Colloid Polym Sci (2009) 287:345–350
DOI 10.1007/s00396-008-1978-8

ORIGINAL CONTRIBUTION

Uptake and release of surfactants from polyampholyte microgel particles

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Received: 7 November 2008 / Revised: 28 November 2008 / Accepted: 28 November 2008 / Published online: 20 December 2008

Abstract Polyampholyte microgel particles, containing both methacrylic acid and 2-(dimethylamino) ethyl methacrylate (a weak base), in a mainly *N*-isopropyl acrylamide network, have been prepared by free-radical dispersion polymerisation. The swelling properties of the particles have been shown to be pH and temperature dependent and to exhibit a minimum in size at the iso-electric point. The uptake and release of cetylpyridinium chloride and Triton X-100, into and from, the polyampholyte microgel particles have been investigated as a function of pH. The absorbed amounts at different pH values have been related to various specific interactions between the surfactant and the microgel network.

Keywords Amphoteric · Microgel · Uptake · Release · Cationic surfactant · Non-ionic surfactant · *N*-isopropylacrylamide

Introduction

Microgel particles, which have potential application in the controlled uptake and release of small molecules for chemical separation and in drug delivery, are cross-linked polymer particles, which can swell/deswell in response to changes in the local environmental conditions (e.g. temperature, solvency of the polymer chains). Charged microgel particles, containing, for example, weak acid or base groups, can respond to changes in pH and ionic strength. Polyampholyte microgel particles contain both positively and negatively charged groups. If these are based on *strong* acids and bases, then, if the charges are balanced, the net *neutral* polyampholyte microgel particles are collapsed at low ionic strength and show a monotonic increase in swelling with increasing electrolyte concentration [1]. More commonly encountered are polyampholyte microgel particles containing *weak* acid groups (e.g. carboxylic acid) and *weak* base groups (e.g. amino groups). Weak polyampholytes normally exhibit a minimum in size with varying pH; this occurs around the pH value corresponding to their iso-electric point (i.e.p.). Such microgel particles are of interest since they may absorb an ionic "active" species in one range of pH values and release it over another range.

Various authors have prepared weak polyampholyte microgel particles [2–7], mostly using an aqueous dispersion polymerisation route.

Ogawa et al. have physically entrapped different types of polymers into polyampholyte microgel particles in order to investigate volume change of the particles in response to pH [8,9]. However, few other studies exist in the literature on the interaction of polyampholyte microgels with solutes and the ones that do generally look at the effect of electrolyte on the swelling properties of the particles [4,10]. In this paper, we describe the properties of polyampholyte microgel particles containing monomers having weak acid and base groups, copolymerised with *N*-isopropylacrylamide (NIPAM). We then investigate the uptake into, and in some cases, the release from, the microgel particles of a cationic and a non-ionic surfactant.

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Experimental section

Materials

N-Isopropylacrylamide (NIPAM) and *N*,*N*′-methylenebisacrylamide (BA; both from Fisher) were recrystallised from hexane and ethanol, respectively. 2-(dimethylamino)ethyl methacrylate (DMAEM, Aldrich) and *tert*-butyl methacrylate (tBMA) were filtered through a basic alumina column. Methacrylic acid (MAAc), "V50" cationic initiator (2,2′-azobis(2 methyl amidino propane) dichloride, 97%), cetylpyridinium chloride surfactant (CPC), non-ionic surfactant Triton® X-100 ($(C_{14}H_{22}O(C_2H_4O)_n)$ $n=9.5$), were used as received from Aldrich. All solutions were prepared with Milli-Q-grade water.

Polyampholyte microgel synthesis

Single-step emulsion polymerisations were carried out in a 100-mL reaction vessel, fitted with a reflux condenser, a magnetic stirrer, a thermometer and a glass nitrogen inlet tube. NIPAM (0.5 g, 69 wt.% of total monomer), DMAEM (0.05 g, 7 wt.%), MAAc (0.04 g, 6 wt.%), tBMA (0.05 g, 7 wt.%) and BA (0.08 g, 11 wt.%),were added into the reaction vessel along with 100 mL of water. The vessel was immersed in an oil bath set at 70 °C. The reaction mixture was purged with nitrogen for 20 min. Once the reaction temperature had been reached, the initiator solution, containing 0.04 g "V50", was added. The polymerisation reaction was allowed to continue for 24 h. The microgel dispersion was then allowed to cool and was subsequently dialysed against Milli-Q water to remove any residual monomer and other impurities, changing the dialysate twice daily for a week.

Characterisation of the microgel particles

The solids contents and, hence, the yield of the various microgel particle preparations were determined gravimetrically. When required, the pH was adjusted by the addition of small quantities of (0.1 M) HCl or NaOH. The diffusion coefficients of the various microgel particles (at a particle concentration of 0.1 wt.%) were determined by dynamic light scattering (DLS), using a Brookhaven Instruments Zeta Plus apparatus, fitted with a 15-mW laser (λ=678 nm) and with the detector set at 90°. The Stokes–Einstein equation was then used to calculate the hydrodynamic diameter of the microgel particles.

The electrophoretic mobility of the particles was determined using a Brookhaven Instruments Zeta-PALS apparatus. The detailed theory behind the electrokinetics of soft particles can be found in a review article by Ohshima [11].

The binding isotherm for CPC and Triton X-100 to the microgel particles was determined using the following (solution depletion) method. A given quantity of a dispersion of microgel particles was added to a known volume of surfactant solution and the system left to equilibrate for at least 7 days. The particles were then separated from solution by centrifugation, at 10,000 rpm for 20 min, using a Sorvall RC 5b Plus centrifuge. The equilibrium surfactant concentration was then determined from a calibration graph of absorbance versus surfactant concentration. The wavelengths used were 259 and 275 nm for CPC and Triton X-100, respectively.

Results and discussion

Characterisation of the polyampholyte microgel particles

Polyampholyte microgel particles, based on NIPAM as the major constituent, but also containing both amine (i.e. weakly basic) functional groups and carboxylic acid groups, as well as a cross-linking monomer, were successfully prepared using the batch precipitation polymerisation process described.

The hydrodynamic diameter of the particles, as a function of pH, is shown in Fig. 1, for dispersions at 25° C and 60° C. At both temperatures the hydrodynamic diameter passes through a minimum value at a pH ~5.2, which one concludes corresponds to the iso-electric point of the microgel particles. As might be expected for microgel particles, largely based on NIPAM monomer, the hydrodynamic diameter is greater at 25° C than at 60° C, over the whole pH range studied. The anomalous, small increase in diameter at pH 5.2 and 60° C is due to the particles being very weakly flocculated, there being no net charge on the

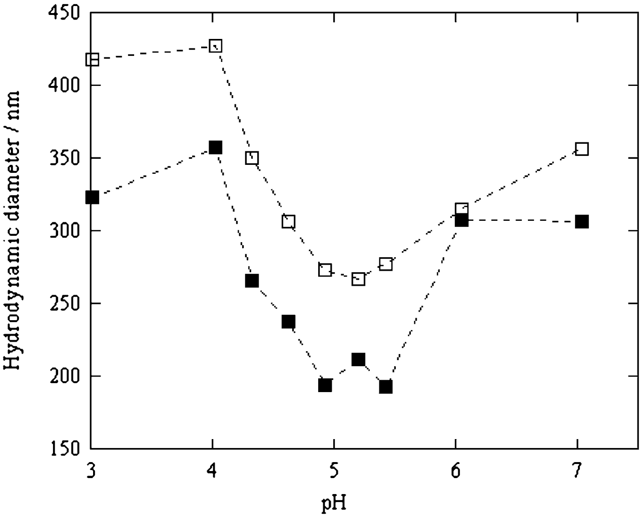

Fig. 1 Hydrodynamic diameter as a function of pH of the polyampholyte microgel particles at (*open square*) 25° C and (*filled square*) 60° C

microgel particles at this pH value. However, at 25° C, even at the iso-electric pH, the particles are sufficiently swollen for the van der Waals interaction between the particles to be too weak to cause any flocculation. The small decrease in diameter in the region of pH 3, at both temperatures, is probably an ionic strength effect, leading to charge screening; the increased ionic strength arises from the necessary addition of acid to adjust the pH to this value.

The corresponding electrophoretic mobility data for the microgel particles, as a function of pH, are shown in Fig. 2, at both 25° C and 60° C. The iso-electric point is clearly at pH ~5.2, as was concluded in the last paragraph. The mobility values on both sides of the iso-electric pH are greater in magnitude at 60° C than at 25° C. This is because the microgel particles are less swollen at 60° C (Fig. 1) and, hence, their charge density (surface plus bulk) is higher at 60° C. The amphoteric nature of these microgel particles arises from the presence of both weak base (DMAEM) and weak acid (MAAc) groups in the polymer network comprising the particles. The pK_a of DMAEM is 8.4 [12]. The pK_a of the carboxyl groups in MAAc is 4.6 [13, 14]. The iso-electric pH is between the two pK_a values, as one would expect.

PolyNIPAM is a temperature-sensitive polymer in aqueous solution, with a lower critical solution temperature (LCST) at 32° C [15]. Likewise, polyNIPAM microgel particles show a volume phase transition (VPT) centred at 32° C, where the particles show a rapid decrease in hydrodynamic diameter over a narrow temperature range [16]. The (de)swelling ratio ($s=v_T/v_{25}$, where v_T and v_{25} are the particle volumes at temperature T, and 25° C, respectively) can be as low as ~0.1, at low cross-link densities [17]. It is well known that by copolymerising NIPAM with a much more hydrophilic (or ionic) monomer, then the VPT of the microgel particles can be shifted to a higher temperature [18–20]. In Fig. 3, the swelling ratio of the polyampholyte microgel particles is shown, as a function of temperature, for three solution pH values. Although it is difficult to locate the VPT precisely from the data presented, it is clear that, at all three pH values, the VPT is significantly higher than 32° C, the value for polyNIPAM itself. At pH 3 and 7, where the microgel particles carry a net charge (positive and negative, respectively) then the VPT is around 45° C or even slightly greater. At pH 5, on the other hand, close to the iso-electric point of the microgel particles, the increase in the VPT is somewhat smaller. The microgel deswelling with increasing temperature is much less than for pure polyNIPAM, i.e. s ~0.87 at pH 3 and 7, where the microgel particles carry a charge, and s ~0.80 at pH 5 where they are virtually neutral. The reduced deswelling, compared to polyNIPAM microgel particles, is, as with the increase in VPT, due to the presence of the more hydrophilic monomers present in the polymer network comprising the microgel particles.

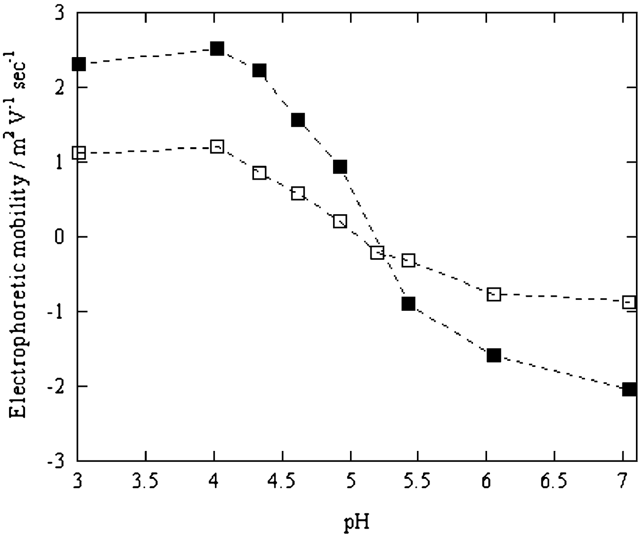

Fig. 2 Electrophoretic mobility as a function of pH of the polyampholyte microgel particles at (*open square*) 25° C and (*filled square*) 60° C

It is clear that even for microgel particles containing ~70 wt.% NIPAM monomer, the dampening effect of the hydrophilic groups present on the temperature response of the microgel particles implies that pH variation is probably going to be a more effective trigger than temperature variation in controlled uptake and release applications. Vincent et al. have investigated several aspects of the interaction of various types of “active species” with microgel dispersions [17,21–27]. It would seem that the actual swelling/deswelling response of microgel particles is a much more important consideration when considering the uptake and release of species such as high molecular weight polymers and nanoparticles, whose dimensions are comparable to the effective mesh size within the microgel particles. For relatively small species, such as the cationic surfactant molecules used in the current studies, it is the *binding strength* of the added molecules to the polymer network comprising the microgel particles which is a much more important consideration.

The uptake and release of surfactants from the polyampholyte microgel particles

Two absorption characteristics of two types of surfactant molecules into the amphoteric microgel particles are considered below: (1) the cationic surfactant, cetylpyridinium chloride (CPC) and (2) the poly(ethylene oxide)-based, non-ionic surfactant, Triton X-100.

1. CPC

The hydrodynamic diameter of the polyampholyte microgel particles, as a function of added CPC concentra-

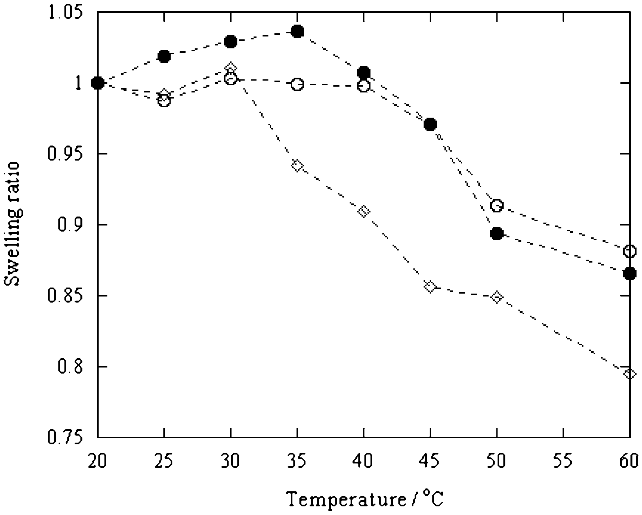

Fig. 3 Swelling ratio of the polyampholyte microgel particles as a function of temperature at (*filled circle*) pH 3, (*open diamond*) pH 5, and (*open circle*) pH 7

tion, is shown in Fig. 4, at pH 3 and pH 7. At pH 3, where the microgel particles are themselves strongly cationic, the hydrodynamic diameter remains virtually invariant with increasing CPC concentration, suggesting that if there is any uptake of the cationic surfactant, then no further swelling occurs. At pH 7, on the other hand, where the microgel particles carry a net negative charge, the hydrodynamic diameter of the microgel particles decreases steadily as a function of increasing CPC concentration. This suggests that there is, as expected, a strong electrostatic attraction of the microgel particles for the CPC molecules at pH 7 (note that the CMC of CPC is ~0.9 mM at 25 °C [28], so the concentration range studied is below the CMC).

The electrophoretic mobility data shown in Fig. 5 are in accord with the hydrodynamic diameter data presented in Fig. 4. At pH 3, the mobility of the particles is independent of CPC concentration, whilst at pH 7 the mobility of the microgel particles becomes less negative with increasing CPC concentration, as CPC molecules are absorbed into their bulk. At the highest CPC concentration studied (0.5 mM), the mobility is very slightly positive. At higher CPC concentrations one might expect the mobility to become even more positive, as further CPC molecules bind to the microgel particles.

The absorption isotherm for CPC into the microgel particles is shown in Fig. 6, at pH 3 and pH 7. Rather surprisingly, at first sight, there does appear to be significant absorption of the CPC molecules at pH 3, where the microgel particles are also cationic, even though this is insufficient to affect either the hydrodynamic diameter (Fig. 4) or the electrophoretic mobility (Fig. 5) of the microgel particles. There must be a non-electrostatic mechanism leading to the absorption. This is most likely hydrophobic bonding of the tails of the surfactant molecules to the isopropyl moieties/*tert*-butyl within the polymer network comprising the microgel particles. The microgel particles must be sufficiently swollen to allow the surfactant molecules to diffuse into the network against the electrostatic repulsion. At pH 7, the absorbed amount, at any given CPC concentration, is higher than at pH 3 (Fig. 6). This is to be expected, since electrostatic attraction of the cationic surfactant head groups to the anionic sites within the microgel particles now plays a major role, as was discussed earlier. However, this does not imply that the hydrophobic

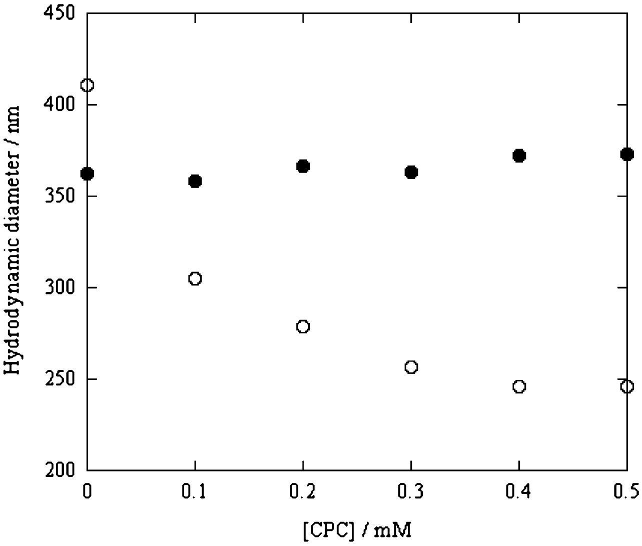

Fig. 4 Hydrodynamic diameter of the polyampholyte microgel particles as a function of CPC concentration (25° C) at (*filled circle*) pH 3 and (*open circle*) pH 7

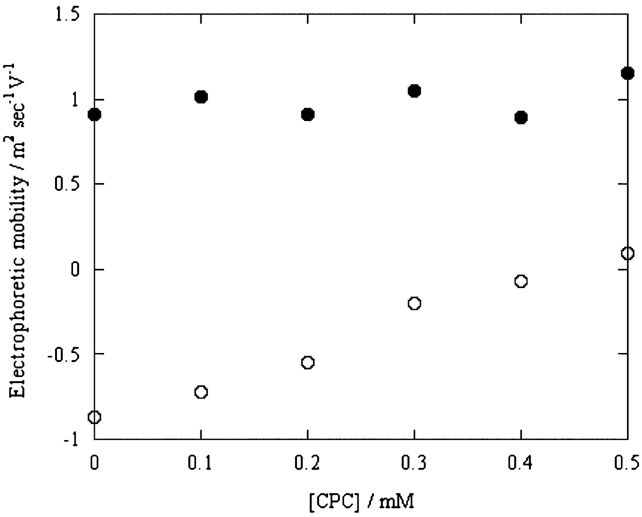

Fig. 5 Electrophoretic mobility of the polyampholyte microgel particles as a function of CPC concentration (25° C) at (*filled circle*) pH 3 and (*open circle*) pH 7

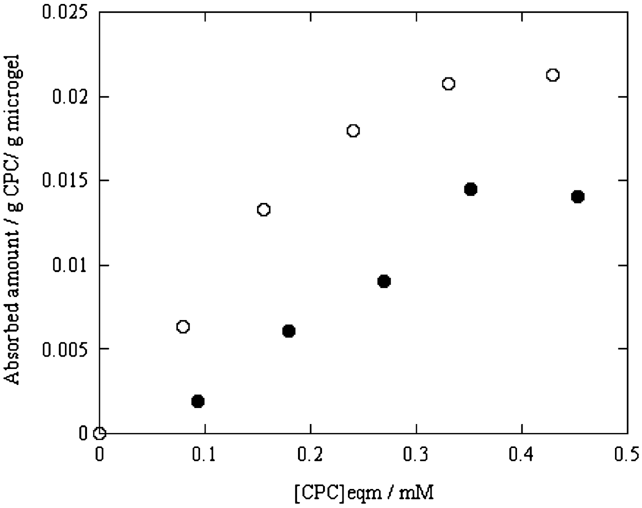

Fig. 6 Absorbed amount of CPC into the polyampholyte microgel particles as a function of equilibrium CPC concentration (25° C) at (*filled circle*) pH 3 and (*open circle*) pH 7

interaction mechanism, operating at pH 3, referred to above, does not contribute in addition. There is no way of telling just how significant the hydrophobic effects are at pH 7. Nerapusri et al. [27] have recently investigated the absorption of CPC molecules into polyNIPAM and poly (NIPAM-co-acrylic acid) microgel particles, over a greater concentration range than here (spanning the CMC in fact) and concluded that surfactant *aggregates* form inside the microgel particles, irrespective of whether the electrostatic or hydrophobic attraction mechanism is dominant.

One implication of the results presented in Fig. 6 is that CPC should be released from the microgel particles, on switching the pH from 7 to 3, although the released amount would be less than 50% (depending on the initial CPC concentration). However, Nerapusri et al. [27], have demonstrated that increased desorption of CPC may be obtained by raising the temperature to ~40 °C, in addition to switching the pH. A “squeezing” mechanism was proposed, whereby, as the microgel particles deswell on raising the temperature, the CPC molecules are (sterically) forced out of the interior of the microgel particles.

2. Triton X-100

The hydrodynamic diameter of the microgel particles, as a function of Triton X-100 concentration, is shown in Fig. 7 for pH 3 and 7. The trends are similar at both pH values. Up to around the CMC for Triton X-100, which is 0.3 mM [29], there is an increase in hydrodynamic diameter. Above the CMC, the hydrodynamic diameter decreases. Similar maxima in size have been observed by this group before [22] in the case of Triton X-100 absorbed into polyNIPAM and poly(NIPAM-*co*-acrylic acid) microgel particles. The initial increase in hydrodynamic diameter is due to the binding of surfactant into the microgel. Clearly, this absorption must, at some concentration, attain a maximum value, and the subsequent decrease in size has been previously ascribed by us [22] to the build-up of free surfactant in solution. This causes an osmotic balance in the reverse direction, leading to shrinkage of the microgel particles.

The absorbed amounts of Triton X-100 into the microgel particles, as a function of surfactant concentration, are shown in Fig. 8 for pH 3 and 7. At pH 3, the absorbed amount is much lower than at pH 7. At pH 3, where the –COOH groups inside the microgel particles are mostly in their unionised form, the surfactant absorbs mainly by a H-bonding mechanism between the ether oxygens in the ethylene oxide head groups of the surfactant molecules and

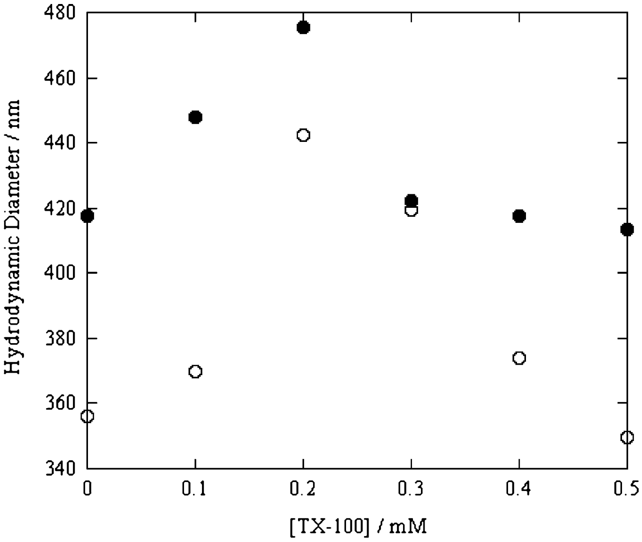

Fig. 7 Hydrodynamic diameter as a function of Triton X-100 concentration (25° C) at (*filled circle*) pH 3 and (*open circle*) pH 7

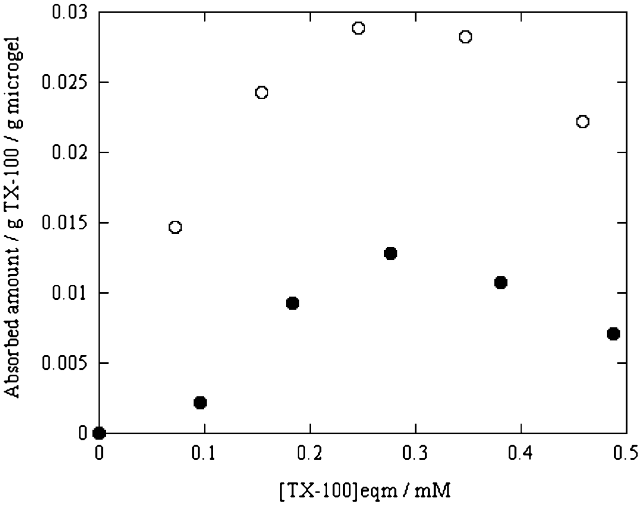

Fig. 8 Absorbed amount of Triton X-100 into the polyampholyte microgel particles as a function of equilibrium Triton X-100 concentration (25(C) at (*filled circle*) pH 3 and (*open circle*) pH 7

the hydrogen on the carboxyl groups inside the microgel particles. At pH 7, there can be no such H-bonding, either with the now largely ionised carboxylic acid groups (or indeed the DMAEM units), so at the first site, it is surprising that the absorbed amounts are so much higher than at pH 3. One can only surmise that the high level of absorption at pH 7 is due a hydrophobic interaction between the Triton X-100 tail group and the largely non-polar DMEAM groups within the microgel particles. At pH 3, the DMAEM groups are strongly protonated and therefore much more polar, so this hydrophobic interaction will be greatly diminished.

It is notable that, above the CMC, there seems to be a slight *decrease* in the absorbed amount of Triton-X100, with increasing Triton-X100 concentration. This behaviour is most unusual, but it is observed at both pH 3 and 7. It should be recalled that the hydrodynamic diameter passes through a maximum around the CMC, again at both pH 3 and 7 (Fig. 7). As explained earlier, the decrease in size of the microgel particles at concentrations above the CMC is caused by the build-up of free surfactant in solution. This decrease in size could have a “squeezing” effect on the Triton X-100 molecules within the polymer network comprising the microgel particles. It is significant in this regard that the cross-link density in these particular microgel particles is rather high (11 wt.% of cross-linking monomer used in the particle preparation), so the average pore size within the microgel particles is likely to be quite small, and comparable in size to the Triton X-100 molecules with their somewhat bulky head groups.

Conclusions

Polyampholyte microgel particles, containing both acid and base groups, have been prepared and characterised. They show the expected swelling profiles as a function of pH for polyampholytes containing weak acid and weak base groups. The uptake and release of both cationic surfactant and non-ionic surfactant molecules has been shown to depend on pH. It is concluded that three types of absorption mechanism play a role, depending on the surfactant type and the pH: electrostatic interactions, H-bonding and hydrophobic bonding.

Acknowledgement MB and BV would like to acknowledge GSK, Weybridge, UK, for provision of research funds to enable this research to be carried out.

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