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SHORT COMMUNICATION

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The interaction between *n*-alkyl trimethylammonium bromides with poly(L-aspartate): a thermodynamics study

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Abstract Specific conductivities of a homologous series of *n*-alkyl trimethylammonium bromides (C_8, C_{10}, C_{12} and C_{14}TABs) in the presence of poly(L-aspartate) in glycine buffer at pH 3.2 and 25 °C have been measured over a range of C_nTAB concentrations. From the conductivity changes, the number of surfactant molecules absorbed onto the polymer, the Gibbs free energies of adsorption and the equilibrium constants have been calculated. A statistical thermodynamics analysis was used to obtain the Gibbs free energies of adsorption. The results obtained using both methods are compared and analysed.

Key words *n*-Alkyl trimethylammonium bromides · Specific conductivity · Poly(L-aspartate) · Gibbs free energy of adsorption

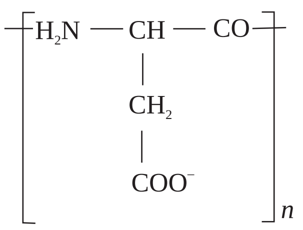
Introduction

With the advent of a range of new polyelectrolytes, comprising both natural backbones, such as polysaccharides, and completely synthetic materials, based on vinyl chemistry, interest in their properties has increased. These macromolecules enjoy a high level of industrial importance in view of their ability to interact with surfactants. Understanding the properties of mixed polymer–surfactant systems has acquired new importance. In fact, such systems have been investigated by a large number of methods, such as equilibrium dialysis [1], surface tension [2], solubility [3], etc.

The case of polymer–surfactant pairs in which the polymer is a polyion and the surfactant is also ionic but bears the opposite charge is of special interest. It should be pointed out that when the respective charges are of the same sign association between the polymer and the surfactant can be expected to be feeble or absent. The fact that the association in the case of oppositely charged polyelectrolytes and surfactants is strong is not surprising since very strong electrical attraction forces are involved. In fact, the association which takes place can be considered to be an ion-exchange process where the electrostatic forces of interaction are reinforced by a cooperative process involving aggregation of the alkyl chains of the bound surfactant molecules. An ion-exchange process would also involve pH shifts as bound hydroxyl (hydronium) ions are displaced by surfactant anions (cations).

A point of interest is the addition of excess surfactant when a second layer of bound surfactant ion, with ionic groups pointing outwards, was attached to the first bound layer through association with the hydrocarbon chains of the first layer.

In previous work we studied the interactions between lysozyme and *n*-alkyl trimethylammonium bromides C_nTAB [4] and between lysozyme and *n*-alkyl sulfates [5] by zeta-potential measurements as a function of concentration and pH. Continuing with our investigation we have studied the interaction of a polypeptide, poly(L-aspartate), the structure of which is shown in Scheme 1, with an aspartic acid monomer unit,



$$\left[H_2N - \underset{\underset{COO^-}{|}}{\underset{CH_2}{\underset{|}{CH}}} - CO \right]_n$$

with a homologous series of C_nTABs (octyl, decyl, dodecyl and tetradecyl) by specific conductivity measurements. The number of C_nTAB molecules adsorbed onto the polymer was determined and the Gibbs free energies of adsorption were calculated on the basis of Page's method. A statistical thermodynamics analysis was used to understand the nature of the interactions between surfactant and polymer.

Experimental

Poly(L-aspartate) (no. P-6762), weight-average molecular mass 31700, residue number 137, was obtained from Sigma Chemical Co. C_8TAB, C_{10}TAB, C_{12}TAB and C_{14}TAB (product nos. 3736, 12144, 86210 and 10294, respectively) were obtained from Lancaster MTM Research Chemicals. The glycine buffer system used was 50 mmol dm^{-3} glycine–hydrochloric acid pH 3.2 (ionic strength 0.0065 mol dm^{-3}).

Specific conductivities were measured at 25 °C using a precision LCR meter (HP4285A) with a colloid dielectric probe (HP E5050A). The colloid dielectric probe was calibrated with aqueous solutions of KCl over the appropriate concentration range using the molar conductivity data of Shedlovsky [6] and Chambers et al. [7]. The measuring cell was immersed in a thermostated bath, with the temperature being controlled to within ±0.01 °C. Water (twice distilled and degassed) was progressively added to a concentrated aqueous solution of surfactant and later to a surfactant plus polyelectrolyte aqueous solution of composition 0.125% w/v using a peristaltic pump (Dosimat, model 655, Metrohm) under the control of a Hewlett-Packard Vectra computer.

Results and discussion

Plots of specific conductivity, κ, for surfactant and poly (L-aspartate) plus surfactant systems are shown in Figs. 1–4 as a function of the molar concentration of surfactant (the polymer concentration was kept constant). These results were analysed to obtain precise values of the critical micelle concentrations (cmc) using the Phillips [8] definition of the cmc as the concentration corresponding to the maximum change in gradient in plots of the solution conductivity versus concentration

$$\left(\frac{\partial^3 \kappa}{\partial m^3}\right)_{m=\mathrm{cmc}} = 0 \ . \qquad (1)$$

The numerical analysis of the data was made by means of a recently developed algorithm based on the Runge–Kutta numerical integration method and the Levenberg–Marquardt least-squares fitting algorithm which allows the determination of precise values of the critical concentrations of drugs and surfactants of low aggregation number [9]. The results of the analysis are shown in Figs. 1–4, where the measured conductivities and Gaussian fits of the second derivative obtained using the previously mentioned algorithm are plotted against molar concentration. The figures show the existence of one minimum of the second derivative and, therefore, of one cmc. This value coincides with the intersection point of the two linear segments of the conductivity–concentration curves. Measurements of aqueous solutions containing only surfactant show two segments with

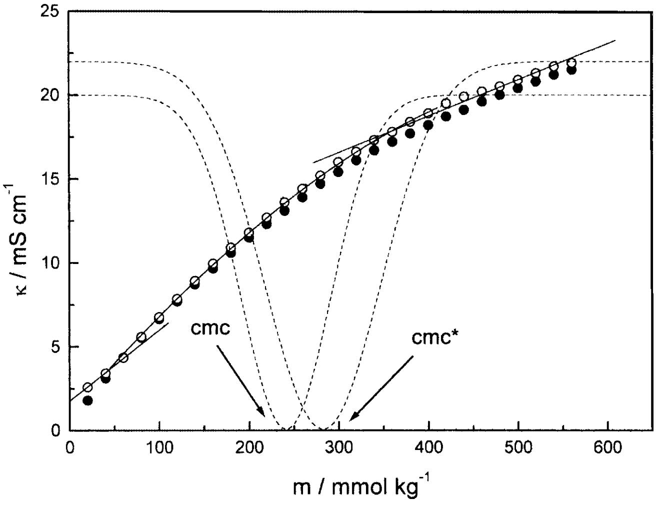


Fig. 1 Specific conductivity, κ, as a function of molality for octyl trimethylammonium bromide (●) and octyl trimethylammonium bromide–poly (L-aspartate) (○). For Figs. 1–5, the *dashed line* represents the second derivative of the conductivity–concentration curve

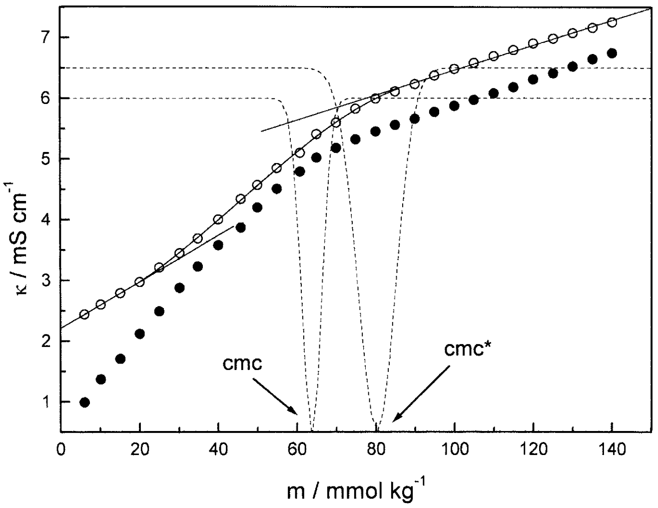


Fig. 2 κ as a function of molality for decyl trimethylammonium bromide (●) and decyl trimethylammonium bromide–poly (L-aspartate) (○)

different slopes as expected, but for the system containing polyelectrolyte plus surfactant three segments with different slopes are obtained. Changes in the slope are due to a variation of the ionic equilibrium in the aqueous medium when different molecular structures appear. Along each segment it can be supposed that kinetic processes remain constant.

If the slope of the polyelectrolyte–surfactant system is lower than that of the surfactant only system, this means that the number of charged particles decreases in the bulk of the solution, i.e. the surfactant is being adsorbed onto the polymer. When the surfactant concentration is increased, caused by a variation in conductivity, no more is adsorbed onto the polymer so it remains in the bulk of the solution and an increment in the slope results. Finally, the free surfactant in the solution reaches a critical concentration and the formation of micelles starts. This mechanism was confirmed by other researchers and other methods [10–12].

Values of the cmc in the presence and absence of polyelectrolyte are shown in Table 1. From this result we can observe how the presence of a polyelectrolyte in the solutions raises the cmc values. This result is to be expected if we consider that the polyelectrolyte acts like an interface that allows surfactant molecules to be adsorbed onto it, which means that more surfactant molecules are needed in the bulk of the solution until the cmc is reached. In Fig. 5 we show the variation of the logarithm of the cmc in mole fraction against the number of alkyl chain carbon atoms. For both systems, with and without polymer, the experimental data show a linear dependence, but the presence of the polymer resulted in a difference between both cmcs, which increases with the alkyl length.

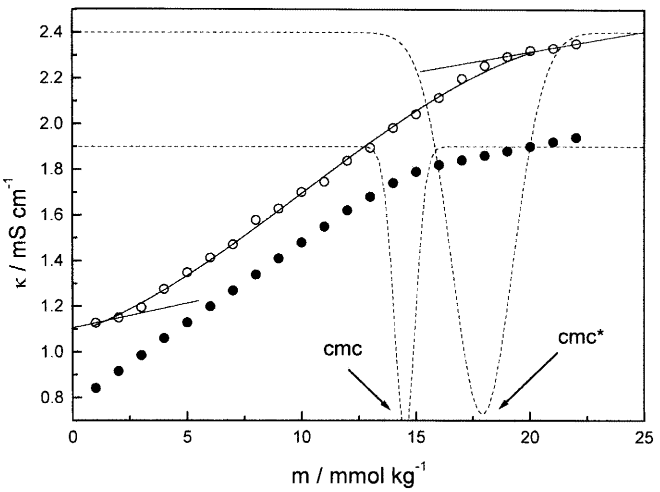


Fig. 3 κ as a function of molality for dodecyl trimethylammonium bromide (●) and dodecyl trimethylammonium bromide–poly (L-aspartate) (○)

Table 1 Critical micelle concentration values for *n*-octyl, *n*-decyl, *n*-dodecyl, and *n*-tetradecyl trimethylammonium bromides (*C_8TAB*, *C_{10}TAB*, *C_{12}TAB*, *C_{14}TAB*) (*cmc*) and for C_8TAB–, C_{10}TAB–, C_{12}TAB– and C_{14}TAB–poly (L-aspartic acid) (*cmc**) systems at 25 °C and the number of adsorbed molecules (*v*)

	cmc (mmol kg^{-1})	cmc* (mmol kg^{-1})	v
C_8TAB	241.0	272.1	214
C_{10}TAB	63.7	80.2	142
C_{12}TAB	14.5	17.9	71
C_{14}TAB	2.6	5.4	37

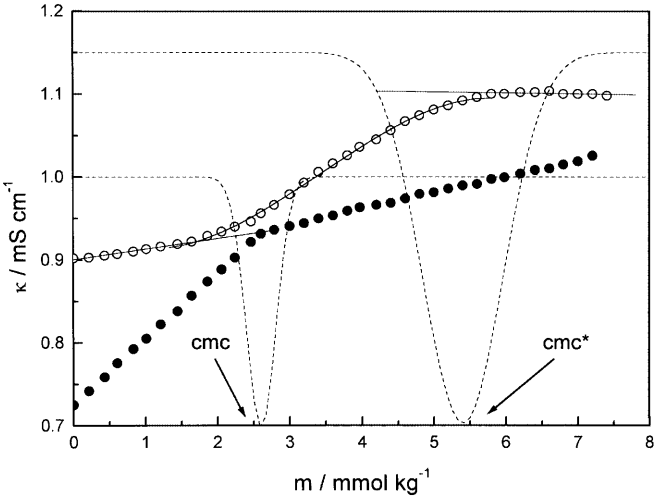


Fig. 4 κ as a function of molality for tetradecyl trimethylammonium bromide (●) and tetradecyl trimethylammonium bromide–poly (L-aspartate) (○)

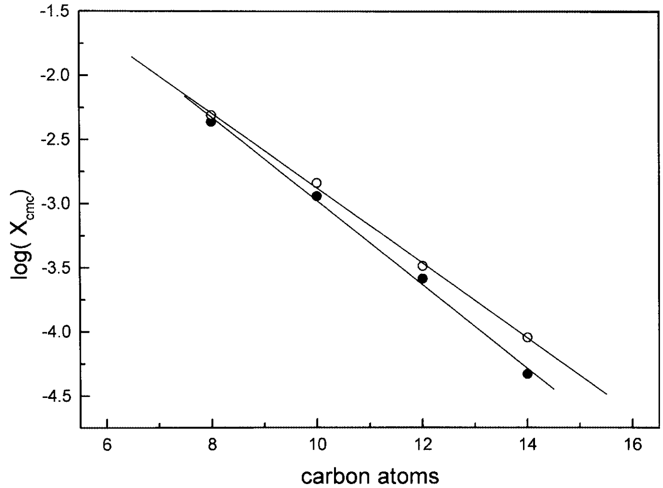


Fig. 5 Logarithm of critical micelle concentration in mole fraction, $\log X_{cmc}$, of *n*-alkyl trimethylammonium bromides as a function of the number of alkyl chain carbon atoms in the absence (●) and presence of poly (L-aspartate) (○)

The average number of surfactant molecules adsorbed onto the polymer, v, can be calculated from the difference between the cmc for surfactant only and the value obtained in the presence of the polymer. This difference is due to the adsorption of the surfactants onto the polymer. v is obtained by dividing the difference by the number of polymer molecules. The results are listed in Table 1. The number of molecules adsorbed increases as the alkyl chain length decreases; these values are lower than the number of residues, 137, for C_{14} and C_{12} and higher for C_{10} and C_8.

In this study the Gibbs free energies of adsorption were calculated using the Pace treatment [13, 14]. The equilibrium constant, K_{eq}, as a molality function, for a two-state transition

Polymer(P) ↔ polymer plus surfactant adsorbed (PS)

can be defined as

$$K_{eq}(m) = \frac{PS(m)}{P(m)} , \tag{2}$$

where P(m) and PS(m) are the fraction of the polymer in the native and adsorbed states, respectively, as a function of the molality of the surfactant, $m \cdot$ P(m) and PS(m) are related to the experimental observable (specific conductivity in our case), $\kappa(m)$, by [15]

$$P(m) = 1 - PS(m) = \frac{\kappa_X(m) - \kappa_{PS}(m)}{\kappa_P(m) - \kappa_{PS}(m)} , \tag{3}$$

where $\kappa_P(m)$ and $\kappa_{PS}(m)$ are the dependencies of the variable on the native and adsorbed state respectively and $\kappa_X(m)$ is an intermediate state. From Eq. (3) the expression for the equilibrium constant can be written as

$$K_{eq}(m) = \frac{PS(m)}{P(m)} = \frac{PS(m)}{1 - PS(m)} = \frac{\kappa_P(m) - \kappa_X(m)}{\kappa_X(m) - \kappa_{PS}(m)} . \tag{4}$$

The Gibbs free energy for monomeric surfactant at a given concentration of surfactant, $\Delta G(m)$, is related to the equilibrium constant by

$$\Delta G(m) = -RT \ln K_{eq}(m) \tag{5}$$

and can be obtained experimentally only in the surfactant concentration range where the change is observed experimentally.

Table 2 Equilibrium constant, K_{eq}, and Gibbs free energies of adsorption, ΔG, calculated from Eqs. (4) and (5), respectively, for the four surfactants under study

Surfactant	K_{eq}	ΔG (kJ mol^{-1})
C_8TAB	7.65×10^{-2}	−6.30
C_{10}TAB	5.18×10^{-2}	−7.33
C_{12}TAB	3.39×10^{-2}	−8.37
C_{14}TAB	2.07×10^{-2}	−9.59

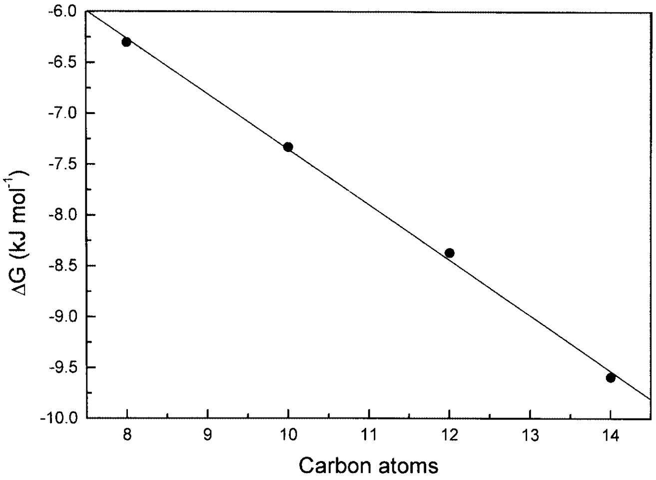


Fig. 6 Gibbs energies of adsorption as a function of the number of alkyl chain carbon atoms

Table 3 Number of arrangements, $\Omega_{n,i}$, entropy, ΔS, and Gibbs free energy, ΔG, for C_{12}TAB and C_{14}TAB

Surfactant	$\Omega_{n,i}$	ΔS (JK^{-1} mol^{-1})	ΔG (kJ mol^{-1})
C_{12}TAB	1.08×10^{40}	766	−3.12
C_{14}TAB	1.43×10^{33}	634	−5.25

The values obtained for the equilibrium constant and the Gibbs free energy are listed in Table 2. These values were fitted to a first-order polynomial, giving the equation (Fig. 6)

$$\Delta G/\text{kJ mol}^{-1} = -(1.89 \pm 0.18) - (0.54 \pm 0.16)n , \tag{6}$$

where n is the number of carbon atoms in the alkyl chain. A regression coefficient of $r^2 = 0.9987$ was obtained. The -CH_2- contribution was found to be about 0.54 kJ mol^{-1}, or 1.34 in kT units. This value is in good agreement with those found for the binding of C_{12}TAB and C_{14}TAB to DNA, 1.19kT [16], and to various carboxylated polyanions, 1.10−1.32 kT [17]. The independent term, −1.89, is obtained when the number of carbon atoms is zero, so it is possible to identify this term with the electrostatic interaction contribution.

To make the statistical analysis of the cooperative ligand binding to the polymer feasible, a simplified model must be constructed which takes into account the structure of the polymer and surfactant, the distribution of binding sites on the polymer, the state of motion of bound ligands and the nature of the interaction between bound ligands [18]. We assume that the polymer is linear, the surfactant is a monocationic ligand, the binding sites exposed to the solvent are equivalent and have the same intrinsic binding constant and the nature of interaction is assumed to be ionic. We consider that the initial interaction between surfactants and proteins is predominantly ionic [19] and the pK_a of the carboxylate side chains of aspartic acid is 3.90, corresponding to 83% of protonation [20] at our experimental pH of 3.2. This last assumption is only applied to C_{14} and C_{12}, which have a lower number of adsorbed molecules than polymer residues.

For *i* ligands binding to *n* binding sites, the number of arrangements, $\Omega_{n,i}$, is given by [21]

$$\Omega_{n,i} = \frac{n!}{(n-i)!\,i!} \quad , \tag{7}$$

which corresponds to an entropy of

$$\Delta S = R \ln \Omega_{n,i} \tag{8}$$

and a Gibbs free energy per ligand bound of

$$\Delta G = -\left(\frac{RT}{i}\right) \ln \Omega_{n,i} \quad . \tag{9}$$

The values obtained for the number of arrangements, the entropy and the Gibbs free energy for C_{12}TAB and C_{14}TAB are shown in Table 3. These values are the Gibbs free energies due to ionic interactions, showing a decrease as the number of adsorbed molecules increases. This fact arises from the saturation of the few specific binding sites, due to the protonation of the polymer, and the subsequent adsorption of surfactant molecules by hydrophobic forces.

The Gibbs free energies calculated using Eq. (5) involve electrostatic and hydrophobic interactions. By subtracting values from this equation and whose Eq. (9), which involve only electrostatic interactions we obtain values for the hydrophobic interaction for C_{14} and C_{12} of 4.29 and 5.25 kJ mol^{-1}, respectively. Hydrophobic interaction must increase with the alkyl chain length, so this seems to be an unexpected result. This event only indicates that hydrophobic interactions become more important as the number of adsorbed molecules increases. In fact for C_{10} and C_8 this number is greater than the number of residues. This can only be explained by assuming that the alkyl chains of the surfactant interact with the alkyl chains of the surfactant adsorbed onto the polymer surface.

The values obtained for the electrostatic interaction are greater than that attributed to this interaction calculated from Eq. (6). This value is just an average of the electrostatic interaction for these surfactants, so for the two smaller surfactants the electrostatic contributions will be remarkably low.

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