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Thermodynamics of the Electrocapillarity of Oil-Water Interfaces

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General electrocapillary equations for the interfaces between two immiscible or partially miscible electrolyte solutions have been derived. The theory includes both nonpolarized and ideal polarized interfaces. The electrocapillary equation for the latter has been derived from the equation for the former as a special case where no common ionic species are distributed between the two phases. Implications of the general electrocapillary equation for oil-water interfaces are indicated.

Recent advances[1-3] in electrochemistry of the interfaces between two immiscible or partially miscible electrolyte solutions allow us to obtain various thermodynamic quantities characterizing the interface from the electrocapillary measurements. Koryta *et al.* have first interpreted the polarizability of the interfaces in terms of the transfer free energies of ions from one solvent to the other.[4] Kakiuchi and Senda have shown that the interface between a nitrobenzene solution of tetrabutylammonium tetraphenylborate and an aqueous solution of lithium chloride has a certain polarized potential region, where the ion transfer current across the interface is negligibly small, and gives an electrocapillary curve of parabolic shape.[5,6] The electrocapillary curves of nonpolarized nitrobenzene–water interfaces have been measured by Gros *et al.*[7] To analyze these electrocapillary data at full length, exact thermodynamic treatment of these interfaces is indispensable. Several thermodynamic treatments so far reported[7-10] suffer from limited applicability due to simplifications and various assumptions introduced.

The purpose of this study is to present a general thermodynamic theory of electrocapillarity for the planar interface between two immiscible or partially miscible electrolyte solutions, which we hereafter call the oil–water interface. In this paper, we first establish the basic electrocapillary equations for a nonpolarized oil–water interface at equilibrium, where some of the ions as well as some of the neutral components can pass through the interface and are distributed between the two phases in equilibrium. Then the electrocapillary equation for an ideal polarized oil–water interface, which is defined as the interface where no ionic species is common in both phases or where each charged species is present in appreciable amounts in only one of the two phases,[11] is derived from the equation for the nonpolarized interface by eliminating the terms involving the common ionic species.

Theoretical

Nonpolarized Oil–Water Interface. *The System*: We shall consider the following cell:

$$\mathrm{M}\,|\mathrm{R1}|\,\mathrm{O}\,|\,\mathrm{W}\,|\,\mathrm{R2}|\,\mathrm{M'}, \qquad \text{(I)}$$

where M and M′ are two pieces of the same metal between which we measure the potential difference, and R1 and R2 are the appropriate reference electrodes, each of which is reversible to one of the ions in the adjoining solution phase. We assume a planar interface between the oil phase (O) and the water phase(W). The oil phase contains i cations, j anions, and k uncharged nondissociating components, which we hereafter simply call neutral components, while the water phase contains p cations, q anions, and h neutral components. These sets of the components are also designated by i, j, k, p, q, and h, respectively, so that these symbols are used to indicate both the set and the number of the components. Suppose that α cations, β anions and l neutral components are able to pass through the interface and are commonly distributed over the two phases; the interface is nonpolarizable with respect to these common ions. In other words, i-α cations, j-β anions, and k-l neutral components stay solely within the oil phase, while p-α cations, q-β anions, and h-l neutral components stay within the water phase. Let the sets of these common cations, anions, and neutral components also be denoted by α, β, and l, respectively.

The number of the intensive variables for this system is $i+j+k+p+q+h+2$ including temperature and pressure, but not all of them are independent. Since $\alpha+\beta+l$ components are common in both phases, there are $\alpha+\beta+l$ equations relating the chemical potentials of the common components in the two phases with each other. In addition, there are two Gibbs-Duhem equations: one for the oil phase and one for the water phase. Moreover, the potential difference between the two terminals of the cell (I) correlates the two electrochemical potentials of the two ions which are reversible to the reference electrodes R1 and R2. The number of the independent intensive variables which define the present system is, therefore, $i+j+k+p+q+h-(\alpha+\beta+l)-1$.

The Electrocapillary Equation: We adopt the concept of a surface phase[12,13] to describe the interface. An exact definition of the surface phase which the present treatment rests on has been given by Eriksson.[14] The analogue of the Gibbs-Duhem equation for the surface phase with a planar interface is[14]

$$-\,\mathrm{d}\gamma = \eta\,\mathrm{d}T - \tau\,\mathrm{d}P + \sum_x \Gamma_x \mathrm{d}\mu_x, \qquad (1)$$

where γ is the interfacial tension, η is the entropy of the surface phase per unit area of the interface, T is the temperature, τ is the thickness of the surface phase, P is the pressure, and Γ_x is the number of moles of the x component per unit area of the interface, which may be called the surface concentration of the x component.

The summation in the right hand side of Eq. 1 includes all the components in the system including ionic species. In Eq. 1 μ_x represents the electrochemical potential for a charged component and the chemical potential for a neutral component. For the present system Eq. 1 takes the form

$$\begin{aligned}-\mathrm{d}\gamma = \eta\,\mathrm{d}T - \tau dP &+ \sum_{i\neq\alpha}\Gamma_i\mathrm{d}\tilde{\mu}_i + \sum_{j\neq\beta}\Gamma_j\mathrm{d}\tilde{\mu}_j + \sum_{k\neq l}\Gamma_k\mathrm{d}\mu_k \\ &+ \sum_{p\neq\alpha}\Gamma_p\mathrm{d}\tilde{\mu}_p + \sum_{q\neq\beta}\Gamma_q\mathrm{d}\tilde{\mu}_q + \sum_{h\neq l}\Gamma_h\mathrm{d}\mu_h \\ &+ \sum_{\alpha}\Gamma_\alpha\mathrm{d}\tilde{\mu}_\alpha + \sum_{\beta}\Gamma_\beta\mathrm{d}\tilde{\mu}_\beta + \sum_{l}\Gamma_l d\mu_l. \end{aligned} \tag{2}$$

In Eq. 2, we have made a distinction between the electrochemical potential, $\tilde{\mu}_x$, for a charged component $x(x=i, j, p, q, \alpha, \beta)$, and the chemical potential, μ_y, for a neutral component $y(y=h, k, l)$. The symbol $\sum_{f\neq g}$ means that the summation covers all the f components except g. There are $i+j+k+p+q+h-(\alpha+\beta+l)+2$ intensive variables and hence three of them are dependent variables as described above.

Suppose that the reference electrodes R1 and R2 are reversible to a cation i' among the cations $i\neq\alpha$(i except α) and an anion q' among the anions $q\neq\beta$(q except β). Furthermore, we choose the anion j' out of $j\neq\beta$ anions as a counter anion of the cation i' to make up an indicator salt[15] $i'j'$ and the cation p' out of the $p\neq\alpha$ cations as a counter cation of the anion q' to make up an indicator salt $p'q'$. Then the electrochemical potentials of the ionic components can be related to the chemical potentials of the salt containing one of the ions: i',j',p', or q'.

In many practical cases, the ions constituting the indicator salts may also be commonly distributed in the two phases. To make the present treatment general enough to include these cases, we further suppose here that, in addition to the common ions, α and β, the ions consituting the indicator salts also are commonly distributed in the two phases. There are then $\alpha+2$ common cations and $\beta+2$ common anions in the system. Although these newly added four ions could be included in the sets α and β, we retain in the following treatment a distinction between these ions and the sets of ions α and β for later convenience when deriving the electrocapillary equation for an ideal polarized oil–water interface. Obviously, this extension does not change the number of independent variables. Then we have the following equations relating the electrochemical potentials of the ionic components with the chemical potential of their salt:

$$\mathrm{d}\mu_{i'j'} = \nu^+_{i'j'}\mathrm{d}\tilde{\mu}_{i'} + \nu^-_{i'j'}\mathrm{d}\tilde{\mu}_{j'} \tag{3-1}$$

$$\mathrm{d}\mu_{ij'} = \nu^+_{ij'}\mathrm{d}\tilde{\mu}_{i} + \nu^-_{ij'}\mathrm{d}\tilde{\mu}_{j'} \qquad (i\neq i', \alpha) \tag{3-2}$$

$$\mathrm{d}\mu_{i'j} = \nu^+_{i'j}\mathrm{d}\tilde{\mu}_{i'} + \nu^-_{i'j}\mathrm{d}\tilde{\mu}_{j} \qquad (j\neq j', \beta) \tag{3-3}$$

$$\mathrm{d}\mu_{\alpha j'} = \nu^+_{\alpha j'}\mathrm{d}\tilde{\mu}_{\alpha} + \nu^-_{\alpha j'}\mathrm{d}\tilde{\mu}_{j'} \tag{3-4}$$

$$\mathrm{d}\mu_{i'\beta} = \nu^+_{i'\beta}\mathrm{d}\tilde{\mu}_{i'} + \nu^-_{i'\beta}\mathrm{d}\tilde{\mu}_{\beta} \tag{3-5}$$

$$\mathrm{d}\mu_{p'q'} = \nu^+_{p'q'}\mathrm{d}\tilde{\mu}_{p'} + \nu^-_{p'q'}\mathrm{d}\tilde{\mu}_{q'} \tag{3-6}$$

$$\mathrm{d}\mu_{pq'} = \nu^+_{pq'}\mathrm{d}\tilde{\mu}_{p} + \nu^-_{pq'}\mathrm{d}\tilde{\mu}_{q'} \qquad (p\neq p', \alpha) \tag{3-7}$$

$$\mathrm{d}\mu_{p'q} = \nu^+_{p'q}\mathrm{d}\tilde{\mu}_{p'} + \nu^-_{p'q}\mathrm{d}\tilde{\mu}_{q} \qquad (q\neq q', \beta) \tag{3-8}$$

$$\mathrm{d}\mu_{\alpha q'} = \nu^+_{\alpha q'}\mathrm{d}\tilde{\mu}_{\alpha} + \nu^-_{\alpha q'}\mathrm{d}\tilde{\mu}_{q'} \tag{3-9}$$

$$\mathrm{d}\mu_{p'\beta} = \nu^+_{p'\beta}\mathrm{d}\tilde{\mu}_{p'} + \nu^-_{p'\beta}\mathrm{d}\tilde{\mu}_{\beta} \tag{3-10}$$

$$\mathrm{d}\mu_{i'q'} = \nu^+_{i'q'}\mathrm{d}\tilde{\mu}_{i'} + \nu^-_{i'q'}\mathrm{d}\tilde{\mu}_{q'} \tag{3-11}$$

$$\mathrm{d}\mu_{p'j'} = \nu^+_{p'j'}\mathrm{d}\tilde{\mu}_{p'} + \nu^-_{p'j'}\mathrm{d}\tilde{\mu}_{j'}, \tag{3-12}$$

where μ_{CA} is the chemical potential of a salt $(\mathrm{C})_{\nu^+_{\mathrm{CA}}}(\mathrm{A})_{\nu^-_{\mathrm{CA}}}$, and ν^+_{CA} and ν^-_{CA} are the stoichiometric numbers for the dissociation of the salt:

$$(\mathrm{C})_{\nu^+_{\mathrm{CA}}}(\mathrm{A})_{\nu^-_{\mathrm{CA}}} = \nu^+_{\mathrm{CA}}\mathrm{C}^{z_\mathrm{C}} + \nu^-_{\mathrm{CA}}\mathrm{A}^{z_\mathrm{A}}, \tag{4}$$

where C and A represent a cation and an anion and z_C and z_A are their ionic charges. By using the Gibbs-Duhem equations for the oil and water phases, we can eliminate any two of the intensive variables in Eq. 1. Usually, it is convenient to eliminate the chemical potentials of the two neutral components, which may be identified as the solvents in each phase, *e.g.*, water in the water phase and an oil in the oil phase. These two components are called the reference components. Since most organic solvents used in electrochemistry of oil–water interfaces have a certain solubility in water and *vice versa*, let l' and l'' out of l neutral components be chosen as the reference components.

The Gibbs-Duhem equations for the oil and water phases may then be written in the form

$$\begin{aligned}\bar{s}^\mathrm{O}\mathrm{d}T - \bar{v}^\mathrm{O}\mathrm{d}P &+ \sum_{i\neq i',\alpha} x^\mathrm{O}_{ij'}\mathrm{d}\mu_{ij'} + \sum_{\alpha} x^\mathrm{O}_{\alpha j'}\mathrm{d}\mu_{\alpha j'} \\ &+ \sum_{j\neq j,\beta} x^\mathrm{O}_{i'j}\mathrm{d}\mu_{i'j} + \sum_{\beta} x^\mathrm{O}_{i'\beta}\mathrm{d}\mu_{i'\beta} + x^\mathrm{O}_{i'j'}\mathrm{d}\mu_{i'j'} \\ &+ x^\mathrm{O}_{i'q'}\mathrm{d}\mu_{i'q'} + x^\mathrm{O}_{p'j'}\mathrm{d}\mu_{p'j'} + \sum_{k\neq l} x^\mathrm{O}_{k}\mathrm{d}\mu_{k} \\ &+ \sum_{l\neq l',l''} x^\mathrm{O}_{l}\mathrm{d}\mu_{l} + x^\mathrm{O}_{l'}\mathrm{d}\mu_{l'} + x^\mathrm{O}_{l''}\mathrm{d}\mu_{l''} = 0, \end{aligned} \tag{5}$$

and

$$\begin{aligned}\bar{s}^\mathrm{W}\mathrm{d}T - \bar{v}^\mathrm{W}\mathrm{d}P &+ \sum_{p\neq p',\alpha} x^\mathrm{W}_{pq'}\mathrm{d}\mu_{pq'} + \sum_{\alpha} x^\mathrm{W}_{\alpha q'}\mathrm{d}\mu_{\alpha q'} \\ &+ \sum_{q\neq q',\beta} x^\mathrm{W}_{p'q}\mathrm{d}\mu_{p'q} + \sum_{\beta} x^\mathrm{W}_{p'\beta}\mathrm{d}\mu_{p'\beta} + x^\mathrm{W}_{p'q'}\mathrm{d}\mu_{p'q'} \\ &+ x^\mathrm{W}_{i'q'}\mathrm{d}\mu_{i'q'} + x^\mathrm{W}_{p'j'}\mathrm{d}\mu_{p'j'} + \sum_{h\neq l} x^\mathrm{W}_{h}\mathrm{d}\mu_{h} \\ &+ \sum_{l\neq l',l''} x^\mathrm{W}_{l}\mathrm{d}\mu_{l} + x^\mathrm{W}_{l'}\mathrm{d}\mu_{l'} + x^\mathrm{W}_{l''}\mathrm{d}\mu_{l''} = 0, \end{aligned} \tag{6}$$

where $\bar{s}$ and $\bar{v}$ are the mean molar entropy and the mean molar volume of the bulk phase and x is the mole fraction. The superscript O and W denote the oil phase and the water phase, respectively. Substituting Eqs. 3, 5, and 6 into Eq. 2 to eliminate the chemical potential terms for l' and l'' and for all the ionic components except i' and q', we obtain

$$\begin{aligned}-\mathrm{d}\gamma &= (\eta - J\bar{s}^\mathrm{O} - K\bar{s}^\mathrm{W})\mathrm{d}T - (\tau - J\bar{v}^\mathrm{O} - K\bar{v}^\mathrm{W})\,\mathrm{d}P \\ &+ \sum_{k\neq l}(\Gamma_k - Jx^\mathrm{O}_k)\mathrm{d}\mu_k + \sum_{h\neq l}(\Gamma_h - Kx^\mathrm{W}_h)\,\mathrm{d}\mu_h \\ &+ \sum_{l\neq l',l''}(\Gamma_l - Jx^\mathrm{O}_l - Kx^\mathrm{W}_l)\,\mathrm{d}\mu_l + \sum_{i\neq i',\alpha}\left(\frac{\Gamma_i}{\nu^+_{ij'}} - Jx^\mathrm{O}_{ij'}\right)\mathrm{d}\mu_{ij'} \\ &+ \sum_{j\neq j',\beta}\left(\frac{\Gamma_j}{\nu^-_{i'j}} - Jx^\mathrm{O}_{i'j}\right)\mathrm{d}\mu_{i'j} + \sum_{p\neq p',\alpha}\left(\frac{\Gamma_p}{\nu^+_{pq'}} - Kx^\mathrm{W}_{pq'}\right)\mathrm{d}\mu_{pq'} \\ &+ \sum_{q\neq q',\beta}\left(\frac{\Gamma_q}{\nu^-_{p'q}} - Kx^\mathrm{W}_{p'q}\right)\mathrm{d}\mu_{p'q} \\ &+ \sum_{\alpha}\left(\frac{\Gamma_\alpha}{\nu^+_{\alpha q'}} - Jx^\mathrm{O}_{\alpha j'}\frac{\nu^+_{\alpha j'}}{\nu^+_{\alpha q'}} - Kx^\mathrm{W}_{\alpha q'}\right)\mathrm{d}\mu_{\alpha q'} \\ &+ \sum_{\beta}\left(\frac{\Gamma_\beta}{\nu^-_{p'\beta}} - Jx^\mathrm{O}_{i'\beta}\frac{\nu^-_{i'\beta}}{\nu^-_{p'\beta}} - Kx^\mathrm{W}_{p'\beta}\right)\mathrm{d}\mu_{p'\beta} \\ &+ \frac{1}{\nu^-_{i'j'}}\Bigg(\Gamma_{j'} - \sum_{i\neq i',\alpha}\frac{z_i}{|z_{j'}|}\Gamma_i - J\sum_{\alpha}\nu^-_{\alpha j'}x^\mathrm{O}_{\alpha j'} - J\nu^-_{p'j'}x^\mathrm{O}_{p'j'} \\ &\qquad - K\nu^-_{p'j'}x^\mathrm{W}_{p'j'} - J\nu^-_{i'j'}x^\mathrm{O}_{i'j'}\Bigg)\mathrm{d}\mu_{i'j'} \end{aligned}$$

$$+\frac{1}{\nu^{+}_{p'q'}}\left(\Gamma_{p'}-\sum_{q\neq q'}\frac{|z_q|}{z_{p'}}\Gamma_q+J\sum_{\beta}\frac{|z_\beta|}{z_{p'}}\nu^{-}_{i'\beta}x^{\mathrm{O}}_{i'\beta}\right.$$

$$\left.-J\nu^{+}_{p'j'}x^{\mathrm{O}}_{p'j'}-K\nu^{+}_{p'j'}x^{\mathrm{W}}_{p'j'}-K\nu^{+}_{p'q'}x^{\mathrm{W}}_{p'q'}\right)\mathrm{d}\mu_{p'q'}$$

$$-\frac{Q^{\mathrm{W}}}{z_{i'}F}\mathrm{d}\tilde{\mu}_{i'}+\frac{Q^{\mathrm{O}}}{|z_{q'}|F}\mathrm{d}\tilde{\mu}_{q'}, \tag{7}$$

where F is the Faraday and Q^{W}, Q^{O}, J, and K are given by

$$\frac{Q^{\mathrm{W}}}{F}=\sum_{p}z_p\Gamma_p-\sum_{q}|z_q|\Gamma_q-J\sum_{\alpha}|z_{j'}|\nu^{-}_{\alpha j'}x^{\mathrm{O}}_{\alpha j'}$$

$$+J\sum_{\beta}z_{i'}\nu^{+}_{i'\beta}x^{\mathrm{O}}_{i'\beta}+J(z_{i'}\nu^{+}_{i'q'}x^{\mathrm{O}}_{i'q'}-|z_{j'}|\nu^{-}_{p'j'}x^{\mathrm{O}}_{p'j'})$$

$$+K(z_{i'}\nu^{+}_{i'q'}x^{\mathrm{W}}_{i'q'}-|z_{j'}|\nu^{-}_{p'j'}x^{\mathrm{W}}_{p'j'}), \tag{8}$$

$$\frac{Q^{\mathrm{O}}}{F}=\sum_{i\neq\alpha}z_i\Gamma_i-\sum_{j\neq\beta}|z_j|\Gamma_j+J\sum_{\alpha}z_\alpha\nu^{+}_{\alpha j'}x^{\mathrm{O}}_{\alpha j'}$$

$$-J\sum_{\beta}|z_\beta|\nu^{-}_{i'\beta}x^{\mathrm{O}}_{i'\beta}-J(z_{j'}\nu^{+}_{i'q'}x^{\mathrm{O}}_{i'q'}-|z_{j'}|\nu^{-}_{p'j'}x^{\mathrm{O}}_{p'j'})$$

$$-K(z_{i'}\nu^{+}_{i'q'}x^{\mathrm{W}}_{i'q'}-|z_{j'}|\nu^{-}_{p'j'}x^{\mathrm{W}}_{p'j'}), \tag{9}$$

$$J=\frac{\Gamma_{l''}x^{\mathrm{W}}_{l'}-\Gamma_{l'}x^{\mathrm{W}}_{l''}}{x^{\mathrm{W}}_{l'}x^{\mathrm{O}}_{l''}-x^{\mathrm{O}}_{l'}x^{\mathrm{W}}_{l''}}, \tag{10}$$

$$K=\frac{\Gamma_{l'}x^{\mathrm{O}}_{l''}-\Gamma_{l''}x^{\mathrm{O}}_{l'}}{x^{\mathrm{W}}_{l'}x^{\mathrm{O}}_{l''}-x^{\mathrm{O}}_{l'}x^{\mathrm{W}}_{l''}}. \tag{11}$$

The electroneutrality condition of the interface can be written in the form

$$\sum_{i\neq\alpha}z_i\Gamma_i+\sum_{p\neq\alpha}z_p\Gamma_p+\sum_{\alpha}z_\alpha\Gamma_\alpha-\sum_{j\neq\beta}|z_j|\Gamma_j$$

$$-\sum_{q\neq\beta}|z_q|\Gamma_q-\sum_{\beta}|z_\beta|\Gamma_\beta=0, \tag{12}$$

from which it can be shown that $Q^{\mathrm{W}}=-Q^{\mathrm{O}}$. Then the last two terms in the right hand side of Eq. 7 become

$$\frac{Q^{\mathrm{O}}}{F}\left(\frac{1}{z_{i'}}\mathrm{d}\mu_{i'}+\frac{1}{|z_{q'}|}\mathrm{d}\mu_{q'}\right)=$$

$$-\frac{Q^{\mathrm{W}}}{F}\left(\frac{1}{z_{i'}}\mathrm{d}\mu_{i'}+\frac{1}{|z_{q'}|}\mathrm{d}\mu_{q'}\right). \tag{13}$$

Since the reference electrodes R1 and R2 in the cell (I) are reversible to i' and q' ions, respectively, we may write[15)]

$$\begin{aligned}\mathrm{d}\tilde{\mu}_{i'}&=-z_i\mathrm{d}\tilde{\mu}^{\mathrm{M}}_{e}+\mathrm{d}\mu^{\cdot\,\mathrm{R1}}_{+}\\&=-z_i\mathrm{d}\tilde{\mu}^{\mathrm{M}}_{e}+s^{\cdot}_{\mathrm{R1}}\mathrm{d}T-v^{\cdot}_{\mathrm{R1}}\mathrm{d}P,\end{aligned} \tag{14}$$

and

$$\begin{aligned}\mathrm{d}\tilde{\mu}_{q'}&=|z_{q'}|\mathrm{d}\tilde{\mu}^{\mathrm{M}'}_{e}+\mathrm{d}\mu^{\cdot\,\mathrm{R2}}_{-}\\&=|z_{q'}|\mathrm{d}\tilde{\mu}^{\mathrm{M}'}_{e}+s^{\cdot}_{\mathrm{R2}}\mathrm{d}T-v^{\cdot}_{\mathrm{R2}}\mathrm{d}P,\end{aligned} \tag{15}$$

where $\tilde{\mu}^{\mathrm{M}}_{e}$ and $\tilde{\mu}^{\mathrm{M}'}_{e}$ are the electrochemical potentials of electron in M and M′, and $\mu^{\cdot}$, $s^{\cdot}$, and $v^{\cdot}$ are linear combinations of the chemical potentials, the molar entropies and the molar volumes of the neutral substances involved in the electrochemical reactions at the reference electrodes[15)] and hence are dependent only on the nature of the reference electrodes. Substitution of Eqs. 13, 14, and 15 into Eq. 7 yields the basic electrocapillary equation for the cell (I),

$$-\mathrm{d}\gamma=\left[\eta-J\bar{s}^{\mathrm{O}}-K\bar{s}^{\mathrm{W}}-\frac{Q^{\mathrm{W}}}{F}\left(\frac{s^{\cdot}_{\mathrm{R1}}}{z_{i'}}+\frac{s^{\cdot}_{\mathrm{R2}}}{|z_{q'}|}\right)\right]\mathrm{d}T$$

$$-\left[\tau-J\bar{v}^{\mathrm{O}}-K\bar{v}^{\mathrm{W}}-\frac{Q^{\mathrm{W}}}{F}\left(\frac{v^{\cdot}_{\mathrm{R1}}}{z_{i'}}+\frac{v^{\cdot}_{\mathrm{R2}}}{|z_{q'}|}\right)\right]\mathrm{d}P$$

$$+\sum_{k\neq l}(\Gamma_k-Jx^{\mathrm{O}}_{k})\mathrm{d}\mu_k+\sum_{h\neq l}(\Gamma_h-Kx^{\mathrm{W}}_{h})\mathrm{d}\mu_h$$

$$+\sum_{l\neq l',l''}(\Gamma_l-Jx^{\mathrm{O}}_{l}-Kx^{\mathrm{W}}_{l})\mathrm{d}\mu_l$$

$$+\sum_{i\neq i',\alpha}\left(\frac{\Gamma_i}{\nu^{+}_{ij'}}-Jx^{\mathrm{O}}_{ij'}\right)\mathrm{d}\mu_{ij'}+\sum_{j\neq j',\beta}\left(\frac{\Gamma_j}{\nu^{-}_{i'j}}-Jx^{\mathrm{O}}_{i'j}\right)\mathrm{d}\mu_{i'j}$$

$$+\sum_{p\neq p',\alpha}\left(\frac{\Gamma_p}{\nu^{+}_{pq'}}-Kx^{\mathrm{W}}_{pq'}\right)\mathrm{d}\mu_{pq'}+\sum_{q\neq q',\beta}\left(\frac{\Gamma_q}{\nu^{-}_{p'q}}-Kx^{\mathrm{W}}_{p'q}\right)\mathrm{d}\mu_{p'q}$$

$$+\sum_{\alpha}\left(\frac{\Gamma_\alpha}{\nu^{+}_{\alpha q'}}-J\frac{\nu^{+}_{\alpha j'}}{\nu^{+}_{\alpha q'}}x^{\mathrm{O}}_{\alpha j'}-Kx^{\mathrm{W}}_{\alpha q'}\right)\mathrm{d}\mu_{\alpha q'}$$

$$+\sum_{\beta}\left(\frac{\Gamma_\beta}{\nu^{-}_{p'\beta}}-J\frac{\nu^{-}_{i'\beta}}{\nu^{-}_{p'\beta}}x^{\mathrm{O}}_{i'\beta}-Kx^{\mathrm{W}}_{p'\beta}\right)\mathrm{d}\mu_{p'\beta}$$

$$+\frac{1}{\nu^{-}_{i'j'}}\left(\Gamma_{j'}-\sum_{i\neq i',\alpha}\frac{z_i}{|z_{j'}|}\Gamma_i-J\sum_{\alpha}\nu^{-}_{\alpha j'}x^{\mathrm{O}}_{\alpha j'}-J\nu^{-}_{p'j'}x^{\mathrm{O}}_{p'j'}\right.$$

$$\left.-K\nu^{-}_{p'j'}x^{\mathrm{W}}_{p'j'}-J\nu^{-}_{i'j'}x^{\mathrm{O}}_{i'j'}\right)\mathrm{d}\mu_{i'j'}+\frac{1}{\nu^{+}_{p'q'}}\left(\Gamma_{p'}-\sum_{q\neq q'}\frac{|z_q|}{z_{p'}}\Gamma_q\right.$$

$$\left.+J\sum_{\beta}\frac{|z_\beta|}{z_{p'}}\nu^{-}_{i'\beta}x^{\mathrm{O}}_{i'\beta}-J\nu^{+}_{p'j'}x^{\mathrm{O}}_{p'j'}-K\nu^{+}_{p'j'}x^{\mathrm{W}}_{p'j'}-K\nu^{+}_{p'q'}x^{\mathrm{W}}_{p'q'}\right)\mathrm{d}\mu_{p'q'}$$

$$+Q^{\mathrm{W}}\mathrm{d}E^{\mathrm{W}-}_{\mathrm{O}+}, \tag{16}$$

where $\mathrm{d}E^{\mathrm{W}-}_{\mathrm{O}+}=(\mathrm{d}\tilde{\mu}^{\mathrm{M}}_{e}-\mathrm{d}\tilde{\mu}^{\mathrm{M}'}_{e})/F$ is the change in the potential of the right hand side terminal, M′, in the cell (I) with respect to the left, M. The superscript W− and the subscript O+ indicate that the reference electrodes are reversible to the anion in the water phase and the cation in the oil phase, respectively. In Eq. 16 there are $k+h+i+p+q-(\alpha+\beta+l)-1$ intensive variables, and hence all of them are independent variables.

Generalization of the Electrocapillary Equation: In the derivations of Eq. 16 we have chosen the chemical potentials of the salts of $\alpha q'$ and $p'\beta$ types as the independent variables for all the salts containing the commonly distributed ions α and β. In principle, we can choose as the independent variables either one of $\mu_{\alpha q'}$, and $\mu_{\alpha j'}$ for each of α and either one of $\mu_{p'\beta}$ and $\mu_{i'\beta}$ for each of β. In the present treatment we consider only the simple cases where all the chemical potentials of the salts of the same type are either simultaneously dependent variables or simultaneously independent variables. There are then four possible cases to choose the sets of the independent variables involving the commonly distributed ions α and β: ($\alpha q'$ and $p'\beta$), ($\alpha q'$ and $i'\beta$), ($\alpha j'$ and $p'\beta$), and ($\alpha j'$ and $i'\beta$). The change of the independent variables among these variables results in the corresponding changes in the coefficients of $\mathrm{d}E^{\mathrm{W}-}_{\mathrm{O}+}$, $\mathrm{d}\mu_{i'j'}$, and $\mathrm{d}\mu_{p'q'}$ in Eq. 16 as well as those of the terms involving the chosen independent variables. Furthermore, the expressions of the coefficients of $\mathrm{d}\mu_{i'j'}$ and $\mathrm{d}\mu_{p'q'}$ depend upon the set of the ions reversible to the reference electrodes R1 and R2. There are four possible cases for the choice of the set of the ions among the ions i', j', p', and q': (i' and p'), (i' and q'), (j' and p'), and (j' and q'). The coefficients of the $\mathrm{d}T$ and $\mathrm{d}P$ terms also depend upon the choice of the set of these ions.

Taking account of these possible cases, we have a general formula for the basic electrocapillary equation for the non-polarized interface:

$$-\mathrm{d}\gamma=\left\{\eta-J\bar{s}^{\mathrm{O}}-K\bar{s}^{\mathrm{W}}-\frac{Q^{\mathrm{W}}}{F}(\mathrm{A}+\mathrm{A}')\right\}\mathrm{d}T$$

$$-\left\{\tau-J\bar{v}^{\mathrm{O}}-K\bar{v}^{\mathrm{W}}-\frac{Q^{\mathrm{W}}}{F}(\mathrm{B}+\mathrm{B}')\right\}\mathrm{d}P$$

$$
\begin{aligned}
&+ \mathrm{Cd}\mu_{i'j'} + \mathrm{Dd}\mu_{p'q'} + \mathrm{Gd}\mu_{\alpha x} + \mathrm{Hd}\mu_{y\beta} + Q^{\mathrm{W}}\mathrm{d}E^{\mathrm{W}\pm}_{\mathrm{O}\pm} \\
&+ \sum_{k\neq l}(\Gamma_k - Jx^{\mathrm{O}}_k)\mathrm{d}\mu_k + \sum_{h\neq l}(\Gamma_h - Kx^{\mathrm{W}}_h)\mathrm{d}\mu_h \\
&+ \sum_{l\neq l'.l''}(\Gamma_l - Jx^{\mathrm{O}}_l - Kx^{\mathrm{W}}_l)\mathrm{d}\mu_l \\
&+ \sum_{i\neq i'.\alpha}\left(\frac{\Gamma_i}{\nu^+_{ij'}} - Jx^{\mathrm{O}}_{ij'}\right)\mathrm{d}\mu_{ij'} + \sum_{j\neq j'.\beta}\left(\frac{\Gamma_i}{\nu^-_{i'j}} - Jx^{\mathrm{O}}_{i'j}\right)\mathrm{d}\mu_{i'j} \\
&+ \sum_{p\neq q'.\alpha}\left(\frac{\Gamma_p}{\nu^+_{\alpha q'}} - Kx^{\mathrm{W}}_{pq'}\right)\mathrm{d}\mu_{pq'} + \sum_{q\neq q'.\beta}\left(\frac{\Gamma_q}{\nu^-_{p'q}} - Kx^{\mathrm{W}}_{p'q}\right)\mathrm{d}\mu_{p'q}, \qquad (17)
\end{aligned}
$$

where G, H, and Q^{W} are given in Tables 1 and 2, and A, A′, B, B′, C, and D are in Tables 3 and 4. In Eq. 17 $\mu_{\alpha x}(x=j'$ or $q')$ and $\mu_{y\beta}(y=i'$ or $p')$ are the chemical potentials of the salts containing α and β, respectively, and $E^{\mathrm{W}\pm}_{\mathrm{O}\pm}$ is the potential of M′ with respect to M in the cell (I), where the plus(minus) sign is taken when the reference electrode is reversible to a cation(anion).

Ideal Polarized Oil–Water Interfaces: When no common ionic species is present between the oil and the water phases the interface may be called an ideal[1] polarized oil–water interface. In general, the ideal polarized oil–water interface permits the equilibrium distribution of neutral compounds between the two phases. In this case the terms involving the common ionic species α and β in Eqs. 8, 9, 16, and 17 vanish. The terms involving the mole fractions of $p'j'$ and $i'q'$ in the two phases also reduce to zero. We then obtain for the ideal polarized oil–water interface corresponding to Eq. 16:

$$
\begin{aligned}
-\mathrm{d}\gamma &= \left[\eta - J\bar{s}^{\mathrm{O}} - K\bar{s}^{\mathrm{W}} - \frac{Q^{\mathrm{W}}}{F}\left(\frac{\dot{s}_{\mathrm{R1}}}{z_{i'}} + \frac{\dot{s}_{\mathrm{R2}}}{|z_{q'}|}\right)\right]\mathrm{d}T \\
&- \left[\tau - J\bar{v}^{\mathrm{O}} - K\bar{v}^{\mathrm{W}} - \frac{Q^{\mathrm{W}}}{F}\left(\frac{\dot{v}_{\mathrm{R1}}}{z_{i'}} + \frac{\dot{v}_{\mathrm{R2}}}{|z_{q'}|}\right)\right]\mathrm{d}P \\
&+ \sum_{k\neq l}(\Gamma_k - Jx^{\mathrm{O}}_k)\mathrm{d}\mu_k + \sum_{h\neq l}(\Gamma_h - Kx_h)\mathrm{d}\mu_h \\
&+ \sum_{l\neq l'.l''}(\Gamma_l - Jx^{\mathrm{O}}_l - Kx^{\mathrm{W}}_l)\mathrm{d}\mu_l \\
&+ \sum_{i\neq i'}\left(\frac{\Gamma_i}{\nu^+_{ij'}} - Jx^{\mathrm{O}}_{ij'}\right)\mathrm{d}\mu_{ij'} + \sum_{j\neq j'}\left(\frac{\Gamma_i}{\nu^-_{i'j}} - Jx^{\mathrm{O}}_{i'j}\right)\mathrm{d}\mu_{i'j} \\
&+ \sum_{p\neq p'}\left(\frac{\Gamma_p}{\nu^+_{pq'}} - Kx^{\mathrm{W}}_{pq'}\right)\mathrm{d}\mu_{pq'} + \sum_{q\neq q'}\left(\frac{\Gamma_q}{\nu^-_{p'q}} - Kx^{\mathrm{W}}_{p'q}\right)\mathrm{d}\mu_{p'q} \\
&+ \frac{1}{\nu^-_{i'j'}}\left(\Gamma_{j'} - \sum_{i\neq i'}\frac{z_i}{|z_{j'}|}\Gamma_i - J\nu^-_{i'j'}x^{\mathrm{O}}_{i'j'}\right)\mathrm{d}\mu_{i'j'} \\
&+ \frac{1}{\nu^+_{p'q'}}\left(\Gamma_{p'} - \sum_{q\neq q'}\frac{|z_q|}{z_{p'}}\Gamma_q - K\nu^+_{p'q'}x^{\mathrm{W}}_{p'q'}\right)\mathrm{d}\mu_{p'q'} \\
&+ q^{\mathrm{W}}\mathrm{d}E^{\mathrm{W}-}_{\mathrm{O}+}, \qquad (18)
\end{aligned}
$$

where $q^{\mathrm{W}}(=-q^{\mathrm{O}})$ is the surface charge density due to the components in the water phase (q^{O} is the surface charge density due to the components in the oil phase) and is defined by

$$
\begin{aligned}
q^{\mathrm{W}} &= F(\sum_p z_p\Gamma_p - \sum_q |z_q|\Gamma_q) \\
&= F(\sum_j |z_j|\Gamma_j| - \sum_i z_i\Gamma_i) = -q^{\mathrm{O}}. \qquad (19)
\end{aligned}
$$

The degree of freedom of Eq. 18 is $k+h+i+j+p+q-l-1$ and, hence, all the intensive variables are independent. When the pair of the ions reversible to the reference electrodes R1 and R2 is not the $i'q'$ pair, one can easily find a corresponding electrocapillary equation using Eq. 17 and Tables 1, 3, and 4 if we omit the terms involving the common ionic species α and β and the mole fractions of $p'j'$ and $i'q'$.

Discussion

Ideal non-polarized interface is characterized by the lack of the degree of freedom concerning the electrical state of the interface; it is not possible to change the electrical potential difference between the interface or the surface charge density if we keep all other intensive variables constant. In the basic electrocapillary equation for the ideal nonpolarized interface represented by Eq. 16, or in more general terms in Eq. 17, there appears the potential difference between the two terminals of the cell (I) as an independent variable. This does not mean that one can apply a voltage to the interface without changing the equilibrium state of the interface. The potential difference between the two terminals can of course be measured, but the change of this potential can be achieved only through the change of the chemical potential of at least one of the salts containing α and β. In fact, the $\mathrm{d}E^{\mathrm{W}-}_{\mathrm{O}+}$ term in Eq. 16 can be rewitten in terms of the chemical potential of one of these salts which has been taken as a dependent variable in Eq. 16.

Let $\mu_{p'\beta'}$ instead of $E^{\mathrm{W}-}_{\mathrm{O}+}$ be the independent variable, where β' is any one of β common anions. By using Eq. 3 the last two terms in the right hand side of Eq. 7 become

$$
\begin{aligned}
&-\frac{Q^{\mathrm{W}}}{z_{i'}F}\mathrm{d}\mu_{i'} + \frac{Q^{\mathrm{O}}}{|z_{q'}|F}\mathrm{d}\mu_{q'} = \\
&-\frac{Q^{\mathrm{W}}}{F}\left(\frac{1}{z_{i'}\nu^+_{i'\beta}}\mathrm{d}\mu_{i'\beta'} - \frac{1}{|z_\beta|\nu^-_{p'\beta'}}\mathrm{d}\mu_{p'\beta'} + \frac{1}{z_{p'}\nu^+_{p'q'}}\mathrm{d}\mu_{p'q'}\right).
\end{aligned}
$$

Therefore, $\mathrm{d}E^{\mathrm{W}-}_{\mathrm{O}+}$ may be rewritten as

$$
\mathrm{d}E^{\mathrm{W}-}_{\mathrm{O}+} = \frac{1}{|z_{\beta'}|\nu^-_{p'\beta'}}\mathrm{d}\mu_{p'\beta'} - \frac{1}{z_{i'}\nu^+_{i'\beta'}}\mathrm{d}\mu_{i'\beta'} - \frac{1}{z_{p'}\nu^+_{p'q'}}\mathrm{d}\mu_{p'q'}.
$$

Necessary changes in Eq. 16 accompanied by the change of the independent variable from $E^{\mathrm{W}-}_{\mathrm{O}+}$ to $\mu_{p'\beta'}$ are given in Table 5. Thus, in ideal nonpolarized oil–water interfaces one can always replace the electromotive force of the cell with the chemical potential of one of the salts containing a common ion. Namely, a change of the chemical potential is always accompanied by a change of the chemical potential and is achieved only through the change of the chemical potential of the salt, as described above. When the interface is ideally polarized, there is no salt whose constituent ion is commonly distributed in both phases. In this case, one can arbitrarily change $E^{\mathrm{W}-}_{\mathrm{O}+}$ by applying a voltage between the two reference electrodes.

Equations 16 and 17 show that the partial derivative of the interfacial tension with respect to the potential drop across the terminals of the cell (I) gives the quantity Q^{W}. This Q^{W} is different from the surface charge density in the water phase q^{W} defined by Eq. 19 for an ideal polarized oil–water interface. First, Q^{W} defined by Eq. 8 contains the terms of the surface concentrations of the ions commonly distributed in the two phases, and, second, in comparison with q^{W}, Q^{W} has four additional terms involving the mole fractions of the salts containing the common ions. Unlike the ideal polarized interfaces, the potential of the electrocapillary maximum of the electrocapillary curve for a nonpolarized oil–water

TABLE 1. COEFFICIENTS G AND H IN Eq. 17

Independent variable		Coefficient	
		G	H
$\mu_{\alpha x}$	$\mu_{\alpha q'}{}^{a)}$	$\sum_\alpha \frac{\Gamma_\alpha}{\nu^+_{\alpha q'}} - J\frac{\nu^+_{\alpha j'}}{\nu^+_{\alpha q'}}x^{\mathrm{O}}_{\alpha j'} - Kx^{\mathrm{W}}_{\alpha q'}$	—
	$\mu_{\alpha j'}$	$\sum_\alpha \frac{\Gamma_\alpha}{\nu^+_{\alpha j'}} - Jx^{\mathrm{O}}_{\alpha j'} - K\frac{\nu^+_{\alpha q'}}{\nu^+_{\alpha j'}}x^{\mathrm{W}}_{\alpha q'}$	—
$\mu_{y\beta}$	$\mu_{p'\beta}{}^{a)}$	—	$\sum_\beta \frac{\Gamma_{\beta'}}{\nu^-_{p'\beta}} - J\frac{\nu^-_{i'\beta}}{\nu^-_{p'\beta}}x^{\mathrm{O}}_{i'\beta} - Kx^{\mathrm{W}}_{p'\beta}$
	$\mu_{i'\beta}$	—	$\sum_\beta \frac{\Gamma_\beta}{\nu^-_{i'\beta}} - Jx^{\mathrm{O}}_{i'\beta} - K\frac{\nu^-_{p'\beta}}{\nu^-_{i'\beta}}x^{\mathrm{W}}_{p'\beta}$

a) This choice of independent variables corresponds to Eq. 16.

TABLE 2. COEFFICIENTS Q^{W} IN Eq. 17 FOR VARIOUS SETS THE INDEPENDENT VARIABLES CONCERNING THE COMMON IONIC SPECIES

Set of independent variables	Q^{W}
$\alpha q'$ and $p'\beta^{a)}$	$F\{\sum_p z_p\Gamma_p - \sum_q \lvert z_q\rvert\Gamma_q - J\sum_\alpha \nu^+_{\alpha j'}z_\alpha x^{\mathrm{O}}_{\alpha j'} + J\sum_\beta \lvert z_\beta\rvert \nu^-_{i'\beta}x^{\mathrm{O}}_{i'\beta} + J(z_{i'}\nu^+_{i'q'}x^{\mathrm{O}}_{i'q'} - \lvert z_{j'}\rvert \nu^-_{p'j'}x^{\mathrm{O}}_{p'j'}) + K(z_{i'}\nu^+_{i'q'}x^{\mathrm{W}}_{i'q'} - \lvert z_{j'}\rvert \nu^-_{p'j'}x^{\mathrm{W}}_{p'j'})\}$
$\alpha q'$ and $i'\beta$	$F\{\sum_p z_p\Gamma_p - \sum_{q\neq\beta} \lvert z_q\rvert\Gamma_q - J\sum_\alpha z_\alpha \nu^+_{\alpha j'} - K\sum_\beta \lvert z_\beta\rvert \nu^-_{p'\beta}x^{\mathrm{W}}_{p'\beta} + J(z_{i'}\nu^+_{i'q'}x^{\mathrm{O}}_{i'q'} - \lvert z_{j'}\rvert \nu^-_{p'j'}x^{\mathrm{O}}_{p'j'}) + K(z_{i'}\nu^+_{i'q'}x^{\mathrm{W}}_{i'q'} - \lvert z_{j'}\rvert \nu^-_{p'j'}x^{\mathrm{W}}_{p'j'})\}$
aj' and $p'\beta$	$F\{\sum_{p\neq\alpha} z_p\Gamma_p - \sum_q \lvert z_q\rvert\Gamma_q + K\sum_\alpha z_\alpha \nu^+_{\alpha q'}x^{\mathrm{W}}_{\alpha q'} + J\sum_\beta \lvert z_\beta\rvert \nu^-_{i'\beta}x^{\mathrm{O}}_{i'\beta} + J(z_{i'}\nu^+_{i'q'}x^{\mathrm{O}}_{i'q'} - \lvert z_{j'}\rvert \nu^-_{p'j'}x^{\mathrm{O}}_{p'j'}) + K(z_{i'}\nu^+_{i'q'}x^{\mathrm{W}}_{i'q'} - \lvert z_{j'}\rvert \nu^-_{p'j'}x^{\mathrm{W}}_{p'j'})\}$
aj' and $i'\beta$	$F\{\sum_{p\neq\alpha} z_p\Gamma_p - \sum_{q\neq\beta} \lvert z_q\rvert\Gamma_q + K\sum_\alpha z_\alpha \nu^+_{\alpha q'}x^{\mathrm{W}}_{\alpha q'} - K\sum_\beta \lvert z_\beta\rvert \nu^-_{p'\beta}x^{\mathrm{W}}_{p'\beta} + J(z_{i'}\nu^+_{i'q'}x^{\mathrm{O}}_{i'q'} - \lvert z_{j'}\rvert \nu^-_{p'j'}x^{\mathrm{O}}_{p'j'}) + K(z_{i'}\nu^+_{i'q'}x^{\mathrm{W}}_{i'q'} - \lvert z_{j'}\rvert \nu^-_{p'j'}x^{\mathrm{W}}_{p'j'})\}$

a) This choice of independent variables corresponds to Eq. 16.

TABLE 3. EXPRESSSIONS OF A, B, AND C IN Eq. 17

Coefficient in Eq. 17	Choice of αx and $y\beta$	Ion reversible to R1	
		i'	j'
A	—	$\dot{s}_{\mathrm{R1}}/z_{i'}{}^{a)}$	$-\dot{s}_{\mathrm{R1}}/\lvert z_{j'}\rvert$
B	—	$\dot{v}_{\mathrm{R1}}/z_{i'}{}^{a)}$	$-\dot{v}_{\mathrm{R1}}/\lvert z_{j'}\rvert$
C	$\left.\begin{matrix}(\alpha q', p'\beta)\\(\alpha q', i'\beta)\end{matrix}\right\}$	$\frac{1}{\nu^-_{i'j'}}(\Gamma_{j'} - \sum_{i\neq j',\alpha}\frac{z_i}{\lvert z_{j'}\rvert}\Gamma_i - J\sum_\alpha \nu^-_{\alpha j'}x^{\mathrm{O}}_{\alpha j'}{}^{a)} - J\nu^-_{i'j'}x^{\mathrm{O}}_{i'j'} - J\nu^-_{p'j'}x^{\mathrm{O}}_{p'j'} - K\nu^-_{p'j'}x^{\mathrm{W}}_{p'j'})$	$\frac{1}{\nu^+_{i'j'}}(\Gamma_i - \sum_{i\neq j',\beta}\frac{\lvert z_j\rvert}{z_{i'}}\Gamma_j - J\sum_\beta \nu^+_{i'\beta}x^{\mathrm{O}}_{i'\beta} - J\nu^+_{i'j'}x^{\mathrm{O}}_{i'j'} - J\nu^+_{i'q'}x^{\mathrm{O}}_{i'q'} - K\nu^+_{i'q'}x^{\mathrm{W}}_{i'q'})$
	$\left.\begin{matrix}(\alpha j', i'\beta)\\(\alpha j', p'\beta)\end{matrix}\right\}$	$\frac{1}{\nu^-_{i'j'}}(\Gamma_{j'} - \sum_{i\neq i'}\frac{z_i}{\lvert z_{j'}\rvert}\Gamma_i + K\sum_\alpha \nu^+_{\alpha q'}x^{\mathrm{W}}_{\alpha q'} - J\nu^-_{i'j'}x^{\mathrm{O}}_{i'j'} - J\nu^-_{p'j'}x^{\mathrm{O}}_{p'j'} - K\nu^-_{p'j'}x^{\mathrm{W}}_{p'j'})$	$\frac{1}{\nu^+_{i'j'}}(\Gamma_{i'} - \sum_{i\neq j'}\frac{\lvert z_j\rvert}{z_{i'}}\Gamma_j + K\sum_\alpha \frac{\lvert z_\beta\rvert}{z_{i'}}\nu^-_{p'\beta}x^{\mathrm{W}}_{p'\beta} - J\nu^+_{i'j'}x^{\mathrm{O}}_{i'j'} - J\nu^+_{i'q'}x^{\mathrm{O}}_{i'q'} - K\nu^+_{i'q'}x^{\mathrm{W}}_{i'q'}$

a) This choice of independent variables corresponds to Eq. 16.

TABLE 4. EXPRESSIONS OF A′, B′, AND D IN Eq. 17

Coefficient in Eq. 17	Choice of αx and $y\beta$	Ion reversible to R2	
		p'	q'
A′	—	$-\dot{s}_{\mathrm{R1}}/z_{p'}$	$\dot{s}_{\mathrm{R2}}/\lvert z_{q'}\rvert^{a)}$
B′	—	$-\dot{v}_{\mathrm{R2}}/z_{p'}$	$\dot{v}_{\mathrm{R2}}/\lvert z_{q'}\rvert^{a)}$
D	$\left.\begin{matrix}(aq', p'\beta)\\(aj', p'\beta)\end{matrix}\right\}$	$\frac{1}{\nu^-_{p'q'}}(\Gamma_{q'} - \sum_{p\neq p'}\frac{z_p}{\lvert z_{q'}\rvert}\Gamma_p + J\frac{z_\alpha}{\lvert z_{q'}\rvert}\nu^-_{\alpha j'}x^{\mathrm{O}}_{\alpha j'} - K\nu^-_{p'q'}x^{\mathrm{W}}_{p'q'} - J\nu^-_{i'q'}x^{\mathrm{O}}_{i'q'} - K\nu^-_{i'q'}x^{\mathrm{W}}_{i'q'})$	$\frac{1}{\nu^+_{p'q'}}(\Gamma_{p'} - \sum_{q\neq q'}\frac{\lvert z_q\rvert}{z_{p'}}\Gamma_q + J\frac{\lvert z_\beta\rvert}{z_{p'}}\nu^-_{i'\beta}x^{\mathrm{O}}_{i'\beta} - K\nu^+_{p'q'}x^{\mathrm{W}}_{p'q'} - J\nu^+_{p'j'}x^{\mathrm{O}}_{p'j'} - K\nu^+_{p'j'}x^{\mathrm{W}}_{p'j'})^{a)}$
	$\left.\begin{matrix}(aq', i'\beta)\\(aj', i'\beta)\end{matrix}\right\}$	$\frac{1}{\nu^-_{p'q'}}(\Gamma_{q'} - \sum_{p\neq p'}\frac{z_p}{\lvert z_{q'}\rvert}\Gamma_p - K\sum_\alpha \nu^+_{\alpha q'}x^{\mathrm{W}}_{\alpha q'} - K\nu^-_{p'q'}x^{\mathrm{W}}_{p'q'} - J\nu^-_{i'q'}x^{\mathrm{O}}_{i'q'} - K\nu^-_{i'q'}x^{\mathrm{W}}_{i'q'})$	$\frac{1}{\nu^+_{p'q'}}(\Gamma_{p'} - \sum_{q\neq q',\beta}\frac{\lvert z_q\rvert}{z_{p'}}\Gamma_q - K\sum_\beta \nu^+_{p'\beta}x^{\mathrm{W}}_{p'\beta} - K\nu^+_{p'q'}x^{\mathrm{W}}_{p'q'} - J\nu^+_{p'j'}x^{\mathrm{O}}_{p'j'} - K\nu^+_{p'j'}x^{\mathrm{W}}_{p'j'})$

a) This choice of independent variables corresponds to Eq. 16.

TABLE 5. CHANGE OF THE TERMS IN Eq. 16 ACCOMPANIED BY THE CHANGE OF AN INDEPENDENT VARIABLES FROM $E^{\mathrm{W}-}_{\mathrm{O}+}$ to $\mu_{i'\beta'}$

$E^{\mathrm{W}-}_{\mathrm{O}+}$	$\mu_{i'\beta'}$
$\sum\limits_{\beta}\dfrac{\Gamma_\beta}{\nu^-_{p'\beta}} - J\dfrac{\nu^-_{i'\beta}}{\nu^-_{p'\beta}}x^{\mathrm{O}}_{i'\beta} - Kx^{\mathrm{W}}_{p'\beta})\mathrm{d}\mu_{p'\beta}$	$\sum\limits_{\beta\neq\beta'}\left(\dfrac{\Gamma_\beta}{\nu^-_{p'\beta}} - J\dfrac{\nu^-_{i'\beta}}{\nu^-_{p'\beta}}x^{\mathrm{O}}_{i'\beta} - Kx^{\mathrm{W}}_{p'\beta}\right)\mathrm{d}\mu_{p'\beta}$ $+\left(\dfrac{\Gamma_{\beta'}}{\nu^-_{p'\beta'}} - J\dfrac{\nu^-_{i'\beta'}}{\nu^-_{p'\beta'}}x^{\mathrm{O}}_{i'\beta'} - Kx^{\mathrm{W}}_{p'\beta'} + \dfrac{1}{\lvert z_{\beta'}\rvert\nu^-_{p'\beta'}}\cdot\dfrac{Q^{\mathrm{W}}}{F}\right)d\mu_{p'\beta'}$
$\dfrac{1}{\nu^+_{p'q'}}X\,\mathrm{d}\mu_{p'q'}$ a)	$\dfrac{1}{\nu^+_{p'q'}}\left(X - \dfrac{Q^{\mathrm{W}}}{z_{p'}F}\right)\mathrm{d}\mu_{p'q'}$ a)
$\dfrac{Q^{\mathrm{W}}}{F}\mathrm{d}E^{\mathrm{W}-}_{\mathrm{O}+}$	$-\dfrac{Q^{\mathrm{W}}}{Fz_{i'}\nu^+_{i'\beta'}}\mathrm{d}\mu_{i'\beta'}$

a) $X = \Gamma_{p'} - \sum\limits_{q\neq q'}\dfrac{\lvert z_q\rvert}{z_{p'}}\Gamma_q + J\sum\limits_{\beta}\dfrac{\lvert z_\beta\rvert}{z_{p'}}\nu^-_{i'\beta'} - J\nu^+_{p'j'}x^{\mathrm{O}}_{p'j'} - K\nu^+_{p'j'}x^{\mathrm{W}}_{p'j'} - K\nu^+_{p'q'}x^{\mathrm{W}}_{p'q'}.$

interface, therfore, does not generally correspond to the potential of zero charge, which, however, can be defined only through an assumption of a dividing surface in the case of nonpolarized interfaces. The difference between Q^{W} and q^{W} originates in the difference in thermodynamic polarizability of the interfaces and is free from any particular model which assumes a physical dividing surface.[16] The surface charge density due to the components in the water phase q^{W} defined by Eq. 19 is conventionally called the surface charge density in water phase and q^{O} the surface charge density in oil phase. Note that the surface charge density $q^{\mathrm{W}}(=-q^{\mathrm{O}})$ is a thermodynamically defined quantity for an ideal polarized oil–water interface and may not correspond to the physical surface charge density.[11,16] For example, the ionic charge due to the hydrophilic group of an amphiphile which is present only in the oil phase and is adsorbed at an oil–water interface should be considered as a part of the "surface charge density in the oil phase" even when the hydrophilic ionic groups protrude into the water phase and are exposed to the aqueous medium, as is the case of the adsorption of phospholipids at the oil–water interface.[17]

In Eqs. 16, 17, and 18 the partial derivative of the interfacial tension with respect to the chemical potential of any one of the neutral components gives the relative surface concentration of the corresponding component, *i.e.*, the surface concentration relativised by the surface concentrations of the two reference components l' and l'', which enter into the measured quantity through J and K terms. Similarly, the partial derivative of the interfacial tension with respect to the chemical potential of any one of the salt components gives the relative surface concentration of the corresponding ionic component. When the mutual solubility between l' and l'' is considerably high, the denominators of Eqs. 10 and 11 become very small. This means that the relative surface concentrations can be significantly different from the actual surface concentrations. This is due to the fact that the relative surface concentrations in Eqs. 16–18 are relativised by the two reference components; hence, this is one of the features of the oil–water interfaces which distinguish them from the metal-solution interfaces.[15]

When there occurs an ion pair formation or an incomplete dissociation of a salt, which may be expected especially in the oil phase having lower dielectric constant, the surface concentration of an ion pair or an undissociated salt appears in the relevant terms in Eq. 17 (and also in Eqs. 16 and 18). Extension of the basic electrocapillary equation to meet these cases is feasible. For example, suppose that the cation $\bar{i}$ in the cations i (except i' and α) and the anion $\bar{j}$ in the anions j (except j' and β) form a neutral ion pair $\bar{i}\bar{j}$ in the oil phase. There then appears an additional term $\Gamma_{\bar{i}\bar{j}}\mathrm{d}\mu_{\bar{i}\bar{j}}$ in Eq. 2, where $\Gamma_{\bar{i}\bar{j}}$ and $\mu_{\bar{i}\bar{j}}$ are the surface concentration and the chemical potential of the ion pair $\bar{i}\bar{j}$. Since the differential of the chemical potential of $\bar{i}\bar{j}$, $\mathrm{d}\mu_{\bar{i}\bar{j}}$, can be written in terms of those of the electrochemical potentials of $\bar{i}$ and $\bar{j}$ ions, $\mathrm{d}\mu_{\bar{i}}$ and $\mathrm{d}\mu_{\bar{j}}$, as

$$\mathrm{d}\mu_{\bar{i}\bar{j}} = \nu^+_{\bar{i}\bar{j}}\mathrm{d}\mu_{\bar{i}} + \nu^-_{\bar{i}\bar{j}}\mathrm{d}\mu_{\bar{j}},$$

where $\nu^+_{\bar{i}\bar{j}}$ and $\nu^-_{\bar{i}\bar{j}}$ are the stoichiometric numbers of the ion pair formation reaction represented by the equation similar to Eq. 4, the term $\Gamma_{\bar{i}\bar{j}}\mathrm{d}\mu_{\bar{i}\bar{j}}$ can be rewritten in the form:

$$\Gamma_{\bar{i}\bar{j}}\mathrm{d}\mu_{\bar{i}\bar{j}} = \Gamma_{\bar{i}\bar{j}}(\nu^+_{\bar{i}\bar{j}}\mathrm{d}\mu_{\bar{i}} + \nu^-_{\bar{i}\bar{j}}\mathrm{d}\mu_{\bar{j}}).$$

Substituting Eqs. 3-1 to 3-3 into this equation, we obtain

$$\Gamma_{\bar{i}\bar{j}}\mathrm{d}\mu_{\bar{i}\bar{j}} = \Gamma_{\bar{i}\bar{j}}\left(\frac{\nu^+_{\bar{i}\bar{j}}}{\nu^+_{\bar{i}j'}}\mathrm{d}\mu_{\bar{i}j'} - \frac{\nu^-_{\bar{i}\bar{j}}}{\nu^-_{i'\bar{j}}}\mathrm{d}\mu_{i'\bar{j}} - \frac{z_{\bar{i}}}{\lvert z_{j'}\rvert}\cdot\frac{\nu^+_{\bar{i}\bar{j}}}{\nu^-_{i'j'}}\mathrm{d}\mu_{i'j'}\right).$$

Consequently, the ion pair formation between the ions $\bar{i}$ and $\bar{j}$ gives rise to additional terms involving the surface concentration of the ion pair, $(\nu^+_{\bar{i}\bar{j}}/\nu^+_{\bar{i}j})\Gamma_{\bar{i}\bar{j}}$, $(\nu^-_{\bar{i}\bar{j}}/\nu^-_{i\bar{j}})\Gamma_{\bar{i}\bar{j}}$, and $(z_{\bar{i}}/\lvert z_{j'}\rvert)(\nu^+_{\bar{i}\bar{j}}/\nu^-_{i'j'})\Gamma_{\bar{i}\bar{j}}$, in the coefficients of $\mathrm{d}\mu_{\bar{i}j'}$, $\mathrm{d}\mu_{i\bar{j}}$, and $\mathrm{d}\mu_{i'j'}$ terms, respectively, in Eq. 17 (and also in Eqs. 16 and 18). Thus the ion pair formation or incomplete dissociation of a salt is easily taken into account in the general electrocapillary equation. The case of the formation of a charged ion pair may be considered similarly.

If we introduce a new function defined by $\xi = Q^{\mathrm{W}}E^{\mathrm{W}\pm}_{\mathrm{O}\mp} + \gamma$, which has been proposed by Parsons[18] for an ideal polarized metal-solution interface, we can replace the independent variable $E^{\mathrm{W}\pm}_{\mathrm{O}\mp}$ with Q^{W} in Eq. 17. Then several useful relationships can be obtained from the cross-differentiation relationship. For example, the Esin–Markov coefficient of a neutral component k, which is defined as the slope of a plot of $E^{\mathrm{W}\pm}_{\mathrm{O}\mp}$ *vs.* the chemical potential of component k at constant T, P, Q^{W}, and chemical potentials of all other components, is related to the rate of the change of the relative surface concentration of a component k with Q^{W} at constant T, P, and composition:

$$\left(\frac{\partial E_{\mathrm{O}\pm}^{\mathrm{W}\pm}}{\partial \mu_k}\right)_{T,P,Q^{\mathrm{W}},\mu\neq\mu_k} = -\left(\frac{\partial(\Gamma_k - Jx_k^{\mathrm{O}})}{\partial Q^{\mathrm{W}}}\right)_{T,P,\mu}$$

(for $k \neq l$).

Similar relations are easily obtained for the Esin–Markov coefficients of the neutral components $h(\neq l)$ and $l(\neq l', l'')$ and of the salts $i'j'$, $p'q'$, αx $(x=j'$ or $q')$, $y\beta(y=i'$ or $p')$, ij'(for $i\neq i'$, α), $i'j$(for $j\neq j'$, β), pq'(for $p\neq p'$, α), and $p'q$(for $q\neq q'$, β). Such cross-differentiation relations have been employed to analyze the Esin-Markov coefficients at the interface between a nitrobenzene solution of tetrabutylammonium tetraphenylborate and an aqueous solution of lithium chloride to detect the specific adsorption of the ions.⁶⁾

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