BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 2326—2329 (1972)

On the Equivalence of Two Expressions for Potentiometric Titration of Polyelectrolytes

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(Received December 3, 1971)

Two expressions for potentiometric titrations of polyelectrolytes are proved to be equivalent, being derived from a common basis. A thermodynamic interpretation of the term representing the non-ideality of polyelectrolyte solutions is also explicitly given.

It has been well known that potentiometric titrations of polyelectrolyte solutions can be described by the equation,[1–4]

$$\mathrm{pH} = \mathrm{p}K_0 + \log(\alpha/1-\alpha) + \Delta \mathrm{p}K \tag{1}$$

Here K_0 and α denote the intrinsic dissociation constant of dissociable sites and the degree of ionization respectively. The last term in Eq.(1) represents the non-ideality of the solution and in ordinary cases arises solely from the electrostatic work accompanying ionization.

On the other hand, the following thermodynamic expression has been presented.[5]

$$(\partial\mu_p/\partial\mu_\mathrm{H})_{m_p,m_s} = \alpha x \tag{2}$$

Here μ_p and μ_H denote the chemical potentials of polymer component and of hydrogen ions, and m_p and m_s the concentrations of ploymer and salt components. Futher x denotes the number of the dissociable sites on a polyion.

However, the equivalence of the two expressions, Eq.(1) and Eq.(2), has not been presented. The purpose of the present study is to derive the two expressions from a common basis and thus to show their equivalence.

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1) A. Katchalsky and J. Gillis, *Rec. Tarv. Chim.*, **68**, 879 (1949).
2) R. Arnold and J. Th. G. Overbeek, *ibid.*, **69**, 192 (1950).
3) A. Katchalsky and S. Lifson, *J. Pholymer Sci.*, **11**, 409 (1953).
4) F. E. Harris and S. A. Rice, *J. Phys. Chem.*, **58**, 725 (1954).
5) A. Shatkay and I. Micheali, *ibid.*, **70**, 3777 (1966).

Theory

For the sake of simplicity, let us take a poly (weak) acid neutralized to various degrees by alkali as a polyelectrolyte. Let us consider a solution containing n_w, n_p, n_s, and n_a moles of water, polyacid, simple salt (uni-uni valent), and alkali. We take a fully protonated species as a polymer component here. Concentrations of solutes are expressed in *m*'s. The counter ions from alkali and those from simple salt are assumed to be of the same species. Since we consider the changes at a constant temperature and pressure, these variables do not appear explicitly in the present formulation.

Let us denote the average number of charged sites on a polyion as i, that is $i=\alpha x$. At equilibrium, i should be determined from the condition of minimum free energy.

$$(\delta G/\delta i)_{n_w,\ m_p,\ m_s,\ m_a} = 0. \tag{3}$$

Here G denotes the Gibbs free energy of the solution. The equation is just the equation for potentiometric titrations. The expression, however, corresponds to an infinitesimal virtual change δi. If the corresponding free energy change can be evaluated, we can obtain Eq.(1). On the other hand we can derive Eq.(2), if we can express the free energy due to a virtual change in terms of some thermodynamic quantities corresponding to quasi-static changes.

We denote the free energy arising from the electrostatic interaction between charges as G^{el}. Self-energy of a polyion, the electrostatic interaction between charged sites on a polyion, is also included in G^{el}. The remaining part of G will be further divided into two parts, G^p and G^s, where G^p represents the contribution from polyions and G^s from all other species. The unitary part of G^p can be divided into three parts; $G_0{}^p$ which is independent of i, $G_1{}^p$ which contains the contributions from the standard free energy of charged and uncharged sites and from their ideal mixing entropy, and $G_2{}^p$ which involves any other contributions depending on i. The cratic part of G^p can be expressed in terms of the ideal term in m_p when neither association nor conformational change occurs. However, it is designated here as $G_3{}^p$ for the purpose of wider applicability.

Let us consider the changes which actually occur in the solution accompanying the virtual change under consideration. At equilibrium, G may be written in terms of species as follows, if we take into account a relation demonstrating the dissociation equilibrium of water, $\mu_w=\mu_{\mathrm{H}}+\mu_{\mathrm{OH}}$.

$$G = (n_w+n_a)\mu_w + n_p\mu_{p,i} + (n_a+n_s)\mu_+ + n_s\mu_- + (n_{\mathrm{H}}-n_{\mathrm{OH}})\mu_{\mathrm{H}}. \tag{4}$$

Here $\mu_{p,i}$ denotes the chemical potential of a polyion having i charged sites, and μ_+ and μ_- those of counter ions and coions. The equation implies that the contribution from excess hydrogen ions n_{H}^{ex} rather than that from total hydrogen ions is necessary to be taken into account when we consider the contribution from hydrogen ion species to the change of G associating with some process. Here the excess hydrogen ions are defined as the remainder resulting from the subtraction of hydroxyl ions from hydrogen ions, $n_{\mathrm{H}}^{ex}=n_{\mathrm{H}}-n_{\mathrm{OH}}$. From the condition of electroneutrality,

$$n_p\delta i = \delta n_a + \delta n_{\mathrm{H}}^{ex}. \tag{5}$$

The virtual change under consideration thus leads to the increase of the excess hydrogen ions by $n_p\delta i$ moles, since the change occurs at constant n_a. The result should not be interpreted as demonstrating that the hydrogen ions produced by the virtual change do not interact with hydroxyl ions and thus do not participate in the dissociation equilibrium of water. In fact, part of hydrogen ions released may be consumed by means of the combination with hydroxyl ions. But as a result of this reaction, exactly the same amount of the latter is also consumed and thus the amount of excess hydrogen ions is not altered. Practically the same result can be obtained, if we notice that except the extremely narrow region near pH 7, either hydrogen or hydroxyl ions are present in great excess so that the difference between the amount of excess ions and that of total ions becomes quite insignificant.

Therefore, corresponding to the virtual change, the number of charged sites on each polyion increases by δi, and $n_p\delta i$ moles of hydrogen ions are released into a solution from these polyions.

Let us evaluate the free energy change G involved in Eq. (3). For the calculation of the free energy other than electrostatic part, we may calculate it in two independent processes. For the process corresponding to the increase of charged sites, the free energy change can be expressed by the change of chemical potentials, since the process does not involve any variation of the number of particles in the system. We may reasonably assume that the interionic interaction other than electrostatic one is negligible except that between polyions. The exception is made here to leave room for the possibility that association of polyions occurs by short range interactions such as hydrogen bonding. According to this assumption, the unitary part of G^s is clearly independent of i and the cratic part can be expressed in terms of the ideal term $\boldsymbol{R}T\ln m$. Therefore G^s remains unchanged under the process considered. As to the remaining part G^p, it can be written as $n_p(\mu_{p,i}-\mu_{p,i}^{el})$. Here $\mu_{p,i}^{el}$ represents the electrostatic part of the chemical potential of a polyion. Corresponding to an increase of $n_p\delta i$ moles of hydrogen ions, the free energy change becomes $n_p\delta i(\mu_{\mathrm{H}}-\mu_{\mathrm{H}}^{el})$. Thus the free energy change except the electrostatic one amounts to,

$$\delta(G-G^{el}) = n_p\delta(\mu_{p,\ i}-\mu_{p,i}^{el})+n_p(\mu_{\mathrm{H}}-\mu_{\mathrm{H}}^{el})\delta i. \tag{6}$$

For the calculation of the change of electrostatic free energy, we regard the process as such that n_p moles of polyions having i charged sites are removed from the solution and exactly the same amount of polyions having $i+\delta i$ charged sites as well as $n_p\delta i$ moles of hydrogen ions are introduced into the solution. Then the total change becomes.

$$\delta G^{el} = n_p\mu_{\mathrm{H}}^{el}\delta i + n_p(\mu_{p,i+\delta i}^{el}-\mu_{p,i}^{el}) = n_p\mu_{\mathrm{H}}^{el}\delta i + n_p\delta\mu_{p,i}^{el}. \tag{7}$$

Adding Eqs. (6) to (7), we obtain

$$(\delta G/\delta i)_{n_w,\, m_p,\, m_s,\, m_a} = n_p[(\delta \mu_{p,i}/\delta i)_{m_p,\, m_s,\, m_a} + \mu_{\mathrm{H}}]. \tag{8}$$

From Eq. (3), the r.h.s. of Eq. (8) should be zero at equilibrium.

Potentiometric Equation. In order to evaluate the derivative on the r.h.s. of Eq. (8), we examine various constituent contributions to $\mu_{p,i}$. In analogy with the classification of G^p, $\mu_{p,i}$ is also divided in the corresponding manner.

$$\mu_{p,i} = \mu_{\mathrm{p}}^0 + \mu_{p,i}^1 + \mu_{p,i}^2 + \mu_{p,i}^3 + \mu_{p,i}^{el}. \tag{9}$$

Since G_0^p is defined as being independent of i, μ_p^0 is also independent of i. As to $\mu_{p,i}^1$, the term can be explicitly written as follows.

$$\mu_{p,i}^1 = -(\boldsymbol{RT} \ln K_0 + \mu_{\mathrm{H}}^0)i + \boldsymbol{RT}[i \ln(i/x) + (x-i)\ln(x-i)/x].$$

Hence,

$$\delta u_{p,i}^1 = \delta i(-\boldsymbol{RT} \ln K_0 - \mu_{\mathrm{H}}^0) + \boldsymbol{RT}(\delta i) \ln(i/x-i). \tag{10}$$

Substituting Eq. (10) into Eq. (8) and rearranging it a little, we obtain

$$\mathrm{pH} = \mathrm{p}K_0 + \log(\alpha/1-\alpha) + (0.434/\boldsymbol{RT}) \times [\delta(\mu_{p,i}^2 + \mu_{p,i}^3 + \mu_{p,i}^{el})/\delta i]. \tag{11}$$

Thus we have derived a potentiometric equation. Comparing Eq. (11) with Eq. (1), we have

$$\Delta \mathrm{p}K = (0.434/\boldsymbol{RT})[\delta(\mu_{p,i}^2 + \mu_{p,i}^3 + \mu_{p,i}^{el})/\delta i]. \tag{12}$$

It can be seen from Eq. (12) that the non-ideal term depends on the non-ideal part of the chemical potential of a *polyion* and not of a *polymer component.* This result has not been explicitly given, though essentially equivalent statements were implicitly presented.[3,4] It may be somewhat significant to give the result in an explicit form, since a confusing expression about the thermodynamic interpretation of the non-ideal term has been reported recently.[6]

For ordinary polyelectrolytes, where a transition between discrete conformations is absent and polymer concentration remains unchanged during ionization, the term $\delta\mu_{p,i}^3$ vanishes. In this case, involved in the term $\mu_{p,i}^2$ are such contributions that the deviation of the mixing entropy of charged and uncharged sites from that of ideal behavior or the free energy due to the expansion of polymer chains. However, these contributions have been considered to be small compared with those involved in the term $\mu_{p,i}^{ei}$.[7] Hence in this case the non-ideal term reduces to

$$\Delta \mathrm{p}K = (0.434/\boldsymbol{RT})(\delta u_{p,i}^{el}/\delta i). \tag{13}$$

If conformational transition depending on ionization occurs, including the association of polymers, then the effect may be involved in the terms $\mu_{p,i}^2$ and $\mu_{p,i}^3$. Thus ΔpK should be expressed in a general form as Eq. (12).[8-10]

Thermodynamic Expression. Since we have derived an ordinary potentiometric equation in the preceding section, it becomes necessary to deduce a thermodynamic expression represented by Eq. (2) in terms of the same model consideration.

It should be noted that the change of the chemical potential of polyions associating with an infinitesimal change δi is independent of whether the change occurs as a virtual one or as a quasi-static one. The difference between these two changes resides in the respect whether the increase of charges on polyions is neutralized by hydrogen ions alone or by both counter ions and hydrogen ions. On account of this, the derivative involved in Eq. (8) can be replaced with one corresponding to quasi-static change.

$$(\delta\mu_{p,\, i}/\delta i)_{m_p,\, m_s,\, m_a} = (\partial\mu_{p,\, i}/\partial i)_{m_p, m_s}. \tag{14}$$

Thus from Eq. (8),

$$(\partial\mu_{p,\, i}/\partial i)_{m_p, m_s} + \mu_{\mathrm{H}} = 0. \tag{15}$$

Changing a variable from i to μ_{H}, we obtain the equation,

$$(\partial\mu_{p,\, i}/\partial\mu_{\mathrm{H}})_{m_p,\, m_s}(\partial\mu_{\mathrm{H}}/\partial i)_{m_p,\, m_s} + \mu_{\mathrm{H}} = 0. \tag{16}$$

According to the definition employed in the present treatment, the chemical potential of a polymer component can be written in terms of the constituent species.

$$\mu_p = \mu_{p,\, i} + i\,\mu_{\mathrm{H}}. \tag{17}$$

Differentiation of Eq. (17) with respect to μ_{H} yields,

$$(\partial\mu_p/\partial\mu_{\mathrm{H}})_{m_p,\, m_s} = (\partial\mu_{p,\, i}/\partial\mu_{\mathrm{H}})_{m_p,\, m_s} + i + \mu_{\mathrm{H}}(\partial i/\partial\mu_{\mathrm{H}})_{m_p,\, m_s}. \tag{18}$$

After Eq. (16) is taken into account, Eq. (18) finally reduces to

$$(\partial\mu_p/\partial\mu_{\mathrm{H}})_{m_p,\, m_s} = i = \alpha x. \tag{2}$$

Thus we have presented the equivalence of the two expressions, Eq. (2) and Eq. (11), by deriving them from a common basis.

Discussion

A brief comment should be added about the implication of the equations and averages under the situation of conformational changes. For the sake of brevity, we consider a solution where two discrete conformations "*a*" and "*b*" are present in equilibrium. In this case, three parameters are necessary to describe the system, which are taken to be i_a, i_b, and i. Here i_a and i_b denote average degrees of ionization of the respective conformations. The fraction of polymers in the "*a*"-conformation, f_a, is given as $(i-i_b)/(i_a-i_b)$. Two parameters i_a and i_b as well as f_a can be generally considered to be solved as the functions of $[m]$ and i from the equations

$$(\delta G/\delta i_a)_{[m],\, i,\, i_b} = 0, \tag{19}$$

and

$$(\delta G/\delta i_b)_{[m],\, i,\, i_a} = 0. \tag{20}$$

Here $[m]$ represents a set of variables n_w, m_p, m_s, and m_a. Hence, a virtual change δi consists of corresponding changes in δi_a, δi_b, and δf_a, which are uniquely determined if δi is given. The equilibrium value of i will be given by Eq. (3) as before. However, the implication of the equation in this case is,

$$(\delta G/\delta i)_{[m]} = (\delta G/\delta i_a)_{[m],\, i,\, i_b}(\delta i_a/\delta i)_{[m]} + (\delta G/\delta i_b)_{[m],\, i,\, i_a}(\delta i_b/\delta i)_{[m]} + (\delta G/\delta i)_{[m],\, i_a,\, i_b} = 0. \tag{21}$$

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[6] G. Torrence, S. Amdur, and J. A. Marinsky, *J. Phys. Chem.*, **75**, 2144 (1971).

[7] L. Kotin and M. Nagasawa, *J. Chem. Phys.*, **36**, 873 (1962).

[8] B. H. Zimm and S. A. Rice, *Mol. Phys.*, **3**, 391 (1960).

[9] M. Nagasawa and A. Holtzer, *J, Amer. Chem. Soc.*, **86**, 538 (1964).

[10] M. Nagasawa and A. Holtzer, *ibid.*, **93**, 606 (1971).

Subsequent equations, except the expressions for $\mu^1_{p,i}$ and $\delta\mu^1_{p,i}$ (Eq. (10)), can be interpreted similarly, if we take into account the relations,

$$\mu_{p,\,i} = f_a\mu_{p,\,i_a} + (1-f_a)\mu_{p,\,i_b} \tag{22}$$

and

$$\mu_{p,\,a} = \mu_{p,i_a} + i_a\mu_{\mathrm{H}} = \mu_{p,i_b} + i_b\mu_{\mathrm{H}} = \mu_p \tag{23}$$

since the conformational equilibrium is attained. Expressions for $\mu^1_{p,i}$ and $\delta\mu^1_{p,i}$ should be regarded as the definitions of them in this case.

From the discussion presented above, most of the equations are proved to hold in the case of conformational changes. However, the implication of averaged quantities such as $\mu_{p,i}$ or i may differ in both situations. Fluctuations from averages are considered to be relatively small in ordinary polyelectrolyte solutions, whereas they become considerably large in solutions where discrete conformations are present in equilibrium.