Colloid Interface Sci 255:194
64. Schott H (1997) J Colloid Interface Sci 189:117
65. Schott H (2001) Colloids Surf A 198:129
66. Schott H, Han SK (1975) J Pharm Sci 64:658
67. Schott H, Royce AE (1984) J Pharm Sci 73:793
68. Schott H (1975) J Colloid Interface Sci 173:265
69. Kavanau JL (1964) Water and solute—water interactions. Holden-Day, San Francisco, pp 52–60
70. Collins KD, Washabaugh MW (1985) Quart Rev Biophys 18:323
71. Schott H (1984) Colloids Surf 11:51
72. Komaromy-Hiller G, Calkins N, von Wabdruszka R (1996) Langmuir 12:916
73. Weckström K (1985) Chem Phys Lett 119:503
74. Weckström K, Zulauf M (1984) J Phys (Paris) 45:137
75. Deguchi K, Meguro K (1975) J Colloid Interface Sci 50:223
76. Materna K, Cote G, Szymanowsky J (2003) J Colloid Interface Sci 260:466
77. Baptista MS, Tran CD (1995) J Phys Chem 99:12952
78. Minardi RM, Schulz PC, Vuano B (1996) Colloid Polym Sci 274(11):1089
79. Schulz PC (1989) Boletín Soc Quím Perú 55:51
80. Kale KM, Cussler EL, Evans DF (1982) J Solution Chem 11:581
81. March J (1992) Advanced organic chemistry: Reactions, mechanisms, and structure. Wiley, New York, pp 250–251
82. March J (1992) Advanced organic chemistry: Reactions, mechanisms, and structure. Wiley, New York, pp 82–87