DONNAN EQUILIBRIA IN POLYMERIC MICELLAR SYSTEMS WITH WEAK POLYELECTROLYTE SHELLS: THE LOWERING OF THE pH VALUE

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When two electrolyte solutions are separated and only some of the ions can cross the boundary, the concentrations of these ions are different on both sides of the boundary. This is the well-known Donnan effect. When weak electrolytes are involved, the imbalance includes also hydrogen ions: there is a difference of pH across the boundary and the dissociation of nondiffusible weak electrolytes is suppressed. The effect is very pronounced when the concentration of the weak electrolyte is high and ionic strength is low. The significance of this phenomenon is discussed for polyelectrolyte solutions, and particularly for block copolymer micelles with weak polyelectrolyte shells. The effect is quite dramatic in the latter case.

Key words: Donnan equilibria; Polyelectrolytes; Copolymer micelles.

For several years we have been studying micellization of block copolymer micelles formed by block copolymers of polystyrene, PS, and poly(methacrylic acid), PMA, in aqueous media. In our earlier studies[1], we have reported dependences of various micellar properties (hydrodynamic radius and electrophoretic mobility) on the pH and ionic strength of the buffers in which these micelles were suspended. As expected, the micellar radius and electrophoretic mobility exhibited a sigmoidal transition from low values at low pH to higher values at high pH. We have interpreted these phenomena as a result of an increasing degree of ionization of the carboxylic groups that leads to expansion of the chains (and therefore of the micellar shells) due to an increasing polyelectrolyte effect. The effective micellar charge and electrophoretic mobility increase simultaneously. However, the S-shaped transition is shifted to significantly higher pH values as compared with the analogous transition region in the linear polymethacrylic acid[2] and cannot be accounted for on the basis of the polyelectrolyte effect only.

Concentration of poly(methacrylic acid) chains in micellar shells is fairly high – about weight 5%, which corresponds to *ca* 0.6 M electrolyte solution. Behavior of the shell is fairly complex. In case of a weak polyelectrolyte, such as PMA, ionization of acid –COOH groups and the spatial concentration of counterions varies from the core/shell interface towards the shell periphery. The polyelectrolyte shell of micelles may be considered as a spherical polyelectrolyte brush. Several theories have been recently developed to describe properties of brushes of various geometries formed by strong and by weak polyelectrolytes[3]. In theoretical studies on polyelectrolyte systems, the concept of an effective variable dissociation constant, K_A^{ef} is often used[4].

It is the main purpose of this paper to show that the above mentioned behavior (at least to a major extent) can be explained by applying the simple and well-known principles of the Donnan equilibria to systems in which a concentrated solution of a weak electrolyte is in a contact with a dilute buffer.

Application of the theory of Donnan equilibrium to polyelectrolyte solutions has been in use at least since the well-known treatment by Flory[5]. Existing literature about polyelectrolytes is so extensive that it seems futile to give specific references. The Donnan effect has been employed for analyzing the expansion of polyelectrolyte coils, polyelectrolyte gels, thermodynamics of polyelectrolyte solutions, *etc*. Donnan equilibria were recently considered by some articles analyzing brushes formed by weak polyelectrolytes (*e.g.* refs[3a,b]), which are physically quite similar to our micelles.

THEORETICAL

Since all polyelectrolyte blocks of PMA (which we designate by HA) in one micelle are inevitably confined in the shell, the system may be regarded as a relatively concentrated constrained solution of a weak acid HA which is separated by an “impermeable membrane” from a solution of another weak acid HB and its salt NaB, which may penetrate freely through the “membrane”. In our calculations we will make the following assumptions:

1. The solutions on both sides of the “membrane” are electroneutral.

2. The ionization constants K_A and K_B of the acids HA and HB, respectively, are independent of the composition of the system.

3. The activities of all species are equal to their molar concentrations, *i.e.*, all activity coefficients are equal to unity at all compositions.

4. Contribution of ionization of water to concentrations of H^+ and OH^- ions is neglected.

5. In relations describing the electroneutrality of solutions, the contributions of H^+ and OH^- ions is neglected. (Under most circumstances, they are orders of magnitude lower than concentrations of the other ions.)

The subscript zero designates quantities on the buffer side, the concentrations on the HA side have no subscript. Thus, the relevant concentrations on the buffer side are

$[HB]_0$, $[H^+]_0$, $[B^-]_0$, $[Na^+]_0$; on the other side they are [HB], $[H^+]$, $[B^-]$, $[Na^+]$, [HA], $[A^-]$.

It is convenient to define two more variables: the stoichiometric concentration of the A entities, $c_A = [HA] + [A^-]$ and their degree of dissociation, $f_A = [A^-]/c_A$.

For our system, we can write three relations for ionization equilibria:

$$[H^+]_0[B^-]_0 = [HB]_0K_B \tag{1}$$

$$[H^+][B^-] = [HB]K_B \tag{2}$$

$$[H^+][A^-] = [HA]K_A \quad . \tag{3}$$

The two electroneutrality equations read: $[Na^+]_0 = [B^-]_0$ and $[Na^+] = [B^-] + [A^-]$. Finally, the assumed equilibrium between the two parts of the system implies that the activities of the diffusible species, formed by compounds HB and NaB in the solution, must be the same in both subsystems, *i.e.*, $[HB]_0 = [HB]$, $[Na^+]_0\,[B^-]_0 = [Na^+]\,[B^-]$.

Thus, our system is fully described by 14 variables: 10 concentration variables described by symbols in brackets, c_A, f_A, K_A, and K_B. Let us assume that the properties of the buffer side are fully known, *i.e.*, that its ionic strength (which is equal to $[Na^+]_0$), its pH (related to $[H^+]_0$, and K_B are given. The quantities $[B^-]_0$ and $[HB]_0$ are then easily obtained from Eqs (*1*) and (*3*). When we further know the analytical concentration, c_A, and the ionization constant, K_A, the above written relations are sufficient for calculation of all the remaining 9 variables. Here, we will present only the most interesting results.

The rearrangement of the aforementioned equations yields the well-known result of Donnan equilibria in systems of strong polyelectrolytes.

$$[Na^+]/[Na^+]_0 = [B^-]_0/[B^-] \tag{4}$$

$$[H^+]/[H^+]_0 = [Na^+]/[Na^+]_0 \tag{5}$$

Thus, the hydrogen ions are distributed between the two parts of the system in the same ratio as the Na^+ counterions. Because the concentration of counterions on the HA side is always higher than on the buffer side, this means that the same applies to the concentration of the H^+ ions, *i.e.*, the pH on the HA side is lower than that on the buffer side.

Quantitatively, the effect can be evaluated when the system of Eqs (*1*)–(*3*) is fully solved. By appropriate manipulations we can convert these equations into

$$f_A(c_A/[Na^+]_0) = (K_A/[H^+]_0)[(1-f_A)/f_A] - [f_A/(1-f_A)]/(K_A/[H^+]_0) \ . \qquad (6)$$

This is an equation of the third order for the unknown f_A; it contains only two parameters $K_A/[H^+]_0$ and $c_A/[Na^+]_0$. This equation has one real root in the interval between zero and one and it is easily solved numerically. We should notice that the parameter $K_A/[H^+]_0$ could be interpreted as

$$\log_{10}(K_A/[H^+]_0) = pH_0 - pK_A \ , \qquad (7)$$

where pH_0 is the pH of the buffer side and pK_A has its usual definition. The parameter $c_A/[Na^+]_0$ relates the concentration of the A component to the ionic strength of the buffer side. It can attain rather high values when c_A is high and ionic strength is low. It should be noticed that Eq. (*6*) does not contain any quantity related to the nature and concentration of the buffer-forming acid HB. Thus, these quantities seem to be irrelevant for our calculation: all buffers with the same pH and ionic strength should behave in the same way.

RESULTS AND DISCUSSION

We have evaluated the f_A values from Eq. (*6*) for a number of values of $K_A/[H^+]_0$ and $c_A/[Na^+]_0$. A short selection of values is presented in Table I. Once f_A is known, the ratio $[H^+]/K_A$ is easily obtained from the rearranged Eq. (*3*)

$$[H^+]/K_A = (1-f_A)/f_A \ . \qquad (8)$$

The decrease in pH, $\Delta pH = pH - pH_0$, where pH is the value on the HA side is then given as

$$\Delta pH = \log_{10}(K_A/[H^+]) - \log_{10}(K_A/[H^+]_0) \ . \qquad (9)$$

Selected results are presented in Table II.

Many interesting properties of weak electrolyte systems are related to the degree of ionization f_A. When following a change of a system with changing pH, it is convenient to designate as a characteristic transition point a situation at which $f_A = 0.5$ (pH = pK_A at this point). For each value of $c_A/[Na^+]_0$, there exists a value of $K_A/[H^+]_0$ yielding $f_A = 0.5$. For values of $c_A/[Na^+]_0$ larger than about ten, the relationship between these values (designated by an asterisk) rapidly approaches a limiting form

$$\{K_A/[H^+]_0\}^* = \{c_A/[Na^+]_0\}^* \quad . \tag{10}$$

TABLE I
Degree of ionization f_A as a function of $\log_{10}(c_A/[Na^+]_0)$ and $\log_{10}(K_A/[H^+]_0)$

$\log_{10}(c_A/[Na^+])$	$\log_{10}(K_A/[H^+])_0$						
	–2	–1	0	1	2	3	4
–2	0.010	0.091	0.909	0.990	0.999	0.999	1.000
–1	0.010	0.091	0.494	0.905	0.990	0.999	1.000
0	0.010	0.087	0.445	0.868	0.984	0.998	1.000
1	0.010	0.067	0.256	0.614	0.915	0.990	0.999
2	0.007	0.030	0.095	0.270	0.618	0.916	0.990
3	0.003	0.010	0.031	0.095	0.270	0.618	0.916
4	0.001	0.003	0.010	0.031	0.095	0.270	0.618

TABLE II
pH shift ΔpH as a function of $\log_{10}(c_A/[Na^+]_0)$ and $\log_{10}(K_A/[H^+]_0)$

$\log_{10}(c_A/[Na^+])$	$\log_{10}(K_A/[H^+])_0$						
	–2	–1	0	1	2	3	4
–2	–0.000	–0.000	–0.000	–0.000	–0.000	–0.000	–0.000
–1	–0.000	–0.002	–0.011	–0.020	–0.017	–	–
0	–0.000	–0.019	–0.096	–0.183	–0.206	–0.205	–
1	–0.018	–0.142	–0.463	–0.799	–0.966	–0.100	–0.100
2	–0.146	–0.514	–0.980	–1.432	–1.604	–1.962	–1.996
3	–0.507	–0.996	–0.142	–1.978	–2.432	–2.791	–2.962
4	–1.000	–1.493	–1.996	–2.492	–2.978	–3.432	–3.791

It is apparent that pH in the shell formed by the weak electrolyte HA drops significantly with increasing ratio of the weak electrolyte concentration and ionic strength, $c_A/[Na^+]_0$. The decrease in pH with increasing ratio $K_A/[H^+]_0$ is also rather large but less significant than the effect of the ionic strength. The shift of the transition between the low and high ionization regime is governed by the ionic strength.

It must be emphasized that the shift of the pH value in the region occupied by a weak electrolyte HA with respect to the bulk buffer solution, HB/NaB, which is in thermodynamic equilibrium with it, is a general phenomenon that occurs without respect to the nature of the weak electrolyte system. Specifically, it is not related to the fact that in polyelectrolytes, many ionizable groups reside on the same macromolecule. Obviously, the finer effects such as interactions among ionizable groups on the same macromolecule, space filling effects, chain deformations and other entropy and enthalpy effects, *etc*., may modify the effect described above. However, it is in principle not necessary to introduce any new concepts into the theory of weak electrolytes, for instance a concept of the effective (*i.e.*, concentration-dependent) K_A^{ef} constant in order to understand the most important contribution to the pH depression. On the other hand, the system studied assumes that the electrolyte groups are attached to the polymer chains which are “tethered” to the hydrophobic micellar core. Therefore, (i) the electrostatic influence that hinders dissociation of –COOH group, which is in the vicinity of ionized $–COO^-$ groups, (ii) counterions condensation, and (iii) the screening effect cannot be neglected in a detailed description.

Let us now examine the system of our major interest, *i.e.*, the amphiphilic block copolymer micelles with weak polyelectrolyte shells suspended in a dilute buffer in more detail. This system is very complex. Since many polyelectrolyte chains are chemically attached to one micellar core, the concentration of ionizable groups in the vicinity of the core may reach almost 1.0 M. Micropolarity within the shell is not constant and the effective dielectric constant varies in the shell. Its value is low close to the core and increases towards the micellar periphery. Dissociation of polyelectrolyte groups increases with the distance from the core-shell interface and concentration of counterions is not spatially constant. Our simplified approach does not capture all details of the polyelectrolyte behavior of the shell. Nevertheless it describes the main feateres of the behavior fairly well (at least at the semi-quantitative level). It shows that such micelles suspended in a dilute buffer may suffer a severe depression of the pH values in the shell. The pH drop may easily reach two units of pH or even more.

CONCLUSIONS

Principles of Donnan equilibria were applied to systems containing relatively concentrated microdomains of a weak polyelectrolyte (*e.g.*, a polyelectrolyte brush, a polyelectrolyte shell of amphiphilic polymeric micelles) in osmotic equilibrium with an outer buffer. It was found that the presence of ions from the outer buffer leads to suppression of the ionization of the weak polyelectrolyte. When the polyelectrolyte is a weak acid, this suppression is accompanied by lowering of the pH value with respect to the outer buffer. When the electrolyte is a weak base, the pH value is increased. The magnitude of the pH shift increases with the increasing ratio of the total molar concentration of the weak electrolyte to the ionic strength of the outer buffer. This effect is common to all weak electrolytes, whether they are low-molecular-weight, polymeric, micellar, or gel-like. It should influence deeply titration curves of weak polyelectrolytes and expansion of their coils. It affects polyelectrolyte gels. However, the largest effect is expected for block copolymer micelles because the local concentration of the ionizable groups close to the core-shell boundary is very high and the pH shift may reach several units of pH.

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