



# An improved method for analyzing isothermal titration calorimetry data from oppositely charged surfactant polyelectrolyte mixtures



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## ARTICLE INFO

### Article history:

Received 8 May 2013

Received in revised form 14 August 2013

Accepted 30 August 2013

Available online 10 September 2013

### Keywords:

Surfactant

Polyelectrolyte

ITC

Satake–Yang

SDS

JR-400

## ABSTRACT

In this work an improved description of isothermal calorimetric titration data for surfactants binding to polyelectrolytes is derived and presented. Mixtures of polyelectrolytes and surfactants show a highly complex association behavior, and often a cooperative adsorption of surfactants, following the Satake–Yang binding isotherm is observed. The binding of surfactants is a multistep process, where a non-cooperative adsorption is followed, at higher coverages, by a cooperative process. Accordingly, three processes are considered in the derivation of the ITC formalism: the non-cooperative and cooperative binding and, as the newly introduced contribution, the transition of non-cooperatively bound surfactants to cooperatively bound state. This approach has been tested on sodium dodecyl sulfate binding to the cationic cellulose derivate JR-400 and the results compared with existing models. While similar binding constants are obtained, different values of the binding enthalpies are found, which should be closer to the real values, thereby yielding a more realistic thermodynamic description.

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## 1. Introduction

Mixtures of surfactants and polymers are both of scientific as well as technological importance, as they are present in a variety of formulations [1]. In general, the behavior of such mixtures is quite complex and becomes even more so if they are oppositely charged. Due to the multitude of combinations of polyelectrolytes and surfactants that can be prepared, and the sensitivity to pH and/or ionic strength, a very broad range of phase behavior, microstructure, and rheological and optical properties can be realized. Several reviews discuss these and other properties of complexes of surfactants with synthetic as well as naturally derived polyelectrolytes [2–9].

Apart from the structural features, the thermodynamic description of such mixtures represents a fundamental step for understanding the complex behavior of surfactants and polyelectrolytes in solution. In particular, from the knowledge of binding enthalpy and entropy, a detailed model for the adsorption process can be inferred. A primary role in that context is played by the binding isotherm. The adsorption of surfactants on polymers in general, and of ionic surfactants on oppositely charged polyelectrolytes in particular, has been shown to be highly cooperative [10–

15], despite the binding mechanisms may vary substantially. Such cooperative binding then can also lead to the formation of quite large and interconnected structures that show much more viscous properties than the individual components [16,17]. However, the origin of the cooperativity can in most cases be ascribed to the hydrophobic interactions among the surfactant hydrophobic tails [11,12].

Several binding isotherm have been derived for the adsorption of surfactants onto polymers [14,18–22]. A model that describes ionic surfactants binding to oppositely charged polyelectrolytes particularly well is the Satake–Yang model [14] based on the Zimm–Bragg theory [23]. It is noteworthy that the same formalism was obtained some years earlier by Gerhard Schwarz, with the aim to describe the binding of small molecules, such as metal ions, dyes, drugs, etc., to polyelectrolytes [20]. In this formalism the polymer is modeled as a linear array of binding sites, which can be free, non-cooperatively occupied or cooperatively occupied. The fraction of occupied binding sites  $\Theta$  is given by [20]:

$$\Theta = \frac{1}{2} \left( 1 + \frac{KuC_f - 1}{(KuC_f - 1)^2 + 4KC_f} \right), \quad (1)$$

with  $Ku$  and  $K$  being the equilibrium constants for the cooperative and non-cooperative binding process, respectively.  $u = Ku/K$  indicates the degree of cooperativity and  $C_f$  is the concentration of free surfactant. The fraction of bound sites which are non-cooperatively occupied is given by [20]:

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$$\chi = \frac{KC_f}{\lambda_0^2} \frac{1 - \Theta}{\Theta}, \quad (2)$$

with  $\lambda_0$  being the larger eigenvalue of the statistical weight matrix [20]:

$$\lambda_0 = 0.5 \left( 1 + KuC_f + \sqrt{(KuC_f - 1)^2 + 4KC_f} \right). \quad (3)$$

The Satake–Yang model is an idealization of the actual binding process of surfactants onto polyelectrolytes, e.g., considering interactions only with the next neighbor and neglecting steric effects which are two of the limitations of the model. Furthermore, the very high cooperativity observed in several mixtures, also of ionic or non-ionic surfactants with neutral polymers, can be alternatively interpreted as a polyelectrolyte induced micellization [3,24–26], a process which would require a different thermodynamic approach. However, despite the stringent approximations of the model, this binding isotherm has been largely employed for the characterization of polymer surfactant mixtures, with  $\Theta$  determined mainly by potentiometric titrations [13,27–29]. These experiments are usually highly accurate, but homemade electrodes are required. Although the Satake–Yang model allows separating the contributions of non-cooperatively and cooperatively bound surfactant to the adsorption isotherm, these quantities cannot be independently determined with electrochemical methods. This problem can be circumvented by the use of isothermal titration calorimetry (ITC) for the thermodynamic characterization of such systems. A further advantage of calorimetric titrations is that, in addition to the binding constants, the binding enthalpies can also be obtained. When combined with a free energy model, ITC measurements result in a complete thermodynamic description of the process. Accordingly, isothermal titration calorimetry has become an increasingly important technique when it comes to characterize the interactions in colloidal systems and several reviews have appeared on the topic [18,30–34]. In particular, ITC has been very frequently employed for determining the interaction between surfactants and polymers, whether being neutral [35–37], oppositely charged [15,18,38–40] or also identically charged [41].

A first approach for an analytical description of the titration curves based on the Satake–Yang model was proposed by Matulis *et al.* [15] and afterwards improved by Lapitsky *et al.* [42]. The authors suggested to describe the heat released per mole of injected surfactant  $\bar{Q}$  by the fraction of injected surfactant binding to the polymer times an average reaction enthalpy  $\Delta\bar{H}$  [42]:

$$\bar{Q} = \frac{C_p(d\Theta/dC_f)}{1 + C_p(d\Theta/dC_f)} \Delta\bar{H}, \quad (4)$$

with  $C_p$  being the concentration of the binding sites and

$$\Delta\bar{H} = \chi\Delta H^{nc} + (1 - \chi)\Delta H^c, \quad (5)$$

where  $\Delta H^{nc}$  and  $\Delta H^c$  are the change in enthalpy associated to the non-cooperative and cooperative binding processes, respectively. Such an approach allows to discern between the non-cooperative and cooperative binding process. However, in this approach the heat arising from non-cooperatively bound surfactant that passes into the cooperatively bound state as their neighboring site are occupied is not taken into account. This leads to an inconsistency in the model as the enthalpy due to rearrangement of surfactant between sites is not considered.

In the following we derive an analytical model that describes a system in which three processes are at work, the non-cooperative binding, the cooperative binding of free surfactants, and the transfer of bound surfactant from the non-cooperatively to the cooperatively bound state, which was not taken into account before and which then renders this a complete description within the

Satake–Yang model. In figure 1 a schematic representation of the three processes, characterized by different binding constants and changes in enthalpy, is reported. This new approach is tested for the binding of sodium dodecyl sulfate to JR-400, a cellulose based cationic polyelectrolyte, using experimental data recently published [43].

## 2. Description of the ITC curves from polyelectrolyte surfactant mixtures

After corrections of the heat of dilutions, the heat of reaction recorded during a calorimetric titration (in our case of a given polyelectrolyte solution that is titrated with a surfactant solution) after each injection is given by the change in amount of species  $X_i$  (surfactant in a given state) weighted for its enthalpy  $H_i$ :

$$Q = \sum_i \Delta X_i H_i. \quad (6)$$

In particular, three states are foreseen for the surfactant: free  $C_f$ , non-cooperatively  $C_b^{nc}$  and cooperatively bound surfactant  $C_b^c$ , each of them defined by an enthalpic content:  $H^f$ ,  $H^{nc}$  and  $H^c$ , respectively. These quantities can be combined as:  $\Delta H^{nc} = H^{nc} - H^f$ ,  $\Delta H^c = H^c - H^f$  and  $\Delta\Delta H = H^c - H^{nc}$ , for the non-cooperative binding and cooperative binding process and for the transition from the non-cooperatively to the cooperatively bound state, respectively.

The system composition is defined by the following set of equations:

$$C_s^{\text{tot}} = C_f + C_b^{nc} + C_b^c, \quad (7a)$$

$$\Theta = (C_b^{nc} + C_b^c)/C_p, \quad (7b)$$

$$\chi = C_b^{nc}/(C_b^{nc} + C_b^c). \quad (7c)$$

According to equation (6) the heat released after each injection is given by

$$Q/V = \Delta C_f H^f + \Delta C_b^{nc} H^{nc} + \Delta C_b^c H^c, \quad (8)$$

with  $V$  being the volume of the reaction vessel and, since during the binding process  $\Delta C_b^{nc} + \Delta C_b^c = -\Delta C_f$ , equation (8) simplifies to:

$$Q/V = \Delta C_b^{nc} \Delta H^{nc} + \Delta C_b^c \Delta H^c. \quad (9)$$

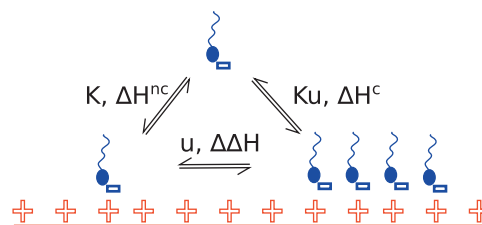
Equation (9) can be rewritten as a function of  $\Theta$  and  $\chi$  substituting from equations (7b) and (7c): and using equation (5):

$$Q/V = C_p \Delta [\Theta(\chi\Delta H^{nc} + (1 - \chi)\Delta H^c)] = C_p \Delta(\Theta\Delta\bar{H}). \quad (10)$$

The heat per injection, normalized by the injected amount of surfactant ( $V\Delta C_s^{\text{tot}} = VC_p\Delta\Theta + V\Delta C_f$ ) is given by:

$$Q/V\Delta C_s^{\text{tot}} = C_p \frac{\Delta(\Theta\Delta\bar{H})}{C_p\Delta\Theta + \Delta C_f}. \quad (11)$$

In differential form:



**FIGURE 1.** Schematic representation of the three equilibria, characterized by different binding constants and enthalpies, which take place when surfactants bind to a polyelectrolyte according to the Yang–Satake model. See text for more details concerning the symbols.

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