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EFFECTS OF DIELECTRIC SATURATION ON PLANAR ELECTRIC DOUBLE LAYERS IN SALT SOLUTIONS

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The effects of dielectric saturation on planar electric double layers in salt solutions are examined by solving the Poisson-Boltzmann equation analytically where the dielectric constant is given as a function of the electric displacement. The activity and the distribution of small ions, the surface potential and the Donnan potential are calculated. The salt exclusion parameter and the Donnan potential decrease while the surface potential increases as a result of the dielectric saturation. The electrostatic entropy is affected considerably by the dielectric saturation while the electrostatic energy is little influenced. Generally, the effects of dielectric saturation on the distribution of small ions and the thermodynamic properties are enhanced by the addition of salt.

1. Introduction

The effects of dielectric saturation on planar electric double layers have been examined in terms of the dielectric constant ϵ which is expressed as a function of the electric field, E [1–3]. Recently, we have proposed the following expression of the dielectric constant ϵ as a function of the electric displacement D, instead of E, from a phenomenological approach [4],

$$\epsilon = (\epsilon_0 + 3\alpha D^2)/(1 + \alpha D^2). \qquad (1)$$

Here ϵ_0 denotes the dielectric constant at a vanishingly small field strength and α is a parameter representing the extent of dielectric saturation. Eq. (1) was compared with other expressions proposed by several authors [4]. Eq. (1) has several advantages over other expressions.

(a) The Poisson-Boltzmann equation can be analytically solved for most cases, since the dielectric constant is given as a function of the electric displacement [see eq. (8)].

(b) The expression has been derived from a general consideration on thermodynamics and electrostatics. Accordingly, the physical basis of eq. (1) is clearer than that proposed by Grahame [1].

(c) The expression is relatively simple as compared with others derived from the statistical mechanical approach [5–8].

(d) The expression is given in a closed form to cover the whole range of D. Therefore, it can be applied to a higher field strength than other series expansions which contain only the terms up to E^2 [2,3].

(e) The dielectric constant at infinitely high field strengths is given as 3, which has been assumed in previous studies. Since eq. (1) is an approximate one, this limiting value of 3 became independent of the material.

In the previous study [4], planar electric double layers were examined in the absence of added salts. In the present study, planar double layers are examined in the presence of simple salts by using eq. (1). As in the foregoing studies [1–3], we confine ourselves to the calculations of the electric potentials, the distribution of small ions, and the thermodynamic quantities. To facilitate these calculations, a model of an assembly of parallel plates with surface charges is employed. This model is convenient to study the thermodynamic properties of planar polyelectrolyte solutions and to understand, for example, the electrostatic properties of the beta-structure of polypeptides [9]. Biological membranes are often highly charged and may have a strong hydration layer in which the dielectric constant is lowered. It is hoped that the

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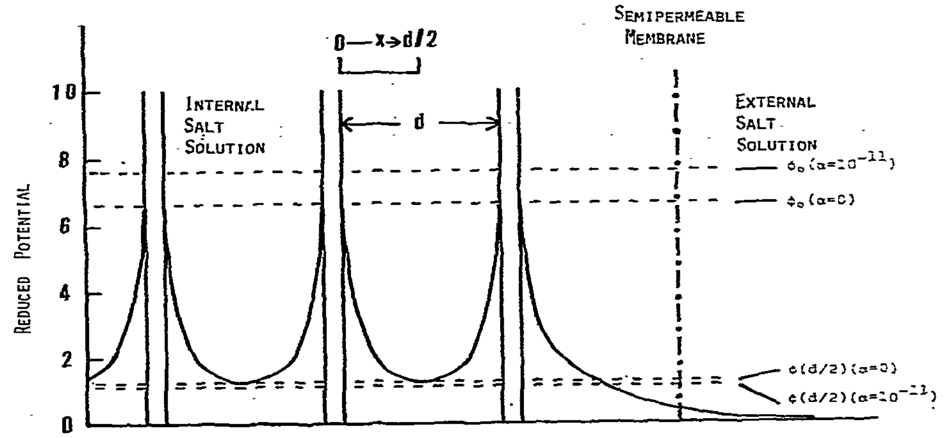

Fig. 1. Schematic representation of the system. Infinitely large plates are placed in a salt solution (C_s) with a uniform interplate distance d. The distance from the surface is denoted as x. The whole solution is in osmotic equilibrium with an external salt solution (C_s') through a semi-permeable membrane. Reduced surface potential ϕ_0 and reduced Donnan potential $\phi(d/2)$ are shown, which are calculated for a particular set of parameters: d = 100 A, surface charge density is 0.01 protonic charge/A^2, $C_s' = 10^{-2}$ M. α is given in the unit of (cm^2/esu)^2. C_s is 1.511×10^{-3} M for $\alpha = 0$ and 1.683×10^{-3} M for $\alpha = 10^{-11}$. Spatial distribution of electric potential is shown only schematically.

present treatment will give a basis for the future analysis of the effect of the dielectric saturation on the property of biological membranes.

As in the previous paper [4], what we wish to present here is a phenomenological approach to the problem. The macroscopic concept of dielectric saturation must have a molecular basis. Therefore, the present problem is to be handled also from a microscopic standpoint. The results of the present treatment must be compated with the results of a molecular dynamical approach, in future.

2. Solution of the Poisson-Boltzmann equation under osmotic equilibrium

Consider a series of parallel plates immersed in a salt solution, in an osmotic equilibrium with an external salt solution through a semi-permeable membrane as depicted in fig. 1. Positive charges are assumed to spread over the surface with a uniform density σ. The added salt is a uni-univalent type and has a common counterion species to that originating from the sites on the surface of plates. The reference point for electric potential $\psi(x)$ is taken in the bulk of the external solution. Accordingly, the potential at the midpoint between two plates $\psi(d/2)$ stands for the Donnan potential. The Donnan potential decreases as the interplate distance d increases and/or as the external salt concentration C_s' increases. In the limit where the Donnan potential is negligible, the system under consideration is reduced to a single plate immersed in an infinite volume of the salt solution.

Concentrations of counterions $C_-(x)$ and coions $C_+(x)$ are given by the Boltzmann law in terms of the external salt concentration C_s' and the reduced potential ϕ, defined as $e_0\,\psi/kT$, where the Boltzmann constant, the protonic charge, and the absolute temperature are denoted as k, e_0, and T, respectively. The concentrations C_s', C_- and C_+ are expressed in (ions/cm^3) unless otherwise stated.

$$C_-(x) = C_s' \exp(\phi), \qquad C_+(x) = C_s' \exp(-\phi). \tag{2}$$

The Poisson–Boltzmann equation is written as follows in terms of the electric displacement D.

$$\mathrm{d}D/\mathrm{d}x = -8\,\pi e_0\, C_s' \sinh(\phi). \tag{3}$$

Differentiation of eq. (3) with respect to x yields,

$$\mathrm{d}^2D/\mathrm{d}x^2 = (8\,\pi e_0^2\, C_s'/kT) \times [1 + (8\,\pi e_0\, C_s')^{-2}\,(\mathrm{d}D/\mathrm{d}x)^2]^{1/2}\,(D/\epsilon). \tag{4}$$

If sinh (ϕ) is written as $z(x)$, then eqs. (3) and (4) can be rewritten as follows.

$$z = -(8\pi e_0 C_s')^{-1}\,(\mathrm{d}D/\mathrm{d}x). \tag{5}$$

$$\mathrm{d}z/\mathrm{d}x = (1+z^2)^{1/2}\,(-e_0/kT)(D/\epsilon). \tag{6}$$

Eq. (6) can be rearranged into eq. (7) if eq. (5) is used.

$$\mathrm{d}(1+z^2)^{1/2} = (8\pi C_s' kT)^{-1}\,(D/\epsilon)\,\mathrm{d}D. \tag{7}$$

Using the boundary condition that $D = 0$ at $x = d/2$ (midpoint), we can carry out the integration of eq. (7).

$$(1+z^2)^{1/2} - (1+z_1^2)^{1/2} = (8\pi C_s' kT)^{-1}\int_0^D (D/\epsilon)\,\mathrm{d}D, \tag{8}$$

where $z_1 = z(x = d/2) = \sinh \phi(d/2)$. (9)

Introduction of eq. (1) into eq. (8) leads to

$$(1+z^2)^{1/2} - (1+z_1^2)^{1/2} = (48\pi C_s' kT)^{-1}\left[D^2 - \frac{\epsilon_0 - 3}{3\alpha}\ln\left(\frac{\epsilon_0 + 3\alpha D^2}{\epsilon_0}\right)\right]. \tag{10}$$

In terms of dimensionless quantities defined below, eqs. (5) and (10) are rewritten into eqs. (11) and (12), respectively.

$$z = -(1/B)\,(\mathrm{d}Y/\mathrm{d}X), \tag{11}$$

$$(1+z^2)^{1/2} - (1+z_1^2)^{1/2} = (\epsilon_0/6B)\left[Y^2 - \frac{\epsilon_0 - 3}{12A}\ln\left(\frac{\epsilon_0 + 12AY^2}{\epsilon_0}\right)\right]. \tag{12}$$

Here $Y = D/D_\mathrm{d}$, $D_\mathrm{d} = 2\epsilon_0 kT/e_0 d$, $B = (\kappa d/2)^2$, $A = \alpha D_\mathrm{d}^2/4$, $X = 2x/d$, and $\kappa^2 = 8\pi e_0^2 C_s'/\epsilon_0 kT$.

Eq. (12) is solved for z and the result is substituted into eq. (11), and the integration is made between $X = 1$ and X; then, we obtain,

$$\int_0^Y z^{-1}\,\mathrm{d}Y = \int_0^Y \mathrm{d}Y\left\{(\epsilon_0/6B)\times\left(Y^2 - \frac{\epsilon_0 - 3}{12A}\ln\frac{\epsilon_0 + 12AY^2}{\epsilon_0} + (1+z_1^2)^{1/2}\right)^2 - 1\right\}^{-1/2} = -\int_1^X B\,\mathrm{d}X = B(1-X). \tag{13}$$

From another boundary condition at the surface $D_0 = D(X = 0) = -4\pi\sigma$ (σ is expressed as esu/cm^2), z_1 can be determined by the following equation.

$$\int_0^{Y_0} z^{-1}\,\mathrm{d}Y = B, \tag{14}$$

where $Y_0 = D_0/D_\mathrm{d}$.

The solution of the Poisson-Boltzmann equation for the case where the dielectric saturation is not taken into account, i.e., $\alpha = 0$, has been given by Verwey and Overbeek [10]. It is pertinent to give the result in the present notations.

$$\phi(x) = \phi(d/2) + B^{-1}\int_0^Y (Y/z)\,\mathrm{d}Y. \tag{15}$$

$$z = \{[Y^2/2B + (1+z_1^2)^{1/2}]^2 - 1\}^{1/2}. \tag{16}$$

3. Distribution and activities of small ions

When z_1 is determined from eq. (14), the Donnan potential and activities of counterions a_- and of coions a_+ can be evaluated as follows.

$$\psi(d/2) = (kT/e_0)\,\phi(d/2) = (kT/e_0)\ln\{z_1 + (1+z_1^2)^{1/2}\} \tag{17}$$

$$a_- = C_s'\{z_1 + (1+z_1^2)^{1/2}\}$$

and

$$a_+ = C_s'\{(1+z_1^2)^{1/2} - z_1\}. \tag{18}$$

In the case of no added salt where the total number of counterions is fixed under a given charge density, there is an upper limit for the counterion activity a_- [4]. In the present system, the number of counterions is not fixed since they can be supplied from a reservoir (the external salt solution). However, limiting values for the counterion activity also exist when C_s' is moderately small. When C_s' is about 10^{-6} M, the limiting values coincide with the results obtained for the case of no added salts for most interplate distances.

The salt concentration of the internal solution C_s is defined as the average or stoichiometric concentration of coins $\langle C_+\rangle$.

Table 1
The Donnan salt exclusion parameter Γ for a charge density of 0.01 e_0/A

C_s' (M)	10^{-3}	10^{-2}	0.1	0.2	0.5
α [a] = 10^{-11}	1.13×10^{-2}	3.40×10^{-2}	9.33×10^{-2}	0.123	0.172
$\alpha = 0$	1.14×10^{-2}	3.53×10^{-2}	0.103	0.139	0.196
ratio [b]	1.00	0.96	0.91	0.88	0.88

[a] α is expressed as $(\mathrm{cm}^2/\mathrm{esu})^2$. [b] Ratio = $\Gamma(\alpha = 10^{-11})/\Gamma(\alpha = 0)$.

$$C_s = \langle C_+\rangle = (2/d)\int_0^{d/2} C_s' \exp(-\phi)\,\mathrm{d}x$$

$$= (C_s'/B)\left\{\int_0^{Y_0} [(1+z^2)^{1/2}/z]\,\mathrm{d}Y - Y_0\right\}. \qquad (19)$$

The analytical or average concentration of counterions C_- is given as follows.

$$\langle C_-\rangle = C_s + C_e = C_s + 2\sigma/(e_0 d), \qquad (20)$$

where C_e denotes the counterion concentration originated from sites on the plates.

Interaction between salt and polyelectrolyte components (charged plates plus counterions) can be described in terms of the well-known Donnan salt exclusion parameter. Some numerical results on the salt exclusion parameter at infinite dilution Γ are given in table 1, i.e.,

$$\Gamma = \lim_{C_e \to 0} (C_s' - C_s)/C_e. \qquad (21)$$

The salt exclusion parameter in this limit Γ decreases as a result of dielectric saturation. Hence the effect of dielectric saturation reduces the repulsive interactions between salt and polyelectrolyte components. However, the effect disappears as C_s' approaches zero and the same limiting value of Γ is obtained at zero salt concentration irrespective of α. This is consistent with the statement that the macroscopic dielectric constant can be used to describe thermodynamic properties of polyelectrolyte solutions in the limit of infinite dilution [11]. Accordingly, the addition of salts causes a deviation from this limiting behavior and effects of dielectric saturation become enhanced as the salt is added.

Activity coefficients of counterions and coins are evaluated from eqs. (18), (19) and (20). Effects of dielectric saturation on activity coefficients of both counterions and coions are almost independent of the external salt concentration in a wide range between 10^{-6} M and 0.5 M. The effects are appreciable only for short interplate distances, where counterions are attracted more strongly to the surface as a result of dielectric saturation. On the other hand, the dielectric saturation has almost no effect on coion activity coefficients.

4. Surface potential of plates and the Donnan potential

Reduced Donnan potential $\phi(d/2)$ is given by eq. (17). An example for a surface charge density of 0.01 $e_0/\text{Å}^2$ is given in table 2. It is to be noted that the dielectric saturation reduces the Donnan potential.

The reduced surface potential ϕ_0 is evaluated as follows

$$\mathrm{d}\phi = -\frac{e_0}{kT} E\,\mathrm{d}x = -\frac{e_0 d}{2\epsilon kT} D\,\mathrm{d}X = -\frac{\epsilon_0}{\epsilon} Y\,\mathrm{d}X. \qquad (22)$$

$$\Delta\phi_0 \equiv \phi_0 - \phi(d/2) = \int_0^1 \frac{\epsilon_0}{\epsilon} Y\,\mathrm{d}X$$

$$= \int_0^1 \frac{(1+\alpha D^2)\,\epsilon_0}{\epsilon_0 + 3\alpha D^2} Y\,\mathrm{d}X$$

$$= \frac{\epsilon_0}{B}\int_0^{Y_0} \frac{Y(1+4AY^2)}{z(\epsilon_0 + 12AY^2)}\,\mathrm{d}Y, \qquad (23)$$

$$\phi_0 = \Delta\phi_0 + \phi(d/2) = \Delta\phi_0 + \ln[z_1 + (1+z_1^2)^{1/2}]. \qquad (24)$$

Table 2
Reduced Donnan potential for a charge density of 0.01 e_0/Å^2 for various interplate distances d and external salt concentrations C_s'

C_s'(M)	10^{-6}	10^{-3}	10^{-2}	0.1	0.5
$d = 10$ Å					
$\alpha = 10^{-11}$ [a]	14.216	7.308	5.006	2.706	1.155
$\alpha = 0$	14.418	7.510	5.208	2.907	1.335
$d = 10^2$ Å					
$\alpha = 10^{-11}$	10.337	3.430	1.177	0.029	0
$\alpha = 0$	10.419	3.511	1.251	0.035	0
$d = 10^3$ Å					
$\alpha = 10^{-11}$	5.882	0.042	0	0	0
$\alpha = 0$	5.892	0.043	0	0	0

[a] α is expressed in (cm^2/esu)^2.

The reduced surface potential ϕ_0 decreases linearly with ln C_s' if C_s' is not too large as shown in fig. 2. It gradually levels off as C_s' becomes large. The dielectric saturation does not affect this logarithmic dependence on C_s' but only increases ϕ_0 by nearly a constant amount. In fig. 2 the difference $[\phi_0(\alpha = 10^{-11}) - \phi_0(\alpha = 0)]$ is also shown. The difference is almost independent of C_s' for small values of C_s'. However, since the potential ϕ_0 itself increases rapidly for small values of C_s', the relative magnitude of the effect of dielectric saturation becomes progressively small as the condition of infinite dilution is approached. The difference is independent of the interplate distance d if d is larger than 100 Å. When d is 10 Å, the differ-

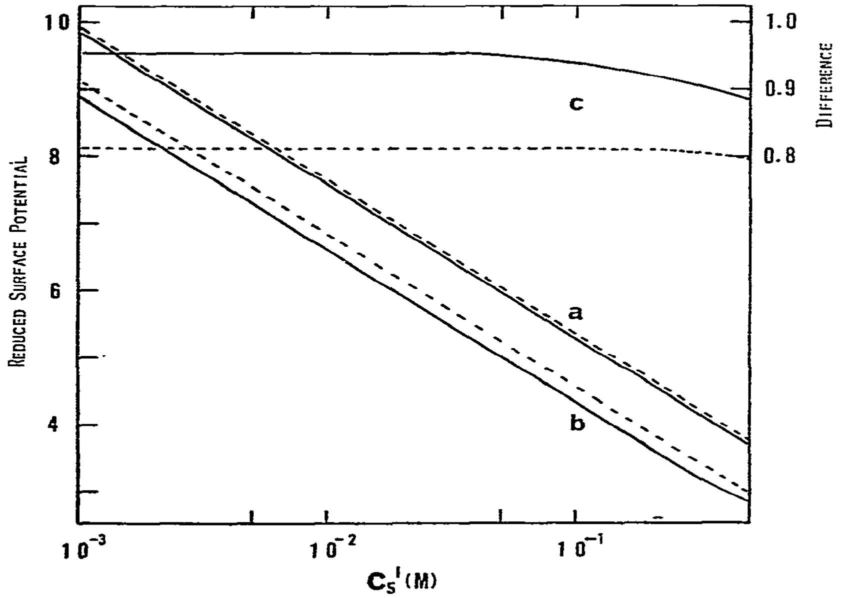

Fig. 2. Reduced surface potential for a charge density of 0.01 protonic charge/Å at different external salt concentrations C_s'. Interplate distance d: 10 Å (dotted lines) and 10^2–10^4 Å (solid lines). Reduced surface potential ϕ_0: (a) $\alpha = 10^{-11}$ and (b) $\alpha = 0$. Differences between curves (a) and (b), $\phi_0(\alpha = 10^{-11}) - \phi_0(\alpha = 0)$, are given by curves (c).

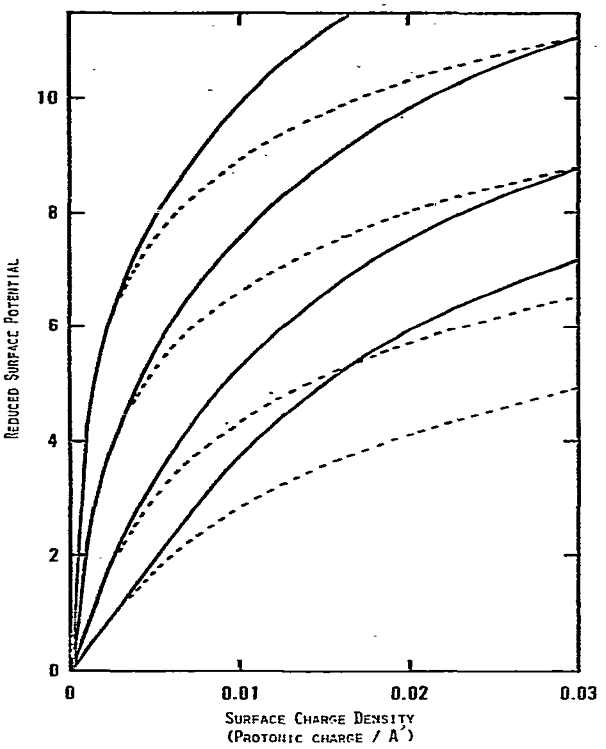

Fig. 3. Potentiometric titration curves for an isolated plate. Solid and dotted curves correspond to $\alpha = 10^{-11}$ and $\alpha = 0$ $(\mathrm{cm}^2/\mathrm{esu})^2$, respectively. Salt concentrations C_s'(M); (from top to bottom) 10^{-3}, 10^{-2}, 10^{-1}, and 0.5.

ence becomes smaller and its dependence on C_s' is further reduced. The reduced surface potential ϕ_0 itself decreases only slightly with the interplate distance d for d smaller than 100 Å but it remains nearly constant for d larger than 100 Å. This constant value corresponds to the potential of an isolated plate immersed in an external salt solution. The dependence of the reduced surface potential in this limit on the surface charge density is given in fig. 3 for different external salt concentrations. The curves in fig. 3 are regarded as the potentiometric titration curves at zero polyelectrolyte concentration.

When the effect of dielectric saturation on the surface potential at a constant (internal) salt concentration is considered, the reference point for the electric potential is taken at the midpoint between two adjacent plates. Therefore, $\Delta\phi_0$ [$= \phi_0 - \phi(d/2)$] should be computed instead of ϕ_0. Values of $\Delta\phi_0$ for a charge density of 0.01 $e_0/\text{Å}^2$ are shown in fig. 4. Linearity between $\Delta\phi_0$ and ln C_s holds if the interplate distance d is larger than 10^3 Å. But the deviation from the linearity occurs when d is smaller than 100 Å. The dielectric saturation again does not affect the dependence of $\Delta\phi_0$ on C_s but increases $\Delta\phi_0$ by nearly a constant amount. Contrary to the Donnan potential or the surface potential, $\Delta\phi_0$ increases considerably with increasing interplate distance d for a range of d smaller than 10^3 Å but it becomes independent of d for d larger than 10^3 Å.

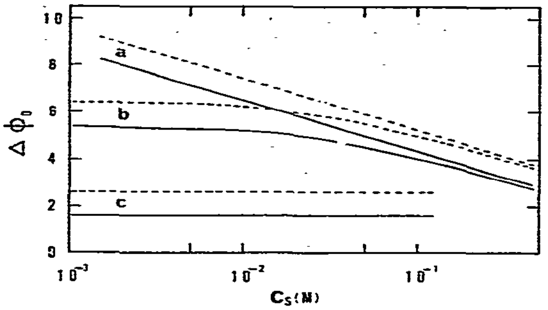

Fig. 4. Reduced surface potential refered to the midpoint between two adjacent plates for a charge density of 0.01 protonic charge/Å at different internal salt concentrations C_s. Solid lines: $\alpha = 0$, dotted lines: $\alpha = 10^{-11}$ $(\mathrm{cm}^2/\mathrm{esu})^2$. Interplate distance d (Å): (a) 10^3 and 10^4, (b) 10^2, and (c) 10.

Effects of dielectric saturation on electric potentials are summarized as follows. Both ϕ_0 at a constant C_s' and $\Delta\phi_0$ at a constant C_s increase due to this effect while the Donnan potential decreases. This is understandable since the spatial distribution of the electric potential is modified by the effect of dielectric saturation in such a way that the potential near a charged plate is increased but it is decreased in the remaining space. This general feature of the potential distribution modified by dielectric saturation has been found already in the absence of added salts [4].

5. Electrostatic energy, entropy, and free energy

The effect of dielectric saturation on the electrostatic energy, the entropy, and the free energy can be examined when these thermodynamic quantities are computed at the same salt concentration. Generally, the internal salt concentration C_s at a given external salt concentration C_s' depends on whether or not the dielectric saturation is taken into account. Thermodynamic quantities as well as C_s have been calculated as functions of C_s' for different values of α. Therefore, the thermodynamic quantities at the same value of C_s are also obtained.

The electrostatic energy and the entropy per unit area of the surface are denoted as U_{el} and S_{el} and evaluated as follows [12].

$$U_{el} = \frac{1}{4\pi} \int_0^{d/2} dx \int_0^{D} E\, dD = \frac{D_d kT}{4\pi e_0}$$

$$\times \left\{ \int_0^{Y_0} \frac{(1+z^2)^{1/2}}{z}\, dY - B(1+z_1^2)^{1/2} \right\}. \tag{26}$$

$$-TS_{el} = kT \left\{ \int_0^{d/2} C_+ \ln(C_+/\langle C_+\rangle)\, dx \right.$$

$$\left. + \int_0^{d/2} C_- \ln(C_-/\langle C_-\rangle)\, dx \right\} \tag{27}$$

$$= (kTd/2)(\langle C_+\rangle + \langle C_-\rangle) \ln C_s'$$

$$-(kTd/2)(\langle C_+\rangle \ln \langle C_+\rangle + \langle C_-\rangle \ln \langle C_-\rangle)$$

$$+ (kTdC_s'/B) \int_0^{Y_0} \sinh^{-1} z\, dY. \tag{28}$$

The corresponding free energy F_{el} is given as follows.

$$F_{el} = U_{el} - TS_{el}. \tag{29}$$

It has been shown [4] that the definition of the electrostatic free energy given by eqs. (25), (27), and (29) is consistent with the Boltzmann distribution of small ions for the case of no added salts. Consistency of the Boltzmann distribution eq. (2) with this definition of the free energy can be also demonstrated in the presence of added salts.

From the above definitions, eqs. (25) and (27), the energy, the entropy, and the free energy are excess quantities refered to a hypothetical solution where all Coulombic interactions between charges are absent. Small ions are distributed uniformly throughout this reference solution. It is to be noted that the electostatic internal energy of the present system is to be regarded as a free energy with respect to the dielectric medium, as pointed out by Bell and Levine [13]. Accordingly, the contribution to entropy from the dielectric saturation as well as the temperature dependence of α and ϵ_0 are included in the term U_{el}. In fig. 5, F_{el}/kT and $-S_{el}/k$ are plotted against the surface charge density for various salt concentrations at a given interplate distance of 100 Å. In the calculation, a value of 10^{-11} (cm^2/esu)^2 was used for α. The effect of dielectric saturation can be evaluated by ratios such as $U_{el}/U_{el}(0)$, where the denominator stands for the value without dielectric saturation (corresponding to the case that $\alpha = 0$). An example is given in fig. 6 for the interplate distance of 100 Å. Effects of dielectric saturation on the electrostatic energy, entropy, and free energy are similar to those found in the case of no

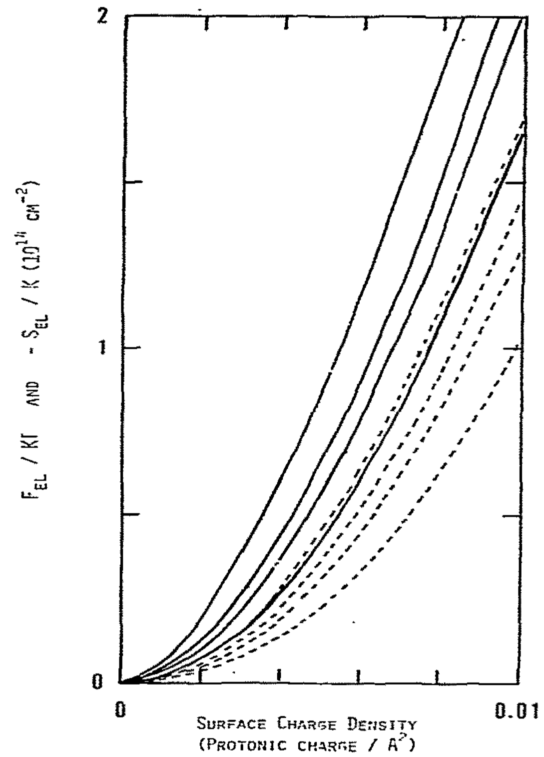

Fig. 5. Electrostatic free energy F_{el} and entropy S_{el} as functions of surface charge density for different internal salt concentrations C_s. F_{el}/kT (———), $-S_{el}/k$ (· · ·), interplate distance 100 Å. Salt concentration C_s(M): (from top to bottom) 10^{-3}, 0.1, 0.2, and 0.5.

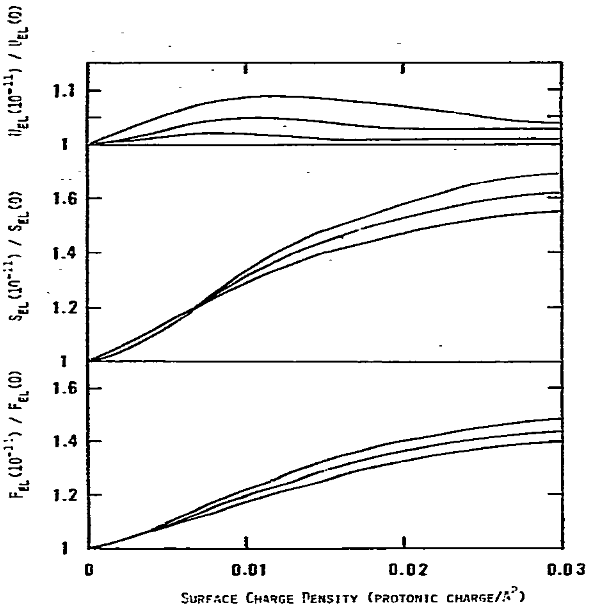

Fig. 6. Effects of dielectric saturation on the electrostatic energy U_{el}, entropy S_{el}, and free energy F_{el} for various surface charge densities and internal salt concentrations C_s. Interplate distance d is 100 Å. Salt concentration C_s(M): (from top to bottom) 0.5, 0.2, and 2×10^{-2}.

added salts [4]. Electrostatic entropy S_{el} is affected considerably while internal energy U_{el} is only slightly affected. The addition of salts does not alter these essential features. For a short interplate distance as 10 Å, the counterion concentration originating from the sites on plates is very high. Under this condition, effects of the dielectric saturation are significant and almost independent of the salt concentration C_s for a range between 0 and 0.1 M. Accordingly, for the interplate distance of 10 Å, thermodynamic quantities at any salt concentration below 0.1 M are almost identical to those obtained in the previous study in the absence of added salts. At large interplate distances, on the other hand, the dielectric saturation has little effect in the absence of added salts. The addition of salts to those solutions causes a deviation from the state of infinite dilution. Therefore, effects of dielectric saturation become more significant on the addition of salts. However, the addition of salts is not as effective as the addition of colloidal electrolytes (equivalent to the decrease of the interplate distance d) to amplify the effect of dielectric saturation.

Numerical calculations were carried out with a FACOM 230-75 computer at the Computation Center of Nagoya University.

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