Linear dependence of the standard ion-transfer potentials of polyanions at the oil | water interface on the surface interaction energy and the charge

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Abstract

The reported linear dependence of standard ion-transfer potentials of heteropolyanions, e.g. [SiW$_{12}$O$_{40}$]$^4^-$, at the nitrobenzene | water interface on the surface charge densities of polyanions cannot be explained completely in terms of the ionic properties and electrostatic energy. A model leading to better understanding is proposed here, in which the ion is solvated with an intermolecular force between the ion and oil or water molecules under electrochemical equilibrium conditions. Assuming that the solvation energy is proportional to the surface area of the polyanion, the partition function of the charged polyanion in the electrostatic potential was derived. The potential detected electrochemically is not a local potential in the vicinity of the ion, but is the potential averaged over each phase. The partition function leads to a linear relation of the potential difference with the interaction energy density and an inverse linear relation with the charge. The potential difference contains no Born-type electrostatic energy. The linear dependence agrees with the experimental result of polyanions, tetralkylammonium ions and simple inorganic anions for various values of radii and charge numbers of the ions. The slope of the linear plot gives the surface energy density or the surface tension at the interface between the ion and the solvent in the first solvation shell. The surface energy of the polyanions is larger than that of the conventional liquid | liquid interface, suggesting a hard solvated shell. The discussion is directed to the energy forming the cavity, the effect of the second solvation shell, the Kelvin effect and the electrostatic contribution except the electrode potential.

Keywords: Linear dependence; Polyanions; Ion transfer; Solvation energy

1. Introduction

Ion transfer taking place in biomembrane systems, solvent extraction and liquid-membrane type ion-selective electrodes is motivated by the difference in the Gibbs energy or the hydrophobicity of ions between two phases. An available measure of the degree of ion transfer is the electrostatic potential difference in the two phases, which can be determined from voltammetry using a polarizable oil | water interface, namely ion-transfer voltammetry [1-3]. It provides not only a convenient criterion for analytical applications but also physicochemical information about the interface such as solvation states, adsorption, orientation, and the kinetics of transferring ions at the oil | water interface.

The electrostatic contribution of the Gibbs energy has frequently been discussed [4] in the context of the electrical work of carrying an ion from one phase into the other with a different dielectric medium, called the Born model [5]. However, the Born model rarely holds [6,7] in the relation between the ionic radius and polarity of the solvent [8], in the difference in solubility of large cations and anions [9], and in the potentiality of penetrating large ions into biological membranes [10]. Several modifications include estimations of the radii of ions [6,11], and correction of the permittivity of solvents by a continuous model [12,13], by non-linear dielectric effects [14,15] and by a statistical model [16,17].

In order to examine in detail the defects of the Born model, one has to remove the ambiguity of evaluating ion radii. A candidate for acquiring a series of ionic data is a heteropolyanion, e.g. [SiMo$_{12}$O$_{42}$]$^{14^+}$ [18,19], because the number of oxygen atoms included in the polyanion is proportional to its spherical volume. An additional advantage of the polyanion is the variety of available charge numbers (-2 to -6). Recently accumulated data [20-23] have led to the empirical conclu-
of the polyanions. The linear relation demonstrates obviously the defect of the Born model. Unfortunately, there is little hope of explaining the linearity using conventional ionic properties because the concept of surface charge holds for macroscopic electric conducting materials rather than ions. The linear dependence on the ionic surface area belongs to the short-range force. Thus it may be a sort of solvophobic effect [7]. A quantity relevant to the surface area is the interfacial interaction between the ion and the solvent. As an attempt to connect the interfacial interaction and the electrochemically detected potential, this paper is devoted to formulating the equilibrium conditions by means of statistical mechanics and applying the formula to the data [23] of ion-transfer potentials of polyanions.

2. Model and derivation

It is assumed that the interaction energy between the polyanion and solvent molecules contributes to the formation of the first solvation shell. When the polyanion is much larger than the solvent molecule, the interaction including the orientation energy for the solvent is proportional to the surface area \( s \) of the polyanion. Letting \( u_j \) be the interaction energy per area of the polyanion in solvent \( j \), then the interaction energy per polyanion is given by \( u_j s \). We define \( v_j \) as a sum of various secondary contributions of the solvation energy. The \( v_j \) includes the energy of forming a cavity of the solvated ion in solvent \( j \), the energy of structuring the second and succeeding solvation shells, and the dependence of the surface energy on the curvature of the ion. Since emphasis is put on the interaction here, ‘secondary’ means secondary attention rather than a quantitatively smaller contribution. These secondary effects are discussed in Section 3. We further define \( \mu_j^\sigma \) as the chemical potential of an imaginary uncharged particle without any chemical interaction with the solvent. That is, \( \mu_j^\sigma \) represents the energy caused by physical collision with the solvent molecules. Then the chemical potential of the solvated polyanion without charge can be expressed by \( \mu_j^\sigma + u_j s + v_j \).

When the polyanion with charge \( z \) is in a local electric potential \( \phi_j^{lel} \), it has an electric energy \( z e \phi_j^{lel} \), where \( e \) is the elementary charge. Taking into account the electrostatic term and the solvation term, we can define the Hamiltonian of the polyanion in solvent \( j \) as

\[
H_j = \mu_j^\sigma + u_j + u_j s + z e \phi_j^{lel} \quad \text{for} \quad j = O \text{ or } W
\]

where \( O \) and \( W \) stand for the oil and water phases respectively. The \( \phi_j^{lel} \) depends on the position of the ion or distances from the other ions whereas \( \mu_j^\sigma, v_j, u_j, s \) are common to all the polyanions. Mutual solvation or coexistence of \( u_O s' \) and \( u_W (s - s') \) in a given phase can be neglected because of the small values of mutual solubility in nitrobenzene and water (0.19 wt.% nitrobenzene in the water phase and 99.76 wt.% nitrobenzene in the nitrobenzene phase).

The solvation energy within the oil |water interface depends on the structure and thickness of the interface, i.e. how sharply the composition (O and W) varies, what is the concentration distribution of the ion, and what is the potential profile within the interface. Since it alters with the distance \( x \) normal to the average interface plane, the Hamiltonian at the interface is given by

\[
H_I = \mu_I^\sigma + u_I + u_I s + z e \phi_I^{lel}(x)
\]

as a function of \( x \).

It is assumed that only the polyanion is transferred across the oil |water interface in a given potential domain. When there are \( n_W, n_O \) and \( n_I \) polyanions respectively in the water, the oil phase and the interfacial domain at temperature \( T \), the canonical partition function of the polyanion in these phases is expressed by

\[
Z = \frac{n!}{n_W! n_O! n_I!} \left( \int \exp \left( - \frac{H_I}{k_B T} \right) dV_J \right)^{n_J}
\]

where \( k_B \) is the Boltzmann constant, \( n = n_W + n_O + n_I \), and \( V_j (j = O, W, \text{and } I) \) is the volume of phase \( j \). The \( H_I = \mu_I^\sigma + u_I + u_I s + z e \phi_I^{lel}(x) \) is expressed by

\[
\frac{1}{V_j} \int g(r) \exp \left[ -z e \phi_I^{lel}(r) / k_B T \right] dV_j
\]

where \( g(r) \) is the weight of the probability at \( r \), the electrochemically detectable potential \( \phi_j \) is expressed by

\[
\exp (-z e \phi_I^{lel} / k_B T) = \frac{1}{V_j} \int g(r) \exp \left[ -z e \phi_I^{lel}(r) / k_B T \right] dV_j
\]

Obviously \( g(r) \) is unity far from the ion under the condition of excess of supporting electrolyte. In contrast, it may deviate from unity especially within the first solvation shell as a result of discrimination be-
between the chemical interaction and the electrostatic interaction. If the volume of all the first solvation shells is much smaller than the volume of each phase as in dilute solution, the contribution of \( g(r) \neq 1 \) may be neglected. Then Eq. (2) is reduced to

\[
Z = \frac{n!}{n_w!n_O!n_I!} \exp \left[ -\frac{n_w}{k_B T} \left( \mu_w^\circ + \nu_w + u_w s + ze \phi_w \right) \right] - \frac{n_O}{k_B T} \left( \mu_O^\circ + \nu_O + u_O s + ze \phi_O \right) - \frac{n_I}{k_B T} \left( \mu_I^\circ + \nu_I + u_I s + ze \phi_I \right)
\]

(4)

It is assumed that the interface is so thin that \( n_I \ll n_O \) and \( n_I \ll n_w \). When using the Stirling formula, the Helmholtz energy defined by \( A = -k_B T \ln Z \) is expressed by

\[
A = k_B T n_w \ln(n_w/n) + n_w \left( \mu_w^\circ + \nu_w + u_w s + ze \phi_w \right) + n_O \left( \mu_O^\circ + \nu_O + u_O s + ze \phi_O \right)
\]

(5)

The polyanions traverse the interface to reach equilibrium until the Helmholtz energy reaches a minimum. Then the equilibrium condition is given by

\[
\frac{\partial A}{\partial n_i} = 0 \quad \text{for} \quad j = O \text{ or } W
\]

(6)

where the partial derivative is taken at constant \( n \) and \( T \). Inserting Eq. (5) into Eq. (6), and carrying out the differentiation, we obtain

\[
k_B T \ln(n_O/n) + \Delta \mu_O^\circ + \nu_O - \nu_w + s(u_O - u_w)
\]

\[
+ ze(\phi_O - \phi_w) = 0
\]

(7)

or

\[
\phi_w - \phi_O = \frac{\Delta \mu_O^\circ}{ze} + \frac{s(u_O - u_w)}{ze} + \frac{\nu_O - \nu_w}{ze}
\]

(8)

where \( \Delta \mu_O^\circ = \mu_O^\circ - \mu_w^\circ \). This equation describes the relation of the equilibrium potential with the interaction energies and the molar ratio in the two phases. At the standard state given by \( n_O = n_w \), the potential difference is expressed by

\[
\phi_w - \phi_O = \frac{\Delta \mu_O^\circ}{ze} + \frac{s(u_O - u_w)}{ze} + \frac{\nu_O - \nu_w}{ze}
\]

(9)

Then, the Helmholtz energy at the standard state becomes

\[
A^\circ / n = -k_B T \ln 2 + \left( \mu_w^\circ + \nu_w + u_w s + ze \phi_w^\circ \right. \\
+ \mu_O^\circ + \nu_O + u_O s + ze \phi_O^\circ \bigg) / 2
\]

(10)

According to the conventional thermodynamics of the electrochemical equilibrium, \( \phi_w^\circ - \phi_O^\circ \) is equal to the standard potential. An equilibrium quantity determined readily from a slow voltammetric experiment is the reversible half-wave potential \( E_{1/2}^{rev} \) [20–23]. It is given by [24]

\[
E_{1/2}^{rev} = \left( \phi_w^\circ - \phi_O^\circ \right) + \Delta E'_{fr} + \frac{RT}{zF} \ln \frac{\gamma_O D_w}{\gamma_w D_O}
\]

(11)

where \( \gamma_j \) and \( D \) are the activity coefficient and the diffusion coefficient of polyanion in phase \( j \) respectively, and \( \Delta E'_{fr} \) is a sum of junction potentials and a potential difference given by reference electrodes. The last term in Eq. (11) has at most a few millivolts contribution even when \( D_O/D_w = 2 \) and \( z = -3 \) for \( \gamma_O = \gamma_w \). When Eq. (11) is combined with Eq. (9) in the standard state, it is reduced to

\[
E_{1/2}^{rev} \approx \Delta E'_{fr} + \frac{s(u_w - u_O)}{ze} + \frac{\nu_w - \nu_O}{ze}
\]

(12)

This is the relation between the observed potential difference and solvation energy. It resembles Uhlig’s equation [25], which describes the dependence of the solubility of a gas on the surface tension. If values of \( u_w - u_O \) are invariant to a series of polyanions and if \( \nu_w = \nu_O \), Eq. (12) predicts the linear variation of \( E_{1/2}^{rev} \) with \( s/ze \).

3. Discussion

3.1. Comparison with experiment

Osakai et al. [21] have estimated surface areas of various polyanions using the number of oxygen atoms \( m \) included in the polyanion, as follows. The oxygen atoms are known to be dispersed throughout the polyanion without localization and are virtually closed packed [18]. Thus \( m \) is proportional to the volume of the polyanion. If the polyanion is a sphere with radius \( a \), its volume and its surface area are, respectively, given by \( (4\pi/3)a^3 = k^3 m \) and \( s = 4\pi a^2 = (4\pi)^{1/3} (3m)^{2/3} k^2 \), where \( k \) is a constant. Using the radius of \( \text{SiW}_{12}O_{40}^4+ \) of 0.56 nm [26] for \( m = 40 \), we have \( s = 0.337 m^{2/3} \text{ nm}^2 \). Inserting this relation into Eq. (12), we have the linear relation between \( E_{1/2}^{rev} \) with \( m^{2/3} / z \) for \( \nu_w = \nu_O \).

Fig. 1 shows the experimental plot (triangles) of \( E_{1/2}^{rev} \) against \( m^{2/3} / |z| \), exhibiting good linearity except for the two points at small values of \( m^{2/3} / |z| \). Substituting the value of slope 0.205 V into 0.337 \( m^{2/3} (u_w - u_O) / ze \), we obtain \( u_O = u_W = 0.098 \text{ J m}^{-2} \). The interfacial energy difference is larger than the energy 0.073 J m\(^{-2}\) at the water | air interface, which is the largest of conventional liquid | liquid interfacial energies [27]. The fact of \( u_O - u_w > 0.073 \text{ J m}^{-2} \) indicates that \( u_w \) and \( u_O \) each should be much larger than
Osakai et al. [21] have proposed linear variation (circles in Fig. 1) of the standard ion-transfer potential with the surface charge density \( |z|/s \), i.e. \( E^{rev}_{1/2} = E^{rev}_{0} + b |z| m^{-2/3} \). The linear relation looks unfamiliar in the context of the relation between \( E^{rev}_{1/2} \) and \( z \) because a balance of the electric energy \( z e \phi \phi \) with the other energy \( K \) demands a functional form of \( \phi = K z e \) rather than \( \phi = K z e \). Thus, it is hopeless to find theoretically any linear relation of \( \phi \) with \( z \). The better linearity (circles) than that of \( E^{rev}_{1/2} \) vs. \( m^{2/3} |z|^{-1} \) (triangles) is probably due to secondary contributions from \( \phi \), discussed in Section 3.3.

We applied Eq. (12) to various data of the standard ion-transfer potentials reported so far. Fig. 2 shows variations of \( E^{rev}_{1/2} \) of inorganic cations, tetraalkyl ammonium ions and simple inorganic anions, where the ionic radii \( a \) were from Goldschmidt–Pauling’s data [12].

The plots of tetraalkylammonium ions obey Eq. (12). The deviation of the plot of tetrapentammonium may be ascribed to a loss of accuracy in \( E^{rev}_{1/2} \). The better linearity (circles) than that of \( E^{rev}_{1/2} \) vs. \( m^{2/3} |z|^{-1} \) (triangles) is probably due to secondary contributions from \( \phi \), discussed in Section 3.3.

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Fig. 2. Plots of standard ion-transfer free energy of inorganic cations, tetraalkyl ammonium ions and simple inorganic anions against \( 4 \pi a^2 / |z| \). The data are from Ref. [31].

3.2. Electrostatic contribution

The Helmholtz energy difference has often been divided into electrostatic and non-electrostatic parts [4], or ionic solvation energy and solution energy of a non-polar gaseous solute [12,13]. We consider the meaning of the electrostatic contribution. The standard Helmholtz energy is the sum of the Helmholtz energy in the oil phase and that in the water phase, i.e. \( A^{\phi} = A^{\phi}_{O} + A^{\phi}_{W} \) under the conditions \( n_{1} \gg n_{O} \) and \( n_{1} \gg n_{W} \). From the derivation of Eq. (10), each contribution is given by

\[
A^{\phi}_{j}/n = - \{ k_{B} T \ln \mu_{j}^{\phi} + v_{j} + u_{j} + z e \phi_{j}^{\phi} \}/2
\]

for \( j = O \) or \( W \) (13)

Reported electrochemical data for the Helmholtz energy difference for ion-transfer are not \( A^{\phi}_{W} - A^{\phi}_{O} \) but \( z F (\phi_{W}^{\phi} - \phi_{O}^{\phi}) \) which is given approximately by Eq. (12). Therefore, they correspond to the electrochemical contribution balanced with the chemical energy difference. The electrochemical contribution, \( z F (\phi_{W}^{\phi} - \phi_{O}^{\phi}) \), presented here does not seem to belong to the electro-
static or the ionic part because it is itself measured. Thus the electrostatic or the ionic contribution may be essentially the chemical term involved in $\nu_w - \nu_O$ in our notation rather than in $zF(\phi_w^O - \phi_w^W)$. The typical electrostatic energy is given by the Born-type equation:

$$\Delta G_{\text{Born}} = \frac{z^2F^2}{8\pi \varepsilon_0 a} \left( \frac{1}{\varepsilon_w} - \frac{1}{\varepsilon_O} \right)$$

or

$$\Delta \phi_{\text{Born}} = \frac{z e}{8\pi \varepsilon_0 a} \left( \frac{1}{\varepsilon_w} - \frac{1}{\varepsilon_O} \right) \tag{14}$$

where $\varepsilon_j$ is the permittivity of the medium $j$. If it is regarded as an essentially electrostatic energy, questions arise as to what is the difference between $\Delta G_{\text{Born}}$ and the well known electrostatic energy $(z e \phi_j)$, and of why $\Delta G_{\text{Born}}$ is not involved in the electrochemical potential difference $z e (\phi_O - \phi_w)$ rather than in $\nu_w - \nu_O$. Experimental results for the polyanions have demonstrated the invalidity of Eq. (14) [23]. The Born equation is valid when the potential profile is inversely proportional to the distance from the charge. Since there is a number of ions in an electrochemical system, the inverse proportionality may not be sustained. The author thinks that superposition of Eq. (14) over a large number of ions generates the electrochemically observed potential as a molecular field or a self-consistent field [29], and theoretical work is now in progress on this problem. Then it may be impossible to abstract the Born-type electrostatic energy from the electrochemically determined potential difference. However, the linear variation of $\Delta G$ with $1/\varepsilon_j$ sometimes observed includes a fascinating implication to be explored in future.

We estimate the deviation of the electrostatic contribution from $z e \phi$ using the Debye–Hückel theory. When the solution includes a univalent supporting electrolyte with concentration $c$, the potential near the polyanion is expressed by

$$\phi^{\text{Le}} = \phi_j + \frac{e}{4\pi \varepsilon_0 \varepsilon_j r} \exp(-\kappa r) \tag{15}$$

where $\phi_j$ is the average potential in solvent $j$ and $\kappa$ is the inverse radius of the ionic atmosphere given by $\kappa^2 = 2e^2c/\varepsilon_j \varepsilon_0 k_BT$. Inserting Eq. (15) into Eq. (3) and expressing $dV$ as the polar coordinate, we have

$$\exp\left( \frac{-ze\phi_j}{k_BT} \right) = \exp\left( \frac{-ze\phi_j}{k_BT} \right) 4\pi \int_a^L \frac{r^2}{V_j} dr \left\{ 1 - \frac{ze^2}{4\pi \varepsilon_0 \varepsilon_j k_BT} \exp(-\kappa r) \right\} \tag{16}$$

where $L$ is the average distance of the closest neighbor polyanions and $V_j$ is the spherical volume with radius $L$. Since values of $e^2/4\pi \varepsilon_0 \varepsilon_j k_BT$ and $\kappa$ are typically 0.7 nm and 1.4 nm respectively, the argument in the exponential is smaller than unity. When we make the Taylor expansion of the exponential term and carry out the integration, we obtain

$$\exp\left( \frac{-ze\phi_j}{k_BT} \right)$$

$$= \exp\left( \frac{-ze\phi_j}{k_BT} \right) \left\{ 1 - \frac{ze^2}{V_j \varepsilon_0 \varepsilon_j k_BT} \int_a^L r e^{-\kappa r} dr \right\}$$

$$= \exp\left( \frac{-ze\phi_j}{k_BT} \right) \left\{ 1 + \frac{ze^2}{V_j \varepsilon_0 \varepsilon_j k_BT} \times \left\{ \kappa^{-1} \left[ L e^{-\kappa L} - a e^{-\kappa a} \right] + \kappa^{-2} \left( e^{-\kappa L} - e^{-\kappa a} \right) \right\} \right\} \tag{17}$$

Because $L = 12$ nm in 1 mmol dm$^{-3}$ polyanion solution, $Le^{-\kappa L}$ is smaller than $ae^{-\kappa a}$. Using the relation $e^2/4\pi \varepsilon_0 \varepsilon_j k_BT = \kappa^2/2c$, we rewrite Eq. (17) as

$$\exp\left( \frac{-ze\phi_j}{k_BT} \right)$$

$$= \exp\left( \frac{-ze\phi_j}{k_BT} \right) \left\{ 1 - z e^{-\kappa a} (1 + \kappa a)/2Vfc \right\} \tag{18}$$

$Vfc$ is the ratio of concentrations of the supporting electrolyte $c_{sp}$ to the polyanion $c_{pol}$. Therefore the deviation from $ze \phi$ is ca. $0.4zC_{sp}/C_{pol}$ when $a = 0.56$ nm. This can be neglected in conventional electrochemical measurements. If it were not neglected, it should show the exponential variation with $a$. This is quite different from both Eq. (12) and the linearity of $1/a$ of the Born equation.

Since Eq. (18) was derived from the integration of Eq. (3), $\phi_j$ thus obtained should not be reflected on $\nu_j$ but should be reflected on the electrode potential. Therefore $\nu_j$ includes no electrostatic effect. More generally, every electrostatic effect may be included in the electrode potential.

3.3. Additional effects

The secondary effects represented by $\nu_j$ are discussed here. They may include the energy of forming a cavity, that of forming the second solvation shell, and variation of the surface energy with the curvature of the ion.

The energy of forming the cavity can be estimated from the enthalpy of vaporization $\Delta H$ of the solvent with spherical cavity $(4/3)\pi a^3$. Since $\mu_j^\infty$ mainly consists of kinetic energy by collision with surrounding particles, the energy of forming a cavity is not involved in $\mu_j^\infty$. Let $V_j$ be the molar volume of solvent $j$. Then
the difference in the energy is expressed by \( \Delta G_{\text{cav}} = (4/3)\pi a^2 (\Delta H_w/V_w - \Delta H_O/V_O) \). The following data for water and nitrobenzene are available: \( \Delta H_w = 45.05 \) kJ mol\(^{-1}\) at 298 K, \( \Delta H_O = 47.7 \) kJ mol\(^{-1}\) at 484 K, \( V_w = 18 \) cm\(^3\) mol\(^{-1}\), \( V_O = 102.7 \) cm\(^3\) mol\(^{-1}\), and \( a = 0.56 \) nm for \([\text{SiW}^7_2\text{O}_{40}]^{4-}\). Correction of the value of \( \Delta H_O \) at 484 K to that at 298 K was estimated from the heat capacity (ca. 0.3 kJ K\(^{-1}\) mol\(^{-1}\)) to give \( \Delta H_O = \Delta H_O^0 + (484 - 298) \times 0.3 = 100 \) kJ mol\(^{-1}\). Then we obtained \( \Delta G_{\text{cav}}/e = 0.7 \) V as a maximum. In this estimation, the value of \( \Delta G_{\text{cav}}/e \) does not vary with the surface area. Therefore the effect of the cavity is negligible.

The effect of the second solvation shell may be approximated roughly as the interaction between the solvents in the second shell and those in the first shell. We denote \( u' \) as the interaction energy density and \( \sigma \) as a radius of the solvent if it is spherical. Then the interfacial energy of the second solvation shell is expressed by \( v_j = 4\pi a(a + 2a_\sigma)^2 u'_j \). When \( v_j \) is inserted into Eq. (12), we obtain

\[
E_{1/2}^{\text{rev}} \approx \Delta E_{\text{rf}} + 4\pi a^2 (u_w - u_O) / ze + 16\pi a (a_w u'_w - a_\sigma u'_O) / ze + \text{(const)}
\]

where \( \text{(const)} \) means the independence of \( a \). This equation suggests that the plot of \( E_{1/2}^{\text{rev}} \) vs. \( 4\pi a^2/|z| \) should deviate from linearity as \( a \) decreases. The deviation of the two points (triangles) at small values of \( m^{2/3}/|z| \) in Fig. 1 seems to reflect this effect.

When we define the interfacial energy at a molecularly sized sphere, the effect of curvature on the surface energy, namely the Kelvin effect, should be taken into account. The apparent surface energy at radius \( a \) is given by [30]

\[
\alpha = \frac{\alpha_0}{1 + 2\delta/a} \quad (20)
\]

where \( \delta \) is the order of the molecular size, e.g. \( 10^{-10} \) m, and \( \alpha_0 \) is the surface energy on a macroscopic plane. Substituting \( 4\pi a^2 \) for \( s \) and replacing \( u_w - u_O \) by \( \alpha \) in Eq. (12), we have

\[
E_{1/2}^{\text{rev}} \approx \Delta E_{\text{rf}} + \frac{\alpha_0 \delta}{ze(1 + 4\sqrt{\pi} \delta/\sqrt{s})} \quad (21)
\]

The value of the correction term \( (1 + 4\sqrt{\pi} \delta/\sqrt{s})^{-1} \) is 0.7 for the smallest polyanions (12th and the 13th in Fig. 1) when \( \delta = 10^{-10} \) m. However, this is just a tentative value because there is a large ambiguity in estimating \( \delta \). The Taylor expansion of Eq. (21) for small values of \( \delta/\sqrt{s} \) shows a quadratic equation of \( a \) similar to Eq. (19). Therefore it is hard to differentiate the Kelvin effect from the second solvation shell effect so far as we are concerned with the relation between \( E_{1/2}^{\text{rev}} \) and \( a \).

The mirror image force of the ion at the interface may be negligibly small because the potential in each phase is controlled externally and because sufficient excess of supporting electrolytes is included in the solution that local potential distribution is minimized.

4. Conclusion

The linear variation of the standard ion-transfer potential of the polyanions with the surface area and the inverse of the charge can be explained by the surface interaction energy between the polyanion and the solvent. Therefore Uhlig’s equation is formally valid if the Helmholtz energy difference is replaced by \(-2F_{1/2}^{\text{rev}}\). The linear dependence holds for the polyanions, tetralkylammonium cations and simple inorganic anions. From the slope of the linear plot, the difference in the surface energy at the ion|water and the ion|nitrobenzene interfaces could be evaluated. The difference in the interfacial energy was specific to a series of ions, probably because the interfacial property is common to a family of ions. Therefore it may be hopeless to express the standard ion-transfer potentials of all the ions as a single equation.

The Helmholtz energy difference measured by electrochemical techniques has no electrostatic part because it is a quantity balanced energetically with the chemical terms. This is a reason why the Born relation does not hold in the ion-transfer potentials of the polyanions. Non-electrochemical determination of the Helmholtz energy might separate the Helmholtz energy into the electrostatic term and the chemical term.

Although we tried to estimate the secondary effects, we could not read a definite conclusion except for the negligibly small cavity effect.

References