[Chem. Pharm. Bull. 23(12)3146—3150(1975)]

UDC 541.132.03 : 576.314

A Theoretical Study of Mobilities and Activity Coefficients of Small Ions in Charged Membranes

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(Received April 15, 1975)

Relation between the activity and mobility of small ions in charged membrane is derived theoretically using a cell model, where each macro-ion attached to the membrane matrix is assumed to be located at the center of individual cell. The result obtained shows that the mobilities of small ion are linearly proportional to the activity coefficient of the corresponding ion species in the membrane. This conclusion is consistent with the experimental results reported in a previous series of papers.

Introduction

The emf. arisen between two electrolyte solutions which are separated by a charged membrane is generally called the membrane potential. The membrane potential is a useful measure for characterizing the membrane-electrolyte systems, because the physical and chemical structures of the membrane, and the interaction between movable species and the molecules constituting the membrane are reflected on the potential difference across the membrane. Due to these reasons and the easiness of the measurements, the membrane potential have been investigated in a variety of fields of natural science including the biological and pharmaceutical sciences, and analytical chemistry.[2] The theory of membrane potential proposed first in 1935 by Teorell,[3] and by Meyer and Sievers[4] was known to be insufficient to describe the experimental data in quantitative manner.[5] Previous papers[6] showed that the discrepancy between the theory and experiments stemmed mainly from the remarkable non-ideal and asymmetric behaviours of activity coefficients and mobilities of small ions in charged membranes. The non-ideality of small ions, especially of the counter-ions, is brought about by the strong electrostatic interaction between the poly-electrolyte constituting the membrane and small ions. The extreme asymmetric behaviours of counter-and co-ions in charged membrane have been adequately represented by the "additivity rule" for the activity coefficients of small ions found empirically in the field of poly-electrolyte solution study.[7] This rule is written as follows;

$$\gamma_+ = \gamma_+{}^\circ \frac{C_- + \phi X}{C_- + X}, \qquad \gamma_- = \gamma_-{}^\circ \tag{1}$$

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[1] Location: *Kita 12 Nishi 6, Kita-ku, Sapporo.*

[2] K. Sollner, *Ann. N.Y. Acad. Sci.*, **148**, 154 (1968); N. Takeguchi and M. Nakagaki, *Biochim. Biophys. Acta*, **219**, 405 (1970); *idem, ibid.*, **233**, 753 (1971); M. Yoshida, N. Kamo, and Y. Kobatake, *J. Membrane Biol.*, **8**, 389 (1972); R. Tamamushi and S. Goto, *Bull. Chem. Soc. Japan*, **43**, 3420 (1970).

[3] T. Teorell, *Proc. Soc. Exptl. Biol.*, **33**, 282 (1935); *idem, Prog. Biophys. Biophys. Chem.*, **3**, 305 (1953).

[4] K.H. Meyer and J.F. Sievers, *Helv. Chim. Acta*, **19**, 649, 665, 987 (1936).

[5] N. Lakshminarayanaiah and V. Subrahmanyan, *J. Polymer Sci.*, **A2**, 4491 (1964); Y. Kobatake, N. Takeguchi, Y. Toyoshima, and H. Fujita, *J. Phys. Chem.*, **69**, 3981 (1965); G.J. Hills, P.W.M. Jacobs, and N. Lakshminarayanaiah, *Proc. Roy. Soc.* **A262**, 257 (1961).

[6] N. Kamo, Y. Toyoshima, H. Nozaki, and Y. Kobatake, *Kolloid Z.Z. Polymere*, **248**, 914 (1971); T. Ueda, N. Kamo, N. Ishida, and Y. Kobatake, *J. Phys. Chem.*, **76**, 2447 (1972); Y. Kobatake and N. Kamo, "Progress of Polymer Science Japan" Vol. 5, Kodansha Scientific, Tokyo, 1973, p. 257.

[7] A. Katchalsky, Z. Alexandrowics, and O. Kedem, "Chemical Physics of Ionic Solutions," John Wily and Sons, Inc, New York, 1966, p. 296; S.A. Rice and M. Nagasawa, "Polyelectrolyte Solutions," Academic Press, New York and London, 1961, 399.

where γ_i, γ_i°, C_-, and X stand for the activity coefficients of i-ion in the membrane, that in free bulk solution, concentration of co-ion and the stoichiometric density of charges fixed in the membrane, respectively. Here, membrane is assumed to have negative fixed charges. The parameter, ϕX $(0<\phi<1)$ is a characteristic constant of membrane-electrolyte combination under consideration, and represents the effective fixed charge density in the membrane.[6]

When the concentration of added salt, and hence the concentration of co-ions, C_- is sufficiently dilute compared with X, γ_+ tends to the value of $\phi\gamma_+^\circ$, which is much smaller than unity. This behaviour of the counter-ions in the membrane or poly-electrolyte solution is contrast to the ordinary electrolyte solution in which γ_i tends to unity at the infinite dilution. This similar phenomenon has been observed for the mobilities of counter-ions in the charged membrane. As shown in previous papers,[6] the mobilities of small ions in the membrane were found to be represented quantitatively by the same functional form as Eq. (1), *i.e.*

$$u_+ = u_+^\circ \frac{C_- + \phi' X}{C_- + X}, \qquad u_- = u_-^\circ \tag{2}$$

Here, ϕ' is a characteristic parameter representing the effect of fixed charges on the mobilities of small ions, and u_i° is the mobility of i-ion in the bulk electrolyte solution. Furthermore, the experimental data on the activity coefficients and mobilities in the membrane showed that $\phi=\phi'$ for a wide range of external salt concentrations.[6] This conclusion has been confirmed even in poly-electrolyte solution by measuring the self-diffusion of small ions.[8]

The relation that $\phi=\phi'$ suggests that the flow equation is written by

$$FJ_i = -u_i^\circ a_i \frac{d\tilde{\mu}_i}{dx} \tag{3}$$

where $\tilde{\mu}_i$ and a_i stand for the electro-chemical potential and activity of i-ion in the membrane phase. This representation for the flux of species i leads to a great simplification in the theoretical analysis of transport process in charged membranes. The significant utilization of Eq. (3) is described elsewhere.[9]

Several authors[10] attempted to derive theoretically the self-diffusion constant of small ions in dilute poly-electrolyte solutions, but their results did not accord with the experimental findings described above. In the present paper, the relation between the activity and mobility of small ions in charged membrane is investigated theoretically by using a cell model. The result obtained is in line with the conclusion drawn from the experimental studies.[6,8]

Basic Equation for Mobilities of Small Ions

The macro-ions constituting the membrane are assumed to localize periodically in the membrane phase with forming a cubic lattice of a lattice constant, $2d$. In other words, the membrane phase is subdivided into unit cell containing a macro-ion, which is regarded as the central ion in the unit cell. In any unit cell, the condition of the electroneutrality is assumed to be satisfied. Then, we confine our consideration to an arbitrary unit cell for calculating the flux of small ions. The electrostatic potential at a point in the cell caused by central ion is denoted by φ. The symmetry requirement of the electrostatic potential at the peripheral surface, R, can be written as

$$(\nabla\varphi)_R = 0 \tag{4}$$

Following the treatment of Katchalsky, *et al.*,[11] it may be assumed that

$$\varphi_R = 0 \tag{5}$$

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[8] T. Ueda and Y. Kobatake, *J. Phys. Chem.*, 77, 2995 (1973).

[9] N. Kamo, M. Oikawa, and Y. Kobatake, *J. Phys. Chem.*, **77**, 92 (1973).

[10] S.R. Coriell and J.L. Jackson, *J. Chem. Phys.*, **39**, 2418 (1963); S. Lifson and J.L. Jackson, *J. Chem. Phys.*, **36**, 2410 (1962); J.L. Jackson and S.R. Coriell, *J. Chem. Phys.*, **38**, 959 (1963); G.S. Manning, *J. Chem. Phys.*, **46**, 2324 (1967); *idem*, *ibid.*, **51**, 934 (1969); G.M. Bell, *Trans. Faraday Soc.*, **60**, 1752 (1964).

[11] A. Katchalsky and Z. Alexandrowicz, *J. Polymer Sci.*, **A1**, 2093 (1963).

since the choice of the reference point of potential is arbitrary. The concentration of i-ion at the surface of a cell is denoted by n_i^R, which is equivalent to the activity of i-ion.[12] The distribution of small ions in a cell is represented by Boltzmann's equation, and the concentration of i-ion n_i at a point $\vec{r}$, is given by

$$n_i = n_i^R \exp(-z_i e\varphi/\boldsymbol{kT}) = n_i^R \exp(-z_i\varepsilon) \tag{6}$$

where ε is the reduced electric potential defined by

$$\varepsilon = e\varphi/\boldsymbol{kT} \tag{7}$$

Here $\boldsymbol{e}$ stands for the electronic charge and $\boldsymbol{k}$, the Boltzmann constant.

When a constant electric field $\vec{\mathbf{E}}$ $(E,0,0)$ is applied in the direction of the x-axis, the local electric potential, ε and local concentration of i-ion, n_i, are changed to ε_E and n_i^E, respectively. Flow of i-ion, $\vec{\mathrm{J}}_i$ can be represented by

$$\vec{\mathrm{J}}_i = (\boldsymbol{kT}/\zeta_i)[\nabla n_i^E + n_i^E z_i \nabla\varepsilon_E + z_i n_i^E \vec{\mathrm{E}}/\boldsymbol{kT}] \tag{8}$$

where ζ_i is the friction constant of an i-ion and assumed to be constant irrespective of salt concentration. When the perturbed quantities, ε_E and n_i^E are linealized as

$$\varepsilon_E = \varepsilon(1+gE) \tag{9}$$

$$n_i^E = n_i^R \exp(-z_i\varepsilon)(1+f_iE) \tag{10}$$

Eq. (8) is transformed to give

$$\vec{\mathrm{J}}_i = -(n_i^R/\zeta_i)\exp(-z_i\varepsilon)[\nabla h_i + z_i\vec{\mathrm{K}}]E \tag{11}$$

under the approximation that the higher order terms of E are neglected. In Eq. (11), $\vec{\mathrm{K}}$ is the unit vector in the direction of the x-axis and h_i is defined as follows;

$$h_i = -\boldsymbol{kT}(f_i + z_i\varepsilon g) \tag{12}$$

To clarify the meaning of h_i, it is instructive to derive the relation between n_i^E and ε_E. Eliminating ε from Eqs. (9) and (10) with use of approximations that $gE \ll 1$ and $z_i\varepsilon_E gE \ll 1$, we obtain the following equation;

$$\begin{aligned} n_i^E &= n_i^R \exp[-z_i\varepsilon_E(1-gE)](1+f_iE) \\ &\simeq n_i^R \exp(-z_i\varepsilon_E)[1-(h_i/\boldsymbol{kT})E] \end{aligned} \tag{13}$$

Since the system is not in equilibrium owing to the externally applied electric field, $\vec{\mathrm{E}}$, the Boltzmann relation no longer retains between n_i^E and ε_E, and the function h_i represents the degree of deviation of n_i^E from the Boltzmann relation at the statistical equilibrium. Since the function f_i and g are periodic, the value of h_i repeates every unit cells. Then, the following boundary condition must be satisfied for h_i;

$$h_i(d, 0, 0) = h_i(-d, 0, 0) \tag{14}$$

The condition of the steady state of the flux of i-ions is given by the equation;

$$\nabla\cdot\vec{\mathrm{J}}_i = 0 \tag{15}$$

which leads to the relation between h_i and ε as follows;

$$-z_i(\nabla\varepsilon)\cdot(\nabla h_i) - z_i\frac{\partial\varepsilon}{\partial x} + \nabla^2 h_i = 0 \tag{16}$$

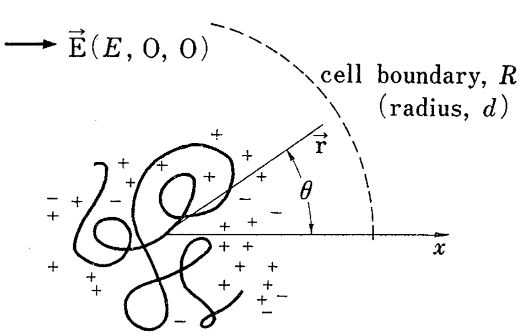

Fig. 1. A Spherical Macro-ion with the Uniform Distribution of Charged Groups in a Spherical Free Volume (Unit Cell)

External electric field, $\vec{\mathrm{E}}$, is applied in a direction parallel to x-axis.

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[12] Z. Alexandrowics and A. Katchalsky, *J. Polymer Sci.*, **A1**, 3231 (1963).

Derivation of Mobility for i-Ion from the Basic Equations

For simplicity of mathematical analysis, we replace the cubic unit cell by a sphere of radius d (see Fig. 1). The center of a spherically coiled macro-ion is taken as the coordinate origin of a cell. Defining q_i by Eq. (17)

$$q_i = h_i + z_i x \tag{17}$$

and introducing Eq. (17) into Eq. (16), we obtain

$$-z_i(\nabla\varepsilon)\cdot(\nabla q_i) + \nabla^2 q_i = 0 \tag{18}$$

Considering the symmetrical requirement, we may write

$$q_i = R_i(r)Q_i(\theta) \tag{19}$$

where r is $(x^2+y^2+z^2)^{1/2}$ and θ, the angle between x-axis and the vector $\vec{r}$. Introducing Eq. (19) into Eq. (18) and rearranging, we obtain the following two equations for θ and r;

$$\frac{d^2Q_i}{d\theta^2} + \cot\theta\frac{dQ_i}{d\theta} = -l(l+1)Q_i \tag{20}$$

$$-z_i r^2\frac{d\varepsilon}{dr}\frac{dR_i}{dr} + r^2\frac{d^2R_i}{dr^2} + 2r\frac{dR_i}{dr} = l(l+1)R_i \tag{21}$$

where $l(l+1)$ is a separating constant. The solution to Eq. (20) is given by $\boldsymbol{P}_l(\cos\theta)$ where $\boldsymbol{P}(\xi)$ is the Lagrangian function of l-th order. Then, q_i can be written by $\sum\limits_l R_{il}\boldsymbol{P}_l(\cos\theta)$. Comparing this equation with Eq. (17), *i.e.* $q_i = h_i(r, \cos\theta) + z_i r\cos\theta$, the value of l must be 0 or 1. When $l=0$, h_i is given by $-z_i r\cos\theta$ since $\boldsymbol{P}_0(\cos\theta)=1$. The relation, $h_i = -z_i r\cos\theta$ together with Eq. (11), however, leads to a trivial solution, *i.e.* $J_{ix}=0$. Then, the value of l is unity and Eq. (19) is recast as follows;

$$q_i = R_i(r)\cos\theta = R_i(r)\boldsymbol{P}_1(\cos\theta) \tag{22}$$

and Eq. (21) is reduced to

$$-z_i\frac{d\varepsilon}{dr}\frac{dR_i}{dr} + \frac{d^2R_i}{dr^2} + \frac{2}{r}\frac{dR_i}{dr} - \frac{2R_i}{r^2} = 0 \tag{23}$$

Boundary condition of Eq. (14) requires that

$$R_i(d) = z_i d \tag{24}$$

In order to solve Eq. (23), another boundary condition is required, which is not known *a priori*. However, it is certain that the boundary condition is independent of the variation of n_i^R. Near the spherical surface, R, ε is approximately equal to zero. Then, Eq. (23) can adequately be approximated by Eq. (25) at the boundary of a cell, R.

$$-z_i\frac{d\varepsilon}{dr}\frac{dR_i}{dr} - z_i\varepsilon\frac{d^2R_i}{dr^2} + \frac{d^2R_i}{dr^2} + \frac{2}{r}\frac{dR_i}{dr} - \frac{2R_i}{r^2} = 0 \tag{25}$$

Integration of Eq. (25) yields

$$-z_i\varepsilon\frac{dR_i}{dr} + \frac{dR_i}{dr} + 2\left(\frac{R_i}{r}\right) = A_i \tag{26}$$

where A_i is an integration constant. It is noted that the value of A_i is not related to n_i^R, since the integration constant is determined only from the boundary condition which is independent of n_i^R as mentioned above.

The total amount of i-ions, T_i, which is passing through the boundary spherical surface, R of $x \geq 0$ in the direction to x-axis is represented as follows;

$$\begin{aligned} T_i &= \int_0^{\pi/2} J_{ix}(r=d)2\pi d^2 \sin\theta d\theta \\ &= \left(\frac{2\pi}{3}d^2\right)(n_i^R/\zeta_i)\left[\frac{dR_i}{dr} + 2\frac{R_i}{r}\right]_{r=d} E \end{aligned} \tag{27}$$

Introducing Eqs. (26) and (5) into the above equation, we obtain

$$T_i = -(2\pi d^2/3)(n_i^R/\zeta_i)A_iE \tag{28}$$

Since the cross-sectional area of a unit cell perpendicular to the x-axis is πd^2, the flow of i-ion, J_i, which is defined as the flux of i-ion per unit area is expressed by

$$J_i = T_i/(\pi d^2) = -\left(\frac{2}{3}\right)\frac{n_i^R}{\zeta_i}A_iE \tag{29}$$

Discussion

Under the present condition, the mobility of i-ion, u_i, is defined as follows;

$$J_i = -u_iC_iz_iE$$

Comparing between this equation and Eq. (29) leads to the following relation.

$$u_iz_i = \frac{2}{3}A_i\gamma_iu_i^\circ \tag{30}$$

In the derivation of the above relation, $u_i^\circ = 1/\zeta_i$ and $\gamma_i = n_i^R/C_i$ are used since $= n_i^R$ is equal to the activity of i-ion as is insisted by Katchalsky, *et al.*[12] and by Oosawa.[13] They showed that the chemical potential of i-ion, μ_i, is represented by

$$\mu_i = \mu_i^\circ + \boldsymbol{RT}\ln n_i^R$$

from the mathematical analysis of the Poisson-Boltzmann equation, where μ_i° stands for the standard chemical potential. Eq. (30) implies that the mobility of counter-ions is proportional to the activity coefficient irrespective of the concentration of the added salt. Comparing the experimental results given by Eq. (1) and (2) with Eq. (30), A_i is equal to $(3z_i)/2$ under the approximation that $\gamma_\pm^\circ = 1$.

Eq. (1) and (2) are interpretated quantitatively as follows; The stoichiometric charges attached to the polymer skeletones, $\boldsymbol{X}$, are partially neutralized due to the strong adsorption of counter-ions (ion-pair or ion-binding), which reduces the fixed charge density of membrane from $\boldsymbol{X}$ to $\boldsymbol{\phi X}$-$\boldsymbol{\phi' X}$ provided that the dissociated small ions behave ideally. If the adsorbed counter-ions are bound so strong that the paired counter-ions are not moved by the electrical field applied externally, the conclusion drawn above is immediately followed. However, it is important to note here that the concept of "ion-binding" is not introduced in the argument presented in this article, and the results obtained are derived only from the flux equation in conjunction with the continuity law.

Alexandrowics, *et al.*[14] have measured the effective fixed charges for both thermodynamic properties and for the dissipative phenomena, (*e.g.* electrophoresis or electrical conductance) in dilute poly-electrolyte solutions. They have concluded that the former is smaller than the latter, which appears to contradict our experimental conclusions. At the present time, we cannot mention the cause of this discrepancy. It is noted, however, that the measurements of the diffusion constant of small ions in the poly-electrolyte solution support the conclusion drawn in the present article.[8] For the case of the membrane or the measurements with use of isotopes, the macro-ions are fixed to the membrane matrix or are not forced to be moved. Contrary to this, the macro-ions are transferred in solution phase in the experiments of electrophoresis and of electrical conductance. Then, it is feasible that the concentration dependence of u_i becomes identical with that of γ_i when the macro-ion are not moved. Further experimental studies are necessary.

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13) F.Oosawa, "Polyelectrolytes" Marcel Dekker, New York, 1971, p. 33.

14) H.E. Auer and Z. Alexandrowics, *Biopolymers*, **8**, 1 (1969).