

Small Systems Thermodynamics of Polymer–Surfactant Complex Formation

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Polymer–surfactant complex formation is described by small systems thermodynamics at three structural levels: macroscopic system, small-system, subsystem. Such complexes are treated as semi-open small systems of surfactants and segments of a polymer molecule. The internal structure of the small system is characterized as a fluctuation product of a collection of open subsystems of surfactant aggregates and polymer segments. The theory unifies and shows the equivalence of different (adsorption, pseudophase separation, chemical equilibrium) concepts of descriptions. It explains that the polymer–surfactant interaction does not depend on the polymer molecular weight, and that the mean aggregation number of surfactants in the complex increases with the bound amount. The isotherm equation of the surfactant binding on the polymer together with its thermodynamic analysis is given.

Introduction

Surfactants in aqueous solution associate into micelles above a critical concentration range. In three-component surfactant solutions the third component often takes part in the micelle formation (solubilization or mixed micelle formation). In the presence of water-soluble polymers a polymer–surfactant complex forms in which surfactant aggregates are distributed along the polymer chain. All of these phenomena are embraced by the main driving force of the aggregation, a force known as the “hydrophobic effect”: the transfer of the surfactant hydrocarbon chain from water into the micelle core.

The first quantitative model of polymer–surfactant interaction^{1,2} was based on two independent co-operative equilibria of the surfactant, viz. surfactant aggregate formation on the polymer chain and free micelle formation. In refs 1 and 2 the binding of the aggregates on the polymer chain was described as an adsorption process; the surfactant aggregation number was considered as a single constant value both for the micelles and the aggregates. The model explained the general features of polymer surfactant systems, that is, the shape of the binding isotherms of ionic surfactants by polymers, the existence of a critical surfactant concentration for interaction, and the appearance of two break points in the colligative properties vs surfactant concentration curves. The size of the aggregates yielded by this theory was confirmed by small-angle neutron-scattering experiments.³

Starting from more general ground, Nagarajan^{4–6} formally applied the multiple chemical equilibrium model for aggregate formation, combining it with the adsorption of the aggregates on the polymer. The polymer-bound surfactant aggregate was defined as a one-component system and the presence of the polymer was taken into account as an interaction of the aggregate with its environment. On the basis of the pseudophase character of the aggregates the “optimum size of the aggregates” was calculated by differentiating the standard free energy of the aggregates with respect to the aggregation number. This approximation is very good in the case of micelles when the aggregation number is high, but if the aggregates are smaller

the optimum size and the thermodynamic mean size may differ considerably. For their molecular interaction model Ruckenstein at al.⁷ applied a similar thermodynamic treatment to that mentioned above.

Nikas and Blankschtein⁸ also started with the multiple chemical equilibrium model, but defined the complex as a two-component system containing a polymer molecule and m_g surfactant aggregates with aggregation number g . These authors erroneously formulated the standard free energy of the complex as the sum of the chemical potential contributions from its constituents; this formulation is correct only for macroscopic systems.^{9,15} In ref 8 the optimum size method was adapted to calculate the mean size of aggregates. However, in the optimization they should have taken into account that the concentration of the surfactant-free polymer is an independent variable that influences the equilibrium condition. Furthermore, the simultaneous minimization of the complex free energy with respect to four different variables is not clear.

Hall¹⁰ described the interaction of polymers with ionic surfactants by means of a simple expression that describes the Donnan equilibrium between a solution of charged colloids and a colloid-free electrolyte solution.

Over the past decade or so research activities related to the polymer–surfactant interaction have increased, but these investigations have mainly focused on the microstructure of the polymer–surfactant complex;^{11–14} thermodynamic treatments are scarce or restricted to special cases.¹⁰ No model-independent general treatment of these complicated systems with a clear distinction between surfactant aggregates and polymer–surfactant complex molecules is available in the literature. The main concern of the present work is to develop a general thermodynamic model of the polymer–surfactant interaction using Hill’s small-systems thermodynamics¹⁵ and to remove some of the constraints imposed on existing models. The polymer–surfactant system will be described at three levels of organization within the same theoretical framework. These are (see Figure 1); (a) subsystem (individual surfactant aggregate combined with the polymer coil); (b) small system (polymer–surfactant complex molecule); and (c) macroscopic system (polymer–surfactant solution).

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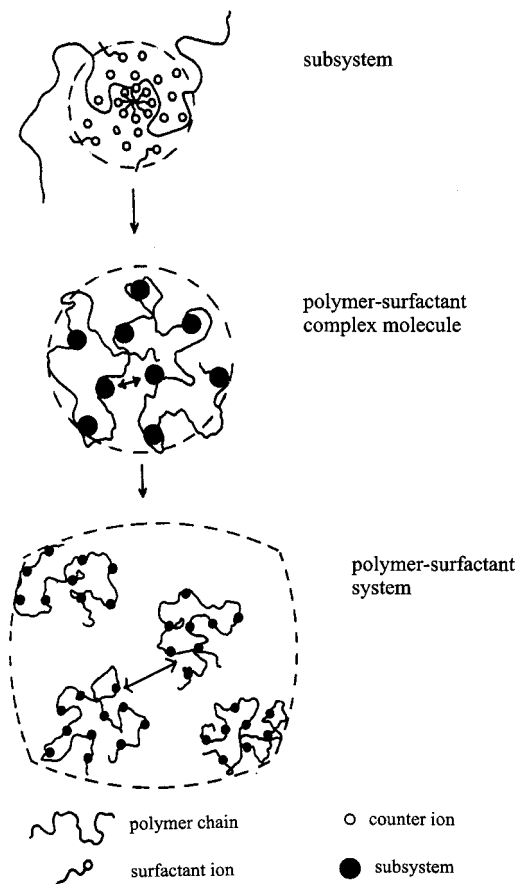


Figure 1. Organization of the polymer-surfactant system.

Theory

Polymer-Surfactant Small System. Let us consider a resting polymer-surfactant complex molecule as a small system open to its surfactant solution environment for the surfactant and closed for the polymer segments. The number of surfactant molecules in this semi-open small system fluctuates around a mean value \bar{q} , resulting in fluctuation of the free energy, volume, and entropy. The Gibbs free energy of the complex, $\bar{G}_{\text{compl}}^o(p, T, \bar{q}, s_o, c_i^s)$, will be given as a function of \bar{q} , the number of segments s_o in the polymer molecule, and of the environmental variables pressure p , temperature T , and the concentration of the components c_i^s in the environmental solution. The change of the Gibbs free energy can be given as

$$d\bar{G}_{\text{compl}}^o = -\bar{S}dT + \bar{V}dp + \mu d\bar{q} + \mu_{\text{seg}} ds_o + \sum \alpha_i^s dc_i^s \quad (1)$$

where the superscript o denotes that the complex is resting and the overbars refer to the fluctuating quantities; μ and μ_{seg} are the chemical potential of the surfactant and the polymer segments, respectively, and the last term represents the change of the free energy with the composition of the environment. Integration of eq 1 yields

$$\bar{G}_{\text{compl}}^o = \bar{q}\mu + s_o\mu_{\text{seg}} + \epsilon \quad (2)$$

where the term ϵ is the consequence of the smallness of the system, that is, that the free energy of the small system is not a homogeneous linear function of the entropy, volume, and number of components. If one takes the differential of eq 2 and subtracts eq 1, it leads to the Gibbs-Duhem relation for small

systems, which can be given at constant T , p , and c_i^s as

$$0 = \bar{q}d\mu + s_o d\mu_{\text{seg}} + d\epsilon \quad (3)$$

Polymer-Surfactant-Solvent Macroscopic System. It is pointed out that it is the macroscopic and not the individual small system that is experimentally observed. For the sake of simplicity let us consider a three-component macroscopic ensemble of water (w), polymer, and surfactant. The surfactant may be present in the form of monomers, in polymer-surfactant complex form, and free micelles. The polymer-surfactant complex molecules, the bare polymer molecules, and the micelles are considered as small systems. The fundamental macroscopic equation can be given as¹⁰

$$dG_t = -S_t dT + V_t dp + \mu_w^s dN_w^s + \mu^s dN^s + \mu_{\text{seg}}^* N_o ds_o + \mu_{q=0}^{\#} dN_o + \mu_{\text{seg}}^{\#} N ds_o + \mu N d\bar{q} + \mu_{\text{compl}}^{\#} dN + \mu^{(\text{mic})} N_{\text{mic}} d\bar{m} + \mu_{\text{mic}}^{\#} dN_{\text{mic}} \quad (4)$$

where the subscript t refers to the total ensemble and the superscript s represents the solution phase; μ^s , μ , and $\mu^{(\text{mic})}$ are the chemical potential of the surfactant in the solution (N^s), in the complex, and in micelles of \bar{m} mean aggregation number, respectively; μ_{seg}^* is the chemical potential of the polymer segments in the bare polymer; $\mu_{\text{compl}}^{\#}$, $\mu_{q=0}^{\#}$, and $\mu_{\text{mic}}^{\#}$ are the chemical potential of the polymer-surfactant complex (N), of the bare polymer (N_o), and of micelles (N_{mic}), respectively. The terms referring to the $d\bar{q}$ and dN derivatives (and similarly the last two terms for micelles) express that the free energy of the system can be changed either by changing the number of complex molecules at constant mean composition or by changing the composition at constant number of complex molecules.

Equation 4 describes a one-phase macroscopic system with three components and on the basis of the Gibbs phase rule the degrees of freedom of the system are only four. This means that at equilibrium six independent relations exist between the variables of eq 4. Two of them follow from the conservation of mass and the remaining four relations are equilibrium conditions. The total number of polymer molecules is

$$N_p = N_o + N$$

and that of the surfactant molecules

$$N_t = N^s + N\bar{q} + N_{\text{mic}}\bar{m}$$

enabling eq 4 to be rewritten as

$$dG_t = -S_t dT + V_t dp + \mu_w^s dN_w^s + \mu^s dN_t + \mu_{q=0}^{\#} dN_p + (\mu_{\text{compl}}^{\#} - \mu_{q=0}^{\#} - \bar{q}\mu^s) dN + (\mu_{\text{seg}}^{\#} + \mu_{\text{seg}}^*) ds_o + (\mu - \mu^s) N d\bar{q} + (\mu_{\text{mic}}^{\#} - \bar{m}\mu^s) dN_{\text{mic}} + (\mu^{(\text{mic})} - \mu^s) d\bar{m} \quad (5)$$

from which the conditions of equilibrium at constant T and p for a closed macroscopic system—when N_p , N_w , and N_t are constant and the polymer is closed for its segments—are the following:

$$\mu = \mu^s \quad (6a)$$

“phase” equilibrium of complex formation or “adsorption” equilibrium of surfactant binding on polymer;

$$\mu^{(\text{mic})} = \mu^s \quad (6b)$$

“phase equilibrium” of micelle formation;

$$\mu_{\text{compl}}^{\#} = \mu_{q=0}^{\#} + \bar{q}\mu^s \quad (6c)$$

“chemical” equilibrium of polymer–surfactant complex formation;

$$\mu_{\text{mic}}^{\#} = \bar{m}\mu^s \quad (6d)$$

“chemical equilibrium” of micelle formation.

Equations 6a and 6c enable one to consider the polymer–surfactant interaction as an adsorption of surfactant on polymer or as a chemical equilibrium within the same theoretical framework. Similarly, the micelle formation can be treated either as a phase equilibrium or as a chemical equilibrium. Indeed, the different concepts are equivalent in the case of noninteracting small systems because

$$(\partial\mu_{\text{compl}}^{\#}/\partial\bar{q})_{T,p,N} = (\partial\bar{G}_{\text{compl}}^o/\partial\bar{q})_{T,p,s_o,c_i} = \mu$$

that is the equilibrium conditions given by eqs 6a and 6c are in integral–differential relation to each other. It is important, however, that in contrast to the macroscopic phases,

$$\mu \neq (\bar{G}_{\text{compl}}^o - s_o\mu_{\text{seg}})/\bar{q}$$

because the polymer–surfactant complex is a small system (see eq 2).

The chemical potential of the corresponding small systems can be expressed in the form

$$\mu_{q=0}^{\#} = \bar{G}_{q=0}^o + kT \ln x_o \quad (7a)$$

$$\mu_{\text{compl}}^{\#} = \bar{G}_{\text{compl}}^o + kT \ln x \quad (7b)$$

$$\mu_{\text{mic}}^{\#} = \bar{G}_{\text{mic}}^o + kT \ln x_{\text{mic}} \quad (7c)$$

for systems that are dilute with respect to the complex molecules and micelles, and the interaction between the small systems can be neglected. x_o , x , and x_{mic} are the mole fraction of the bare polymer, the complex, and the micelles in the ensemble, respectively. Using the equilibrium condition given in eq 6c and eqs 7a and b, the following general relation can be derived:

$$\bar{G}_{\text{compl}}^o - \bar{G}_{q=0}^o + kT \ln x/x_o = \bar{q}\mu^s \quad (8)$$

The chemical potentials in eq 5 refer to a macroscopic system in which the small system is fluctuating, that is, the time or ensemble average of the small systems should be described. To derive the mean quantities, the free energy of the macroscopic system is given in a different form by distinguishing the complex molecules as individual chemical components as

$$dG_t = -S_t dT + V_t dp + \mu_w^s dN_w^s + \mu^s dN^s + \sum_{q=0} \mu_q^{\#} dN_q + \sum_{m=2} \mu_m^{\#} dN_m \quad (9)$$

in which $\mu_q^{\#}$ and $\mu_m^{\#}$ are, respectively, the chemical potential of the complex containing q surfactant molecules and of the micelle with aggregation number m ($m = 1$ represents the monomer, i.e., $N_1 \equiv N^s$). It is important to note that q and m are parameters here, in contrast to eq 4 where \bar{q} and \bar{m} are thermodynamic variables. If we introduce the notations

$$N_p = \sum_{q=0} N_q = N_o + \sum_{q=1} N_q$$

$$N_t = N^s + \sum_{q=1} qN_q + \sum_{m=2} mN_m$$

eq 9 can be rewritten as

$$dG_t = -S_t dT + V_t dp + \mu_w^s dN_w^s + \mu_{q=0}^{\#} dN_p + \mu^s dN_t + \sum_{q=1} (\mu_q^{\#} - \mu_{q=0}^{\#} - q\mu^s) dN_q + \sum_{m=2} (\mu_m^{\#} - m\mu^s) dN_m \quad (10)$$

The conditions of equilibrium are

$$\mu_q^{\#} = \mu_{q=0}^{\#} + q\mu^s \quad \text{for each } q \quad (11a)$$

$$\mu_m^{\#} = m\mu^s \quad \text{for each } m \quad (11b)$$

Equations 9–11 correspond to a multiple chemical equilibrium model. It can be shown that eqs 5 and 10 are identical at equilibrium and only at equilibrium.

If P_q denotes the probability of finding a complex molecule with q surfactant in the macroscopic ensemble ($P_q = N_q/\sum N_q$) and P_m is the analogous quantity with micelles, then the relations

$$\mu_{\text{compl}}^{\#} = \sum P_q \mu_q^{\#} \quad (12a)$$

$$\mu_{\text{mic}}^{\#} = \sum P_m \mu_m^{\#} \quad (12b)$$

hold at equilibrium. From eqs 12a and 7b it follows that

$$\bar{G}_{\text{compl}}^o = \sum P_q \bar{G}_q^o + kT \sum P_q \ln P_q \quad (12c)$$

where the last term is due to an additional entropy contribution because the surfactant may be distributed among complex molecules of different composition.

Subsystem Formation. General experience suggests that the polymer–surfactant complex formation is a “critical” phenomenon: it starts from a critical surfactant concentration similarly to the micelle formation. This is interpreted by the collective interaction of surfactant molecules with the polymer, that is, the surfactants interact with the polymer segments in the form of aggregates called subsystems or simply aggregates.

Because the subsystem is also a small system that is open for both the surfactants and polymer segments (!) its aggregation number n as well as the number of the involved segments s are fluctuating quantities. Furthermore, the number of subsystems (a) in the individual complex molecule also fluctuates, which makes it difficult to treat the problem. However, relaxation time measurements^{16–18} suggest that the polymer–surfactant complex formation is similar to the micelle formation. The formation or decomposition of the aggregates is a very slow process compared with the fast surfactant monomer exchange between the aggregate and its environmental solution. This is a strong argument for supposing independent fluctuations of a and n , that is: $\bar{q} = \bar{a}\bar{n}$ where

$$\bar{n} = \sum_n \sum_s P_{ns} n \quad \text{and} \quad \bar{a} = \sum_a P_{a,n} a$$

The free energy of the resting complex, which consists of a aggregates of \bar{n} surfactant molecules and \bar{s} polymer segments, can be given in the form

$$\bar{G}_{\text{compl},a}^o = a\bar{G}_{\text{sub}}^o + s_a\mu_{\text{seg}}^o - kT \ln \frac{a!}{a_o!(a_o - a)!} + \bar{G}_{\text{conf}} + \bar{G}_{\text{int}} \quad (13)$$

where $a_o = s_o/\bar{s}$ and the interaction between the surfactants and segments in the subsystem is involved in the standard free energy of the mean subsystem \bar{G}_{sub}^o . The third term on the right-hand side of eq 13 results from the distribution of the subsystems among a_o sites within the small system, \bar{G}_{conf} is the mean conformational free energy of the polymer, and the last term represents the interactions between the subsystems. When the complex is in internal equilibrium

$$d\bar{G}_{\text{compl},a}^o = 0 = d(\bar{G}_{\text{conf}} + \bar{G}_{\text{int}})$$

and integration from $a = 0$ yields

$$\bar{G}_{\text{conf}} - \bar{G}_{\text{conf},o} + \bar{G}_{\text{int}} = 0$$

because G_{int} is zero if $a = 0$. Equation 13 can be simply written as

$$\bar{G}_{\text{compl},a}^o = a\bar{G}_{\text{sub}}^o + s_a\mu_{\text{seg}}^o + \bar{G}_{\text{conf},o} - kT \ln \frac{a!}{a_o!(a_o - a)!} \quad (14)$$

Equation 14 suggests that the polymer–surfactant interaction is determined by the surfactant aggregate formation in spite of the complicated interactions within the complex molecule. The interactions between the subsystems are compensated by the conformational change of the polymer. Therefore, the complex formation does not depend on the degree of polymerization insofar as the polymer is long enough to form the same subsystem as has been found experimentally.^{19,20} Equation 14 leads to a binding isotherm equation that predicts monotonic increase of the bound surfactant with the surfactant chemical potential, in contrast to that predicted in ref 8 where stepwise binding was derived from a molecular interaction model. In the present theory stepwise binding may be expected only in the case of certain polymer mixtures or copolymers when two distinct \bar{G}_{sub}^o values characterize the interaction.

Because $\bar{G}_{q=0}^o = s_o\mu_{\text{seg}}^o + \bar{G}_{\text{conf},o}$ the equilibrium condition given in eq 11a can be expressed as

$$\mu_{\text{compl},a}^{\#} - \mu_{q=0}^{\#} = a\bar{G}_{\text{sub}}^o - kT \ln \frac{a_o!}{a!(a_o - a)!} + kT \ln x_a/x_o = a\bar{n}\mu^s \quad (15)$$

from which

$$x_a = x_o \frac{a_o!}{a!(a_o - a)!} \exp\{(a\bar{n}\mu^s - a\bar{G}_{\text{sub}}^o)/kT\} \quad (16)$$

The total mole fraction of the small systems (that of the polymer molecules) is

$$x_p = \sum_{a=0}^{a_o} x_a = x_o(1 + \lambda)^{a_o} \quad (17)$$

where $\lambda = \exp\{(\bar{n}\mu_s - \bar{G}_{\text{sub}}^o)/kT\}$. The relative bound amount is defined as the number of bound surfactant molecules per saturated amount.

$$B = \frac{\overline{anx_p}}{a_o\bar{n}x_p} = \frac{\lambda}{1 + \lambda} \quad (18)$$

because $\bar{a} = \sum ax_a/\sum x_a$ and $\sum ax_a = x_o a_o \lambda(1 + \lambda)^{a_o-1}$. If $\bar{n} = 1$ then eq 18 is a Langmuir isotherm equation. With increasing number of surfactant molecules in the subsystem the binding curve has a sigmoidal shape, as has been widely observed. Equation 18 can be given in a more practical form as

$$\ln \frac{B}{1 - B} = -\Delta/kT + \bar{n} \ln x^s \quad (19)$$

where $\Delta = \bar{G}_{\text{sub}}^o - \bar{n}\mu_s^s$ is the standard free energy change of the mean subsystem formation. If eq 19 is applied for free micelle formation, then $\ln x_{\text{mic}}$ stands instead of the term $\ln[B/(1 - B)]$. The distribution of the surfactant among the different forms in the polymer–surfactant solution can be given as

$$\begin{aligned} x_{\text{tot}} &= x^s + \overline{anx_{\text{compl}}} + \bar{m}x_{\text{mic}} \\ &= x^s + \frac{\lambda}{1 + \lambda} a_o \bar{n} x_p + \bar{m}(x^s)^{\bar{m}} \exp(\bar{m}\mu_o^s - \bar{G}_{\text{mic}}^o) \end{aligned} \quad (20)$$

in which x_{tot} is the total amount of surfactant in monomer mole fraction units. The last term is derived for micelles from eqs 6d and 7c. Equation 20 is restricted to dilute systems because the interactions between the small systems were neglected.

If we suppose that the dependence of \bar{n} and Δ on x^s is slight or negligible, then the important thermodynamic parameters \bar{n} , Δ , and a_o or \bar{s} can be estimated from eq 19. If the concentration of surfactant in complex c_b (the bound surfactant) is measured at constant polymer concentration, then the initial slope ($B \ll 1$) of the $\ln c_b$ vs $\ln c^s$ plot gives the mean aggregation number of the surfactant. The c_b vs x^s function has an inflexion at $B = 1/2$ (when $x^s = x_{\text{infl}}^s$ and $c_b = c^*$), from which

$$\bar{G}_{\text{sub}}^o/\bar{n} - \mu_o^s = kT \ln x_{\text{infl}}^s$$

and

$$\bar{s} = \frac{\bar{n}c_p}{2M_o c^*}$$

where c_p is the polymer concentration in g/volume and M_o is the molar mass of the polymer segment.

Similarly to the critical micelle formation concentration, a critical surfactant concentration for complex formation x_{cr}^s or c_{cr} has been defined as a break point in the colligative properties vs surfactant concentration plots. c_{cr} can be interpreted as the pseudophase separation concentration or solubility of the surfactant subsystems. This approximation is less justifiable than with micelle formation because the mean aggregation number of surfactant in polymer–surfactant complex was experimentally found to be significantly smaller than the micelle aggregation numbers; furthermore, the equilibrium monomer concentration is not constant with increasing number of aggregates in the polymer–surfactant complex molecules.

Discussion

It is mentioned that eq 19 is similar to the relations obtained by an adsorption model.^{1,2} The main difference is that \bar{n} and Δ in eq 19 are mean quantities and theoretically depend on x^s . With increasing x^s the size distribution of the aggregates shifts

to larger values; consequently, the mean size increases and the free energy of formation also changes. At different x^s values the mean small systems are “different objects”. In the case of free micelle formation²¹ the mean aggregation number rapidly increases from $m = 1$ to a high value within a narrow range of x^s . Above this range the mean aggregation number remains practically constant with increasing number of micelles, in view of which the micelle formation can be well characterized by constant \bar{m} and Δ_{mic} in the important concentration range that is available for experimental study.

The situation is not the same if the aggregates are formed in a polymer complex. The existence of a critical concentration range of x^s , when \bar{n} rapidly increases, is expected. However, x^s cannot tend towards a constant value as with micelle formation because the number of aggregates in the complex molecule is limited. Consequently, with increasing B the increase of x^s and that of the mean aggregation number is predicted. Zana et al.²² concluded from fluorescence probe studies that the surfactant aggregation number increases with increasing surfactant concentration and with decreasing polymer concentration (both of these lead to higher B). It can be concluded that the correct thermodynamic analysis of the binding isotherm requires the determination of \bar{n} as a function of x^s (or B) by an independent method.

From the thermodynamic point of view the surfactant aggregation can be completely described by the distribution function of the standard free energy change of aggregate formation with respect to the composition: ΔC_m^o for the micelles and $\Delta G_{n,s}^o$ for the aggregates in polymer–surfactant complexes. The free energy of formation can be calculated from the size distribution of the aggregates at equilibrium. Unfortunately, there is no available experimental method for determining the distribution of the aggregates, and analysis is restricted to the mean values. In general, the experimental binding isotherm has two, more or less well-defined critical concentrations, viz. c_{cr} and c_{infl} , where the corresponding $\Delta \bar{G}_{\text{sub}}^o/\bar{n}$ or $\Delta \mu_o = (\partial \Delta \bar{G}_{\text{sub}}^o/\partial \bar{n})_B$ values can be determined. It is again mentioned that these are different thermodynamic quantities, that is, the standard free energy of aggregate formation per monomer and the standard free energy change of the transition of a monomer from the solution to the aggregate (phase) are identical only for macroscopic systems.

According to eq 1 the standard free energy of the mean small system depends on its size and the environmental variables, in our case, on the concentration of the dilute surfactant solution c^s . The change of the monomer surfactant concentration from c_{cr} to cmc is of practical importance. If the surfactant is nonionic, the concentration change in this narrow range can be neglected. However, in the case of ionic surfactants, c^s determines the ionic strength of the solution, and, in turn, this strength has a strong influence on the electrical free energy contribution to the free energy of the aggregate formation. The presence of excess electrolyte simplifies the situation because the ionic strength is constant and the environment of the surfactant aggregates can also be considered constant.

Some experimental results²³ measured earlier with sodium dodecyl sulfate (NaDS) and various vinyl polymers [polyvinylpyrrolidone (PVP), poly(vinyl alcohol) (PVA), and poly(ethylene oxide) (PEO)] in the presence of 0.1 M NaCl are re-evaluated in light of the theory. The measured and calculated parameters are collected in Table 1. The activity coefficient of the surfactant was taken as unity; the concentration of the surfactant micelles at the critical concentration was approximated as 1×10^{-4} M in monomer units. A magnitude difference

TABLE 1. Thermodynamic Parameters of NaDS–Polymer Complexes in 0.1 M NaCl Solution

	c_{cr} (mM)	c_{infl} (mM)	\bar{n}	$(c_b/c_p)_{\text{sat}}$ (mmol/g)	$\Delta \bar{G}_{\text{sub}}^o/\bar{n}$ (kJT)	\bar{s}
NaDS	1.44	—	93	—	−10.4	—
PVA–NaDS	1.31	(≥ 1.44)	39	(> 4)	(≥ −10.6)	—
PVP–NaDS	0.94	1.25	44	3.5	−10.7	114
PEO–NaDS	1.06	1.25	50	11	−10.7	103

in the micelle concentration results in only 0.02 kT difference in the calculated standard free energy. The experimental $\ln c_b$ vs $\ln x^s$ relation was found to be linear in a sufficiently wide concentration range, thereby allowing the mean aggregation number to be estimated. The saturated bound amount cannot be determined in the case of the PVA because the half-saturation was not reached below the critical micelle formation concentration.

The difference in the free energy of formation per monomer between the micelle and the aggregates in polymer complexes is only a few tenths of a kT. It can be concluded from the data in Table 1 that the interaction of the bulky vinylpyrrolidone is similar to that of the small ethylene oxide or vinyl alcohol segments. Though there is no doubt about the specific role of the interacting components, the claimed strong specificity of the polymers in the interaction^{11–14} seems to be overemphasized (at least for the polymers dealt with here). It is also possible that the dramatic difference in the complex formation due to the change of the surfactant head group for a nonionic or cationic one stems from a very small change in the interaction energies, leading to a “yes or no” effect when the free energy of aggregate formation becomes less negative than that of the micelle formation. The molecular interaction models must also be carefully interpreted because any adjustable interaction parameter may produce a serious “effect” in the polymer–surfactant interaction.

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List of symbols

a :	number of surfactant aggregates in a polymer–surfactant complex
α_i^s :	partial derivative of the mean small system free energy with respect to the concentration of the i th component in the environmental solution
B :	relative bound amount of surfactant on polymer
c_i^s :	concentration of the i th component in the environmental solution of small systems
Δ :	standard free energy change of the mean surfactant aggregate (subsystem) formation in polymer complex
ϵ :	excess free energy of the mean small system
G_t :	total Gibbs free energy of the polymer–surfactant–water system
\bar{G}_{compl}^o :	Gibbs free energy of the mean polymer–surfactant complex molecule (mean small system) with fixed center of mass
$G_{\text{compl},a}^o$:	Gibbs free energy of the resting complex molecule containing a surfactant aggregates
\bar{G}_{sub}^o :	Gibbs free energy of the resting mean subsystem (surfactant aggregate in polymer–surfactant complex molecule)
\bar{G}_{mic}^o :	Gibbs free energy of the resting mean micelle (mean small system)
μ_i :	chemical potential of the i th component in the mean small system (refers to surfactant without subscript)
\bar{G}_{conf}^o :	mean conformational free energy of the polymer

\bar{G}_{int} :	free energy contribution due to the interaction between the surfactant aggregates in a polymer–surfactant complex molecule
$\mu^{(\text{mic})}$:	chemical potential of surfactant in the mean (free) micelle
μ_{seg}^* :	chemical potential of polymer segments in the bare polymer
μ_i^s :	chemical potential of the i th component in the environmental solution of mean small systems (refers to surfactant without subscript)
μ_o^s :	standard state chemical potential of the surfactant in solution phase
$\mu_q^\#$:	chemical potential of the polymer surfactant complex containing q surfactant molecules ($q = 0$ refers to the bare polymer)
$\mu_{\text{compl}}^\#$:	chemical potential of the mean polymer–surfactant complex
$\mu_{\text{mic}}^\#$:	chemical potential of the mean (free) micelle
m :	aggregation number of (free) micelles ($m \geq 2$)
n :	aggregation number of surfactants in a polymer complex ($n \geq 1$)
N :	number of complex molecules
N_p :	total number of polymer molecules
N_o :	number of bare polymer molecules
N_i^s :	number of the i th component in the environmental solution of small systems (refers to surfactant without subscript)
N_m :	number of micelles of m aggregation number
N_{mic} :	total number of free micelles
P_q :	probability of finding a polymer–surfactant complex containing q surfactants in the macroscopic ensemble
P_m :	probability of finding a free micelle of m aggregation number
q :	total number of surfactant molecules in a polymer–surfactant complex molecule
s_o :	degree of polymerization
s :	number of polymer segments interacting with a single surfactant aggregate (subsystem)
\bar{S} :	entropy of the mean small system

\bar{V} :	volume of the mean small system
x_k :	mole fraction of the k th small system in the macroscopic ensemble [k : bare polymer (o); polymer–surfactant complex (no subscript); micelles (mic)]
x^s :	mole fraction of surfactant monomers in the environmental solution of small systems

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