

**BINDING OF CETYLPYRIDINIUM CATION BY POLY(ACRYLIC ACID).  
EFFECT OF POLYMER CHARGE DENSITY<sup>1</sup>**

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**Abstract:** The effect of polymer charge density on the binding of cetypyridinium cation (CP<sup>+</sup>) to poly(acrylic acid) (HPA) has been investigated by using a potentiometric technique based on surfactant cation-selective membrane electrode. The amount of binding,  $\beta$ , has been determined at constant polyelectrolyte concentration ( $m_p = 5 \times 10^{-4}$  monomol/kg) and at five degrees of ionization of the acid ( $\alpha = 0.0, 0.27, 0.53, 0.76, \text{ and } 1.0$ ) in aqueous solutions without added simple electrolyte at 25 °C. It has been observed that appreciable binding of CP<sup>+</sup> cation to PA<sup>-</sup> anion starts at the total detergent concentration about  $1 \times 10^{-5}$  mol/kg which is well below the critical micellization concentration, cmc, of this surfactant. The free surfactant concentration at this point is still lower, about  $3 \times 10^{-7}$  mol/kg. A surprising finding is that the onset of binding is independent on the degree of ionization,  $\alpha$ , of the acid. On the contrary, the plateau region which is reached for  $\beta$  values below 1 depends considerably on  $\alpha$ . In this range,  $\beta$  values increase with increasing degree of ionization. Above the plateau, at free surfactant concentrations higher than  $5 \times 10^{-4}$  mol/kg,  $\beta$  again increases sharply and even reaches values higher than 1. This has been attributed to the formation of the second layer of bound surfactant.

<sup>1</sup> Dedicated to the memory of Professor Jože Šiftar

## INTRODUCTION

A striking feature of polymer/ surfactant systems is their mutual complexation in dilute aqueous solutions. The case of polyelectrolyte/ionic surfactant pairs in which the polyion and surfactant ion carry the opposite charge is of special interest. The association in this case is especially strong and usually starts at surfactant concentrations well below the critical micellization concentration, cmc. A convenient way to characterize various polyion/surfactant ion systems is in terms of critical aggregation concentration, cac, which is defined as the total surfactant concentration at the onset of cooperative binding [1-5]. Cac can be several orders of magnitude lower than the cmc depending on the nature of the polyion and surfactant ion. The lowest cac values have been obtained for polyelectrolytes with high linear charge density. Another important parameter in describing polyelectrolyte/surfactant interactions is the amount of binding defined as the fraction of charges on the polymer chain that are occupied by surfactant ions [6-10]. The amount of binding and the related parameters are also influenced by various polyion properties.

The effect of the linear charge density parameter of the polyion on the above mentioned surfactant binding parameters has been studied thoroughly for different types of polyelectrolytes. The results, obtained by various methods, show that in general the cac values increase with increasing charge density on the polyion [1-5], but are influenced also by the specific nature of the polymer backbone [2,4,10,11]. In addition, there is no simple relationship between the amount of binding and the polyion linear charge density. Kwak et al. [7] have investigated binding of dodecyltrimethylammonium, DTMA<sup>+</sup>, and tetradecyltrimethylammonium, TTMA<sup>+</sup>, cations by several synthetic and naturally occurring polyelectrolytes containing carboxylic groups as fixed charges. They have concluded that, although the charge density of the polymer is an important parameter, other factors such as hydrophobic character, flexibility, and detailed local structure of the polymer also strongly influence the binding process. To isolate the effect of the charge density from the effect of the chemical structure we have decided to investigate the binding of a cationic surfactant, cetylpyridinium chloride (CPC), to

polyacrylate anion (PA<sup>-</sup>). Poly(acrylic acid), HPA, is a flexible relatively hydrophilic polyelectrolyte for which the charge density can be varied by changing the degree of ionization,  $\alpha$ , of the acid. The degree of ionization,  $\alpha$ , appears in the linear charge density parameter,  $\lambda$ , in the following way [12]

$$\lambda = \frac{\alpha e_0^2}{4\pi\epsilon_0\epsilon kTb} \quad (1)$$

Here  $e_0$  is the protonic charge,  $\epsilon_0$  and  $\epsilon$  are the permittivity of vacuum and the dielectric constant of solvent,  $k$  is the Boltzmann constant, and  $b/\alpha$  is the linear charge spacing between two adjacent charges on the polyacrylic chain. Obviously, the latter depends on the degree of ionization. The structural value of  $b/\alpha$  is in the case of the fully ionized sodium salt of polyacrylic acid (NaPA,  $\alpha = 1.0$ ) equal to 0.252 nm [12] and gives the value 2.83 for  $\lambda$  in aqueous solutions at 25 °C. Parameter  $\lambda$  can thus be varied by changing  $\alpha$ . The aspects of the influence of polyion charge density were studying by Hansson and Almgren [4] for binding of DTMA<sup>+</sup> to sodium (carboxymethyl)cellulose, NaCMC, with various degrees of carboxymethylation resulting in different linear charge densities of the polyion. They have found that cac and cooperativity increase with increasing charge density of the polyelectrolyte. We wanted to compare their results with findings in CP<sup>+</sup>/PA<sup>-</sup> system.

One of the fundamental and necessary methods to study interactions between polyelectrolytes and surfactants is the determination and analysis of surfactant binding isotherms. They can be obtained by various experimental procedures such as potentiometry or equilibrium dialysis. Potentiometric method is among the most sensitive ones and has been used very successfully in the past decades [6-10]. It is based on the use of surfactant ion-selective electrodes, which make it possible to determine the amount of free surfactant in a polymer/surfactant solution and thereby the binding isotherm. We have constructed a membrane electrode selective to CP<sup>+</sup> ions in order to study the binding of this surfactant cation to PA<sup>-</sup> anion at various degrees of ionization.

## EXPERIMENTAL SECTION

### Materials

As a starting material poly(acrylic acid), HPA (K & K Laboratories, Inc., Plainview, N. Y.) with a molecular weight around 10 000 g/mol was used. Prior to use, an aqueous solution of the acid was exhaustively dialyzed against water [12]. The concentration of the stock solution of HPA was determined by potentiometric titration with a standard NaOH solution. From the acid, the sodium salt, NaPA, was prepared by adding to the acid a corresponding amount of NaOH. By mixing HPA and NaPA stock solutions of known concentrations, the solutions of polyacrylate anion, (H,Na)PA, with various degrees of ionization ( $\alpha = 0.0, 0.27, 0.53, 0.76,$  and  $1.0$ ) were obtained. For the study of binding, a constant concentration of  $\text{PA}^-$ , equal to  $m_p = 5 \times 10^{-4}$  monomol/kg, was used in all experiments.

The surfactant, N-cetylpyridinium chloride, CPC (Kemika, Zagreb), was thoroughly purified by repeated recrystallization from acetone and vacuum dried at 50 °C. Surfactant stock solutions, either in pure water or in aqueous polyelectrolyte solutions, were prepared by weight from dried substances. The triple distilled water was used in all experiments.

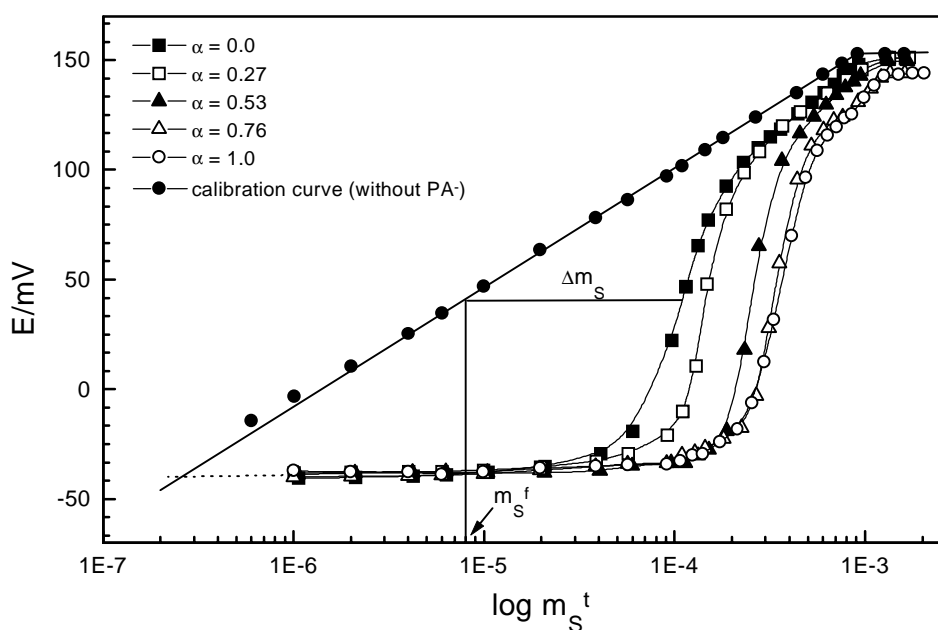
### Emf-Binding Studies

PVC-membrane electrode selective to  $\text{CP}^+$  surfactant cation was constructed as described in the literature [6]. The binding isotherms were determined in aqueous solutions without added simple electrolyte at 25 °C. The membrane electrode potential was determined relative to the standard calomel electrode. The emf was measured with an ISKRA pH meter MA 5740. First, the calibration curve presenting the dependence of the emf on the surfactant concentration in the absence of  $\text{PA}^-$  was recorded. Afterwards, the binding isotherms were determined in the presence of constant polyelectrolyte concentration for various  $\alpha$  values. The titration technique was used to vary the surfactant concentration in a wide range from slightly below  $1 \times 10^{-6}$  mol/kg to about  $2 \times 10^{-3}$  mol/kg. The upper concentration is already above the cmc value for CPC in water.

The reported cmc values in the literature range from  $5.8 \times 10^{-4}$  mol/kg at 25 °C to  $7.0 \times 10^{-4}$  mol/kg at 30 °C [8].

## RESULTS AND DISCUSSION

Potentiometric measurements are shown in Figure 1. The calibration curve obtained in the absence of polyacrylate is a straight line in a wide concentration range from nearly  $1 \times 10^{-6}$  mol/kg to the cmc. The slope of the line equals 56 mV/decade which is somewhat lower than the theoretical value 59.1 mV/decade. However, the

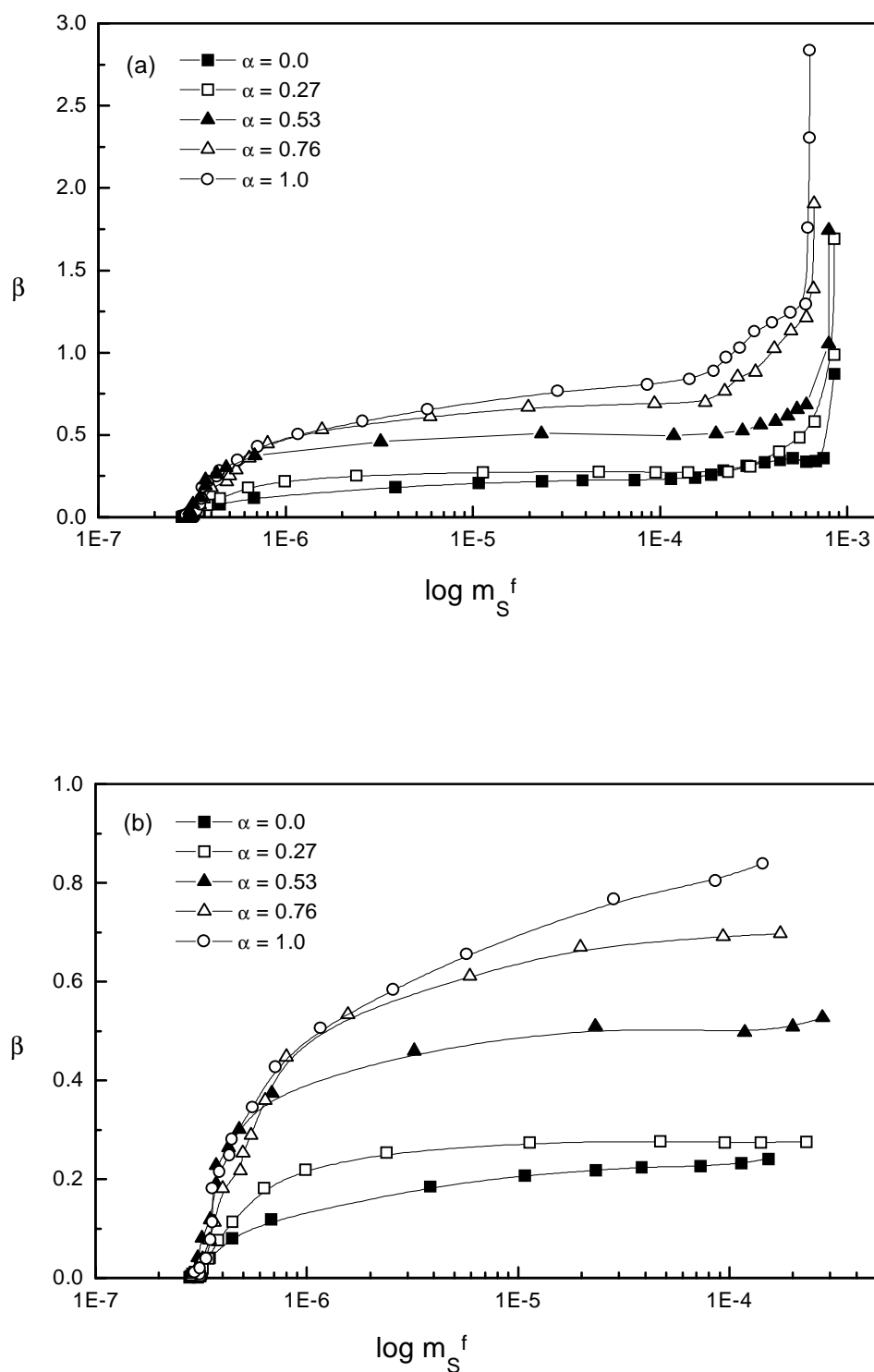


**Figure 1.** Response of the  $CP^+$  electrode to changes in CPC concentration in aqueous solutions without added simple electrolyte at 25 °C: (●) calibration curve in solutions without added  $PA^-$  ( $m_p = 0$ ) and (■, □, ▲, △, ○) potentiometric curves in solutions with added  $PA^-$  ( $m_p = 5 \times 10^{-4}$  m) at various degrees of ionization,  $\alpha$  (values for  $\alpha$  are given in the picture);  $\Delta m_s$  is the amount of  $CP^+$  bound by polyelectrolyte and  $m_s^f$  is the corresponding equilibrium concentration of free  $CP^+$  cations.

reproducibility of the calibration is very good. The observed potentiometric curves in the presence of  $\text{PA}^-$  at various  $\alpha$  values deviate from the calibration line due to the binding of surfactant by polyelectrolyte as indicated in Figure 1. Here,  $\Delta m_s$  represents the amount of  $\text{CP}^+$  bound to  $\text{PA}^-$ . From this, the amount of binding,  $\beta$ , was calculated from expression [6]

$$\beta = \frac{\Delta m_s}{m_p} = \frac{m_s^t - m_s^f}{m_p} \quad (2)$$

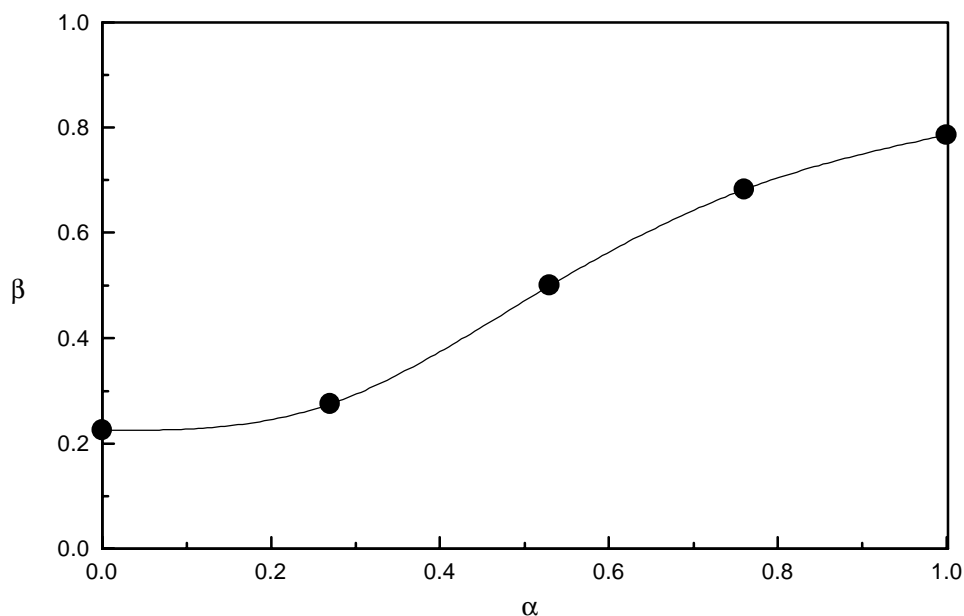
where  $m_s^t$  and  $m_s^f$  are the total and the free surfactant concentrations, respectively, expressed in mol/kg, and  $m_p$  is the constant polyion concentration in monomol/kg. The resulting binding isotherms, i.e., plots of the amount of binding  $\beta$  vs.  $\log m_s^f$ , are presented in Figures 2(a) and 2(b). They have a typical sigmoidal shape associated with the cooperative character of binding of surfactants to polymers. The initial steep rise of  $\beta$  is observed at approximately the same free surfactant concentration ( $\sim 3 \times 10^{-7}$  mol/kg) irrespective of the degree of ionization of the polyacid. The influence of  $\alpha$  on the amount of binding  $\beta$  is seen later in the part of the isotherms where  $\beta$  already reaches the relatively constant plateau value. Here,  $\beta$  depends strongly on  $\alpha$ . The first finding is somewhat surprising. In NaCMC solutions [4] with different linear charge density parameters,  $\lambda$  (ranging from 0.8 to 3.0), the onset of binding of  $\text{DTMA}^+$  was found to shift towards lower free surfactant concentrations with increasing  $\lambda$ . At the same time, the initial slope of the binding isotherm, which is a measure of the extent of cooperativity, increased with increasing  $\lambda$ . On the contrary, the amount of binding in the plateau region where  $\beta$  levels off showed no regular dependence on charge density in the system NaCMC/ $\text{DTMA}^+$ . For binding of  $\text{CP}^+$  to  $\text{PA}^-$  (cf. Figure 2(b)), the slope of the cooperative part of the isotherms also increases with increasing  $\lambda$  (which parallels  $\alpha$ ). However, the onset of binding seems to be independent on  $\lambda$ . At present, it is difficult to explain these differences but they could be ascribed to a less flexible character of NaCMC in comparison with NaPA. Also, the surfactant head group in our study is different than in reference [4].



**Figure 2.** (a) Binding isotherms of CP<sup>+</sup> cations to poly(acrylate) anion, PA<sup>-</sup>, in aqueous solutions without added simple electrolyte at 25 °C for various degrees of ionization,  $\alpha$ , of the acid. (b) The enlargement of the plot for free surfactant concentrations below  $5 \times 10^{-4}$  mol/kg ( $\beta \leq 1$ ). Symbols as in Figure 1.

At higher free surfactant concentrations (above  $m_s^f \approx 5 \times 10^{-4}$  mol/kg, cf. Figure 2(a)),  $\beta$  again increases and even reaches values higher than 1. The sharp increase of  $\beta$  beyond the plateau has already been observed for example in binding of tetradecyltrimethylammonium bromide, TTMAB, by poly(methacrylic) acid and by poly(acrylic) acid [13]. In the case of polyacrylate, this finding was attributed to the formation of a second layer of adsorbed surfactant. This is also visually observed when performing the titration. In this range, solutions developed turbidity, at first very marked but later less and less pronounced.

Let us return to the part of the binding isotherms below  $\beta = 1$  (see the enlargement of binding isotherms for  $\beta \leq 1$  in Figure 2(b)). As mentioned before, the plateau values of  $\beta$  depend considerably on  $\alpha$ . They are plotted against  $\alpha$  in Figure 3. The  $\beta$  values for  $\alpha = 0.27, 0.53,$  and  $0.76$  lie on a straight line, giving intersections at  $\alpha = 0.0$  equal to  $0.05$  and at  $\alpha = 1.0$  equal to  $0.90$ , respectively. The observed average  $\beta$



**Figure 3.** *Dependence of the amount of binding,  $\beta$ , in the plateau region of binding (at free surfactant concentration  $m_s^f \cong 5 \times 10^{-5}$  mol/kg) on the degree of ionization,  $\alpha$ .*



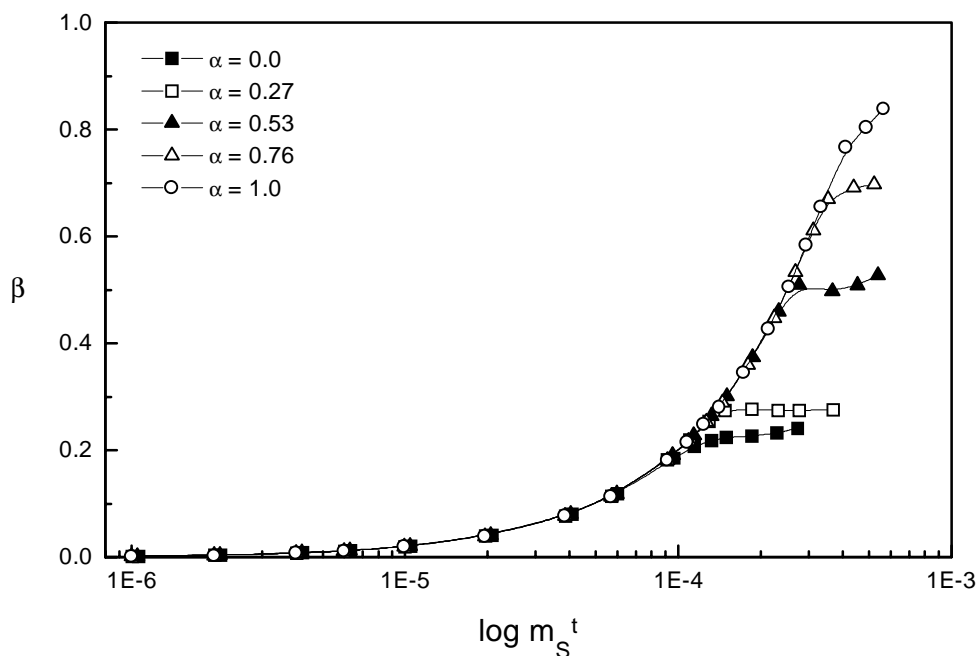
value for the fully ionized acid ( $\alpha = 1.0$ ) is around 0.79. In fact, above the leveling off of the binding isotherm for NaPA  $\beta$  increases from about 0.5 to 0.9 (cf. Figure 2(a)). The higher  $\beta$  value would concord with the straight line drawn through the middle three points in Figure 3. Recently determined amount of binding of  $\text{CP}^+$  to NaPA by fluorimetry [14] is 0.8 and agrees well with the potentiometric result in this paper. Similar  $\beta$  values were obtained also for binding of alkylpyridinium ions with shorter chain lengths to NaPA. For dodecylpyridinium chloride, DPC, and for tetradecylpyridinium bromide, TPB, binding tends to level off above  $\beta \approx 0.70$  [8]. We can conclude from this that our determination is reasonable.

The straight line through  $\beta$  vs.  $\alpha$  for the middle points (cf. Figure 3) would predict nearly no cooperative binding of  $\text{CP}^+$  to the acid, HPA ( $\alpha = 0.0$ ). The intersection at  $\alpha = 0.0$  gives  $\beta$  around 0.05. However, it has to be stressed that neutral polymers also interact cooperatively with ionic detergents in water. Cabane has shown [15] that poly(ethylene oxide) chain cooperatively interacts with the interface of surfactant micelle by replacing water molecules in the vicinity of the surfactant head group. The polymer is wrapped around the aggregated surfactant. In summary, we can say that the obtained influence of the charge density on the amount of binding is reasonable.

Figure 4 shows the dependence of  $\beta$  on the logarithm of the total surfactant concentration ( $\log m_s^t$ ). We can see that the total surfactant concentration at which cooperative binding of  $\text{CP}^+$  to  $\text{PA}^-$  starts is about  $1 \times 10^{-5}$  mol/kg. This is nearly two orders of magnitude lower than the cmc and is in the literature ascribed to the cac value [3]. We have to stress also that  $m_s^t$  (i.e. cac) at the onset of binding seems to be independent on the linear charge density of the polyion, i.e. on the degree of ionization  $\alpha$ , as was discussed previously for the influence of  $\alpha$  on the concentration of free surfactant at the point where appreciable binding starts.

Usually, besides potentiometrically cac values are very often determined fluorimetrically [16]. Unfortunately, alkylpyridinium cations are quenchers of fluorescence and consequently they cannot be investigated by this very sensitive method. There are in fact no fluorimetrically determined cac values for alkylpyridinium surfactants published in the literature. So we can compare our results only with the results for similar

cationic surfactants, e.g. alkyltrimethylammonium salts. The  $cac$  for DTMAB/NaPA is  $3 \times 10^{-5}$  mol/kg [2] and the results obtained from the binding isotherms [7] are in good agreement with fluorimetry. Taking into account that the surfactant in our study has longer hydrocarbon chain and different head group the obtained lower  $cac$  is understandable. In addition, the onset of binding of  $CP^+$  to  $PA^-$  is comparable to the result obtained for binding of  $CP^+$  to a strong polyelectrolyte sodium (polystyrenesulfonate), NaPSS, which has the same linear charge density parameter as the fully ionized poly(acrylic) acid, that is NaPA ( $\alpha = 1.0$ ). It has been observed by potentiometric and calorimetric experiments [10] that appreciable binding of  $CP^+$  to  $PSS^-$  also starts at approximately  $m_s^t \approx 1 \times 10^{-5}$  mol/kg as in the  $PA^-$  case. The difference is, however, that in NaPSS solutions this cationic surfactant is almost completely associated with the polyanion ( $\beta \approx 1$ ) [10,14] whereas in NaPA solutions the amount of binding is weaker ( $\beta \approx 0.78$ ). Another indication of stronger interaction of  $CP^+$  cations with  $PSS^-$



**Figure 4.** The amount of binding,  $\beta$ , as a function of the logarithm of the total surfactant concentration ( $\log m_s^t$ ). Symbols as in Figure 1.

anions is the concentration of free surfactant ions,  $m_s^f$ , at the onset of binding. This is around  $1 \times 10^{-8}$  mol/kg in the presence of 0.01 M NaCl [10] and is expected to be even lower in solutions without added salt. For CP<sup>+</sup>/PA<sup>-</sup> system  $m_s^f$  is considerably higher, around  $3 \times 10^{-7}$  mol/kg (see discussion above and Figure 2). This difference in binding of cationic surfactants to polyelectrolytes with the same charge density but different side groups on the polymer chain has previously been ascribed to the more hydrophobic character of the PSS<sup>-</sup> anion [5, 11, 14].

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## POVZETEK

Z uporabo potenciometrične tehnike, osnovane na uporabi surfaktantne ionoselektivne elektrode, smo proučevali vpliv gostote naboja na polimeru na vezavo cetilpiridinijevega kationa (CP<sup>+</sup>) na poliakrilno kislino (HPA). Stopnjo vezanja,  $\beta$ , smo določili pri konstantni koncentraciji polelektrolita ( $m_p = 5 \times 10^{-4}$  monomol/kg) in za pet stopenj ionizacije kisline ( $\alpha = 0.0, 0.27, 0.53, 0.76, \text{ and } 1.0$ ) v vodnih raztopinah brez dodanega enostavnega elektrolita pri 25 °C. Opazili smo, da se znatno vezanje CP<sup>+</sup> kationa na PA<sup>-</sup> anion prične, ko je celotna koncentracija detergenta okrog  $1 \times 10^{-5}$  mol/kg, kar je precej pod kritično micelno koncentracijo, cmc, za ta surfaktant. Koncentracija prostega surfaktanta v tej točki je še nižja, okrog  $3 \times 10^{-7}$  mol/kg. Presenetljiva ugotovitev je, da je pričetek vezanja neodvisen od stopnje ionizacije kisline,  $\alpha$ . Nasprotno pa je območje, kjer  $\beta$  doseže približno konstantno vrednost, precej odvisno od  $\alpha$ . Stopnja vezanja v tem področju narašča z naraščajočo stopnjo ionizacije. Pri koncentracijah prostega surfaktanta nad  $5 \times 10^{-4}$  mol/kg  $\beta$  ponovno močno naraste in celo doseže vrednosti, ki so večje od 1. To smo pripisali možnosti, da surfaktant tvori drugo vezano plast.