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On the Gibbs Adsorption Equation for Electrolyte Solutions

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A general method is developed to derive the Gibbs adsorption equation in the form applicable to aqueous solutions of electrolytes, either strong or weak, composed of multi-components. Assuming that the solution is ideal, the chemical potentials of solute electrolytes are represented by their concentrations, and the lowering of surface tension is calculated as a function of variations of these concentrations. Explicit expressions for surface excesses of various species are obtained on aqueous solutions of two strong electrolytes having a common cation, such as sodium dodecyl sulfate and NaCl, and on solutions containing a weak acid adjusted its ionization by addition of alkali, such as fatty acid or soap, in the presence of an added salt. The convention for drawing the Gibbs dividing plane is discussed when the Gibbs adsorption equation is represented in terms of all the species in solution.

For the experimental verification of the Gibbs adsorption isotherm, aqueous solutions of surface-active substances are the most appropriate to be examined, but, owing to the electrolytic nature of most of the well-defined surfactants, the Gibbs adsorption equation has to be cast into a form applicable to such multi-component systems. Nevertheless, considerable controversy has been raised about it, since Brady[1)] and Hutchinson[2)] first gave an equation for a solution of strong electrolyte, in which each constituent ionic species contributes to the lowering of surface tension.[3-7)] Later it was shown, however, that when an excess amount of salt is added, the electric double layer reduces the contribution of counter ion, and only the surfactant ion is responsible for surface activity.[8-11)] Davies[12)] derived an approximate form of the Gibbs adsorption equation for a solution of strong electrolyte, which gave the results cited above in both extreme cases, *i.e.*, in the absence and excess presence of added salt.[13,14)] Recently, Tajima[15)] succeeded to find an exact equation for aqueous solution of strong electrolytes.

In the present work, we will develop a general method to derive the Gibbs adsorption equation in the form applicable to aqueous solutions of electrolytes, either strong or weak, composed of multi-components. This method is first adapted to a solution of two strong electrolytes having a common cation, *i.e.*, NaD and NaCl, where D^- may be any anion other than Cl^-. Then it is extended to treat aqueous solutions containing a weak electrolyte, HD, such as a solution of HD, NaOH and NaCl, or solutions of NaD, HCl, and NaCl, or NaD, NaOH, and NaCl, in the latter two of which HD is generated by hydrolysis. The binary system containing HD or NaD alone will appear as a limiting case of ternary or quaternary systems cited above.

Our approach is general and purely thermodynamic. The Gibbs adsorption equation is expressed in terms of chemical potentials of added solute components. The method is applicable to any multi-component systems. The assumption is made that the solution is dilute and ideal, in spite of electrolytes involved, so that the activity coefficients of solute components are put equal to unity. The lowering of surface tension is then given as a function of variations of concentrations of added solute components.

Principles of the Method

Our starting equation is given by

$$-\mathrm{d}\gamma = \sum_{\mathrm{i}} \Gamma_{\mathrm{i}} \mathrm{d}\mu_{\mathrm{i}}, \tag{1}$$

where γ is the surface tension, Γ_{i} is the surface excess referred to a dividing plane set at an unspecified position of the interface between two phases (vapor and solution), and μ_{i} is the chemical potential or may be the electrochemical potential (in the solution phase). The suffix, i, represents the chemical species, either nonionic or ionic, and the summation extends over all species actually present in the system (solution).[16-18)] In the three-component system concerned, i stands for H_2O, Na^+, D^-, and Cl^-, and in the case of hydrolysis occurring, it should include HD, H^+, and OH^-. In the four-component systems, all these species must be taken into account.

It should be noticed that values of Γ_{i} thus given are not definite unless the position of the dividing plane is specified. When n_{i} moles of species i are distributed between vapor and solution phases, in which its molar concentrations are C_{i}' and C_{i}, respectively, the surface excess, Γ_{i}, is given by

$$A\Gamma_{\mathrm{i}} = n_{\mathrm{i}} - V'C_{\mathrm{i}}' - VC_{\mathrm{i}}, \tag{1a}$$

where A is the area of the plane interface. Volumes of the vapor phase and the solution phase, V' and V, are not definite as far as the location of dividing plane is unspecified, while the system is closed and $V'+V$ is constant. Consequently, values of Γ_{i} remain indefinite at this stage.[16-18)]

Let ν neutral components be added to make up the solution, where ν is 3 or 4. When HD is involved, two ionization equilibria are set up. The condition for equilibrium is determined by

$$\mu_\lambda = \mu_{\mathrm{H}^+} + \mu_{\mathrm{a}}, \tag{2}$$

where λ is H_2O or HD and a is OH^- or D^-. It should be noticed that μ_λ stands for the chemical potential of water component or the weak acid added as well as that of unionized H_2O or HD.[17)] Furthermore, the chemical potential of a (uni-univalent) strong electrolyte can also be represented by the sum of the potentials of its constituent ions:

$$\mu_\lambda = \mu_{\mathrm{k}} + \mu_{\mathrm{a}}, \tag{3}$$

where λ is NaD, HCl, NaOH, or NaCl, and k and a are the corresponding cation and anion, respectively.

By means of Eqs. 2 and 3 we eliminate all the chemical potentials of ionic species except for one, and then we can express the decrease in surface tension in terms of the variations of chemical potentials of added neutral components and that of the single ionic species. As the chemical potential of a single ion cannot be altered by itself, the relevant term should not appear, and it is actually found that the condition is satisfied by the electroneutrality among surface excesses of ionic species. Equation 1 is then written in a form

$$-\mathrm{d}\gamma = \sum_{\lambda=1}^{\nu} \Gamma_\lambda \mathrm{d}\mu_\lambda, \tag{4}$$

where λ runs over all ν neutral components actually added, including water as 1. Γ_λ is here expressed by an algebraic sum of Γ_i, when started from Eq. 1, but it represents the surface excess of added neutral component, λ.

In a ν-component system composed of two phases (vapor and solution), the number of degrees of freedom is $\nu-1$ at constant temperature. Consequently, a term of Eq. 4 must vanish, and for dilute solutions the solvent, water, term is chosen, so that the coefficient of $\mathrm{d}\mu_{H_2O}$, *i.e.*, Γ_1, is put equal to zero.18) This procedure is equivalent to set the dividing plane of the interface at a definite position, which makes the surface excesses of solute components definite. In Appendix an alternative definition of surface excesses is given, which eventually agrees with the above.

The Gibbs adsorption equation is now given by

$$-\mathrm{d}\gamma = \sum_{\lambda=2}^{\nu} \Gamma_\lambda^{(1)} \mathrm{d}\mu_\lambda, \tag{5}$$

where the superfix, (1), for Γ_λ implies that the dividing plane is placed at such a position that the surface excess of water, 1, is zero. An algebraic sum of $\Gamma_i^{(1)}$ will replace for $\Gamma_\lambda^{(1)}$. In the following we will omit the superfix, (1), for the sake of brevity, which will not cause any confusion.

It remains to express the chemical potentials of added neutral solutes by their concentrations. In the present work we make an assumption that the solution is ideal so that the activity coefficients of the solute components are unity. Then the chemical potential of an unionized solute species (or a weak electrolyte), λ=HD, has a form

$$\mu_\lambda = \mu_\lambda^\circ + RT \ln C_\lambda, \tag{6}$$

where C_λ is the molar concentration of λ and the superfix, $\circ$, refers to the standard state. The chemical potential of a strong electrolyte has a form

$$\mu_\lambda = \mu_\lambda^\circ + RT \ln C_k C_a, \tag{7}$$

where C_k and C_a are the molar concentrations of cation and anion, respectively. The concentrations, C_λ, C_k, and C_a, can be expressed by the concentrations of added neutral solutes and the degree of ionization.

Ternary System: H_2O+NaD+NaCl

We consider an aqueous solution of NaD and NaCl, where NaD may be an anionic surfactant. Hydrolysis of NaD is not taken into account, and accordingly, the ionization of water is not involved either. Then we have four chemical species in solution, and Eq. 1 is written as

$$-\mathrm{d}\gamma = \Gamma_{H_2O}\mathrm{d}\mu_{H_2O} + \Gamma_{Na^+}\mathrm{d}\mu_{Na^+} + \Gamma_{D^-}\mathrm{d}\mu_{D^-} + \Gamma_{Cl^-}\mathrm{d}\mu_{Cl^-}. \tag{8}$$

Using Eqs. 3 for chemical potentials of NaD and NaCl, Eq. 8 is converted into

$$-\mathrm{d}\gamma = \Gamma_{H_2O}\mathrm{d}\mu_{H_2O} + \Gamma_{D^-}\mathrm{d}\mu_{NaD} + \Gamma_{Cl^-}\mathrm{d}\mu_{NaCl} + (\Gamma_{Na^+} - \Gamma_{D^-} - \Gamma_{Cl^-})\mathrm{d}\mu_{Na^+}. \tag{9}$$

As the chemical potential of Na^+ cannot be varied by itself, the last term should not appear, but its coefficient vanishes owing to the electroneutrality condition

$$\Gamma_{Na^+} = \Gamma_{D^-} + \Gamma_{Cl^-}. \tag{10}$$

According to the phase rule, the system must have two degrees of freedom at constant temperature, so that we may put

$$\Gamma_{H_2O} = 0, \tag{11}$$

which defines the position of dividing plane and the surface excesses of solutes. Eq. 9 then becomes

$$-\mathrm{d}\gamma = \Gamma_{D^-}\mathrm{d}\mu_{NaD} + \Gamma_{Cl^-}\mathrm{d}\mu_{NaCl}. \tag{12}$$

It is evident that Γ_{D^-} is identical with the surface excess of NaD and Γ_{Cl^-} is that of NaCl.

If the molar concentrations of added NaD and NaCl are represented by C and C_S, respectively, the concentrations of ions are

$$\begin{aligned} C_{Na^+} &= C + C_S, \\ C_{D^-} &= C, \\ C_{Cl^-} &= C_S. \end{aligned} \tag{13}$$

Substituting Eqs. 13 into Eqs. 7 for NaD and NaCl, and putting them into Eq. 12, we obtain

$$-\mathrm{d}\gamma = RT[\Gamma_2 \mathrm{d}\ln C + \Gamma_3 \mathrm{d}\ln C_S], \tag{14}$$

where

$$\Gamma_2 = \left(1 + \frac{C}{C+C_S}\right)\Gamma_{D^-} + \frac{C}{C+C_S}\Gamma_{Cl^-}, \tag{14a}$$

$$\Gamma_3 = \frac{C_S}{C+C_S}\Gamma_{D^-} + \left(1 + \frac{C_S}{C+C_S}\right)\Gamma_{Cl^-}. \tag{14b}$$

Solving Eqs. 14a and b, we have the surface excesses or the adsorbed amounts of ions of NaD and NaCl:

$$\Gamma_{D^-} = \left(1 - \frac{C}{2(C+C_S)}\right)\Gamma_2 - \frac{C}{2(C+C_S)}\Gamma_3, \tag{15a}$$

$$\Gamma_{Cl^-} = -\frac{C_S}{2(C+C_S)}\Gamma_2 + \left(1 - \frac{C_S}{2(C+C_S)}\right)\Gamma_3. \tag{15b}$$

The surface excess of Na^+ is given by

$$\Gamma_{Na^+} = \Gamma_{D^-} + \Gamma_{Cl^-} = \frac{1}{2}(\Gamma_2 + \Gamma_3). \tag{15c}$$

The equations derived by Tajima15) reduce to Eqs. 15a and 15b, if the activity coefficients of solutes are substituted by unity, instead of being given by the Debye-Hückel limiting law. Eqs. 14 and 15 are applicable to solutions of sodium dodecyl sulfate in the presence or absence of NaCl, provided that no (surface) hydrolysis occurs. It is easy to show that no surface hydrolysis occurs unless HCl is added, as far as HD is a strong acid.19)

When HD is generated by hydrolysis, as in solutions of sodium carboxylate, three additional species, HD, H^+, and OH^-, must be taken into account. Such a system will be treated as a special case of the quaternary systems below.

Quaternary Systems

When we consider an aqueous solution of HD, NaOH, and NaCl, in which HD is a weak acid such as fatty acid, there are seven chemical species in it. Clearly these species are also produced in solutions of NaD and NaCl, either in the presence or absence of HCl or NaOH. Then the Gibbs adsorption equation, Eq. 1, for these quaternary systems is commonly written as

$$-\mathrm{d}\gamma = \Gamma_{\mathrm{H_2O}}\mathrm{d}\mu_{\mathrm{H_2O}} + \Gamma_{\mathrm{HD}}\mathrm{d}\mu_{\mathrm{HD}} + \Gamma_{\mathrm{H^+}}\mathrm{d}\mu_{\mathrm{H^+}} + \Gamma_{\mathrm{OH^-}}\mathrm{d}\mu_{\mathrm{OH^-}} + \Gamma_{\mathrm{Na^+}}\mathrm{d}\mu_{\mathrm{Na^+}} + \Gamma_{\mathrm{D^-}}\mathrm{d}\mu_{\mathrm{D^-}} + \Gamma_{\mathrm{Cl^-}}\mathrm{d}\mu_{\mathrm{Cl^-}}, \tag{16}$$

For these systems the electroneutrality of surface excesses of ionic species

$$\Gamma_{\mathrm{H^+}} + \Gamma_{\mathrm{Na^+}} = \Gamma_{\mathrm{D^-}} + \Gamma_{\mathrm{OH^-}} + \Gamma_{\mathrm{Cl^-}}. \tag{17}$$

holds.

There exist ionization equilibria given by Eqs. 2 for water and the weak acid, and these equilibrium conditions can be substantially represented by the molar concentrations of added HD or NaD, C, and of added NaCl, C_S, if the activity coefficients of solutes are assumed to be unity.

When the apparent ionic product of water is defined by K_W, Eq. 2 may be put as

$$C_{\mathrm{H^+}}C_{\mathrm{OH^-}} = K_\mathrm{W}. \tag{18}$$

Similarly, when the degree of ionization of the weak acid is α and its ionization constant is K, then the concentrations of unionized and ionized acid species are given by

$$C_{\mathrm{HD}} = (1-\alpha)C, \qquad C_{\mathrm{D^-}} = \alpha C, \tag{19}$$

and Eq. 2 reduces to

$$C_{\mathrm{H^+}}\frac{\alpha}{1-\alpha} = K. \tag{20}$$

By means of the electroneutrality condition of the solution

$$C_{\mathrm{H^+}} + C_{\mathrm{Na^+}} = C_{\mathrm{D^-}} + C_{\mathrm{OH^-}} + C_{\mathrm{Cl^-}}, \tag{21}$$

we can obtain $C_{\mathrm{H^+}}$ and α as a function of C and C_A or C_B for the individual systems, where C_A and C_B are the molar concentrations of added HCl and NaOH, respectively. It is ready to substitute the variations of solute concentrations, C, C_A or C_B, and C_S, for the differentials of chemical potentials.

(I) H_2O+HD+NaOH+NaCl

For this system Eqs. 3 are used for NaOH and NaCl, and Eq. 16 is modified into a form composed of terms for added neutral components and a term of $\mathrm{d}\mu_{\mathrm{OH^-}}$. It is found that the coefficient of the last term is equal to zero owing to Eq. 17, and we have

$$-\mathrm{d}\gamma = (\Gamma_{\mathrm{H_2O}}+\Gamma_{\mathrm{H^+}}-\Gamma_{\mathrm{D^-}})\mathrm{d}\mu_{\mathrm{H_2O}} + (\Gamma_{\mathrm{HD}}+\Gamma_{\mathrm{D^-}})\mathrm{d}\mu_{\mathrm{HD}} + (\Gamma_{\mathrm{Na^+}}-\Gamma_{\mathrm{Cl^-}})\mathrm{d}\mu_{\mathrm{NaOH}} + \Gamma_{\mathrm{Cl^-}}\mathrm{d}\mu_{\mathrm{NaCl}} \tag{23}$$

As the number of degrees of freedom of the system should be 3 at constant temperature, the solvent, water, term is put equal to zero.

$$\Gamma_{\mathrm{H_2O}} + \Gamma_{\mathrm{H^+}} - \Gamma_{\mathrm{D^-}} = 0 \tag{24}$$

Equation 24 implies that the dividing plane of two phases be drawn at such a position as to make the surface excess of added water zero. The left-hand side of Eq. 24 is equal to the surface excess of water component, since either H^+ or H_2O is generated by the dissociation of HD or the reaction of HD with OH^-, the amount of which being equal to that of D^- formed. The water component should be considered to contain H^+ or OH^- as well as H_2O, when weak electrolytic solute is present, and its surface excess should be $\Gamma_{\mathrm{H_2O}}+\Gamma_{\mathrm{H^+}}=\Gamma_{\mathrm{H_2O}}+\Gamma_{\mathrm{OH^-}}$, when the solute is absent. Thus we obtain

$$-\mathrm{d}\gamma = (\Gamma_{\mathrm{HD}}+\Gamma_{\mathrm{D^-}})\mathrm{d}\mu_{\mathrm{HD}} + (\Gamma_{\mathrm{Na^+}}-\Gamma_{\mathrm{Cl^-}})\mathrm{d}\mu_{\mathrm{NaOH}} + \Gamma_{\mathrm{Cl^-}}\mathrm{d}\mu_{\mathrm{NaCl}}, \tag{25}$$

where $\Gamma_{\mathrm{HD}}+\Gamma_{\mathrm{D^-}}$ is the total surface excess of the weak acid added, $\Gamma_{\mathrm{Na^+}}-\Gamma_{\mathrm{Cl^-}}$ is clearly equal to the surface excess of NaOH, and $\Gamma_{\mathrm{Cl^-}}$ is totally assignable to that of NaCl.

For the ideal solution, the chemical potential of HD is given by Eq. 6, and those of NaOH and NaCl are given by Eqs. 7, in which

$$C_{\mathrm{Na^+}} = C_\mathrm{B} + C_\mathrm{S}, \qquad C_{\mathrm{Cl^-}} = C_\mathrm{S}. \tag{26}$$

Replacing Eqs. 18, 19, and 26 into Eq. 21, and combining it with Eq. 20, we have an equation for $C_{\mathrm{H^+}}$ or α, which can give $\mathrm{d}C_{\mathrm{H^+}}$ or $\mathrm{d}\alpha$ in terms of $\mathrm{d}C$ and $\mathrm{d}C_\mathrm{B}$ explicitly.

The final form of the Gibbs equation is then written as

$$-\mathrm{d}\gamma = RT\{\Gamma_2\mathrm{d}\ln C+\Gamma_\mathrm{B}\mathrm{d}\ln C_\mathrm{B}+\Gamma_3\mathrm{d}\ln C_\mathrm{S}\}, \tag{27}$$

where

$$\Gamma_2 = \left(1+\frac{\alpha^2C}{Q_\mathrm{B}}\right)(\Gamma_{\mathrm{HD}}+\Gamma_{\mathrm{D^-}}) - \frac{\alpha C}{Q_\mathrm{B}}(\Gamma_{\mathrm{Na^+}}-\Gamma_{\mathrm{Cl^-}}), \tag{27a}$$

$$\Gamma_\mathrm{B} = -\frac{\alpha C_\mathrm{B}}{Q_\mathrm{B}}(\Gamma_{\mathrm{HD}}+\Gamma_{\mathrm{D^-}}) + \left(\frac{C_\mathrm{B}}{Q_\mathrm{B}}+\frac{C_\mathrm{B}}{C_\mathrm{B}+C_\mathrm{S}}\right)\Gamma_{\mathrm{Na^+}} - \frac{C_\mathrm{B}}{Q_\mathrm{B}}\Gamma_{\mathrm{Cl^-}}, \tag{27b}$$

$$\Gamma_3 = \frac{C_\mathrm{S}}{C_\mathrm{B}+C_\mathrm{S}}\Gamma_{\mathrm{Na^+}} + \Gamma_{\mathrm{Cl^-}}, \tag{27c}$$

and

$$Q_\mathrm{B} = \alpha(2-\alpha)C - C_\mathrm{B} + 2C_{\mathrm{OH^-}} = -\alpha^2C + C_\mathrm{B} + 2C_{\mathrm{H^+}}. \tag{27d}$$

Solving Eqs. 27a, b, and c, the surface excesses or the adsorbed amounts of the weak acid, Na^+ and Cl^- are obtained as follows:

$$\Gamma_{\mathrm{HD}} + \Gamma_{\mathrm{D^-}} = \frac{C_\mathrm{B}+C_\mathrm{S}}{H_\mathrm{B}}\left\{\left(1+\frac{Q_\mathrm{B}+C_\mathrm{S}}{C_\mathrm{B}+C_\mathrm{S}}\right)\Gamma_2 + \left(\frac{Q_\mathrm{B}}{C_\mathrm{B}}+\frac{C_\mathrm{S}}{C_\mathrm{B}+C_\mathrm{S}}\right)\frac{\alpha C}{C_\mathrm{B}}\Gamma_\mathrm{B} - \frac{\alpha C}{C_\mathrm{B}+C_\mathrm{S}}\Gamma_3\right\}, \tag{28a}$$

$$\Gamma_{\mathrm{Na^+}} = \frac{C_\mathrm{B}+C_\mathrm{S}}{H_\mathrm{B}}\left\{\alpha\Gamma_2+\frac{Q_\mathrm{B}+\alpha^2C}{C_\mathrm{B}}\Gamma_\mathrm{B}+\Gamma_3\right\}, \tag{28b}$$

$$\Gamma_{\mathrm{Cl^-}} = \frac{C_\mathrm{B}+C_\mathrm{S}}{H_\mathrm{B}}\left\{-\frac{\alpha C_\mathrm{S}}{C_\mathrm{B}+C_\mathrm{S}}\left(\alpha\Gamma_2+\frac{Q_\mathrm{B}+\alpha^2C}{C_\mathrm{B}}\Gamma_\mathrm{B}\right) + \left(1+\frac{Q_\mathrm{B}+\alpha^2C}{C_\mathrm{B}+C_\mathrm{S}}\right)\Gamma_3\right\}, \tag{28c}$$

and

$$H_B = 2\alpha C + 2C_S + 2C_{OH^-} = 2C_B + 2C_S + 2C_{H^+}. \tag{28d}$$

This kind of equations is applicable to the solutions of monolauryl phosphoric acid in the presence of NaOH, as studied recently by Nakagaki, Handa, and Shimabayashi,[20] when it is modified for a uni-divalent acid instead of HD.

In particular, in the absence of added NaOH, $\Gamma_B = \Gamma_B/C_B = 0$, and also in the absence of added NaCl, $\Gamma_3 = 0$. Then we have

$$\Gamma_{HD} + \Gamma_{D^-} = \left(1 - \frac{\alpha^2 C}{2\alpha C + 2C_{OH^-}}\right)\Gamma_2. \tag{29}$$

This case corresponds to that often cited for illustration of the Traube's rule and Langmuir's deduction of fatty acid solutions,[21] which has been treated as $\alpha = 0$.

(II) $H_2O+NaD+HCl+NaCl$

For this system Eq. 16 is rearranged, by using Eqs. 3 for NaD, HCl, and NaCl, into a form composed of terms of added neutral components and a term of $d\mu_{Cl^-}$. The coefficient of the last term is found to vanish owing to Eq. 17. Thus we have

$$\begin{aligned}-d\gamma &= (\Gamma_{H_2O}+\Gamma_{OH^-})d\mu_{H_2O} + (\Gamma_{HD}+\Gamma_{D^-})d\mu_{NaD}\\ &\quad + (\Gamma_{Cl^-}-\Gamma_{Na^+}+\Gamma_{HD}+\Gamma_{D^-})d\mu_{HCl}\\ &\quad + (\Gamma_{Na^+}-\Gamma_{HD}-\Gamma_{D^-})d\mu_{NaCl}.\end{aligned} \tag{30}$$

By the requirement of phase rule, the number of variables must be 3 at constant temperature, and accordingly, the dividing plane should be set in such a way that

$$\Gamma_{H_2O} + \Gamma_{OH^-} = 0. \tag{31}$$

This means that the surface excess of added water, $\Gamma_{H_2O}+\Gamma_{OH^-}$, is zero, as OH^- has arisen from water by self ionization or by the reaction with D^- but H^+ is generated from HCl as well as from water. Then Eq. 30 becomes

$$\begin{aligned}-d\gamma &= (\Gamma_{HD}+\Gamma_{D^-})d\mu_{NaD}\\ &\quad + (\Gamma_{Cl^-}-\Gamma_{Na^+}+\Gamma_{HD}+\Gamma_{D^-})d\mu_{HCl}\\ &\quad + (\Gamma_{Na^+}-\Gamma_{HD}-\Gamma_{D^-})d\mu_{NaCl}.\end{aligned} \tag{32}$$

The chemical potentials of the three neutral components are given by Eqs. 7 in which

$$\begin{aligned}C_{Na^+} &= C + C_S,\\ C_{Cl^-} &= C_A + C_S.\end{aligned} \tag{33}$$

After straightforward calculation we have

$$-d\gamma = RT\{\Gamma_2 d\ln C + \Gamma_A d\ln C_A + \Gamma_3 d\ln C_S\} \tag{34}$$

where

$$\begin{aligned}\Gamma_2 &= \left(1 - \frac{\alpha(1-\alpha)C}{Q_A}\right)(\Gamma_{HD}+\Gamma_{D^-})\\ &\quad + \left(\frac{(1-\alpha)C}{Q_A} + \frac{C}{C+C_S}\right)\Gamma_{Na^+} - \frac{(1-\alpha)C}{Q_A}\Gamma_{Cl^-},\end{aligned} \tag{34a}$$

$$\begin{aligned}\Gamma_A &= \frac{\alpha C_A}{Q_A}(\Gamma_{HD}+\Gamma_{D^-}) - \frac{C_A}{Q_A}\Gamma_{Na^+}\\ &\quad + \left(\frac{C_A}{Q_A} + \frac{C_A}{C_A+C_S}\right)\Gamma_{Cl^-},\end{aligned} \tag{34b}$$

$$\Gamma_3 = \frac{C_S}{C+C_S}\Gamma_{Na^+} + \frac{C_S}{C_A+C_S}\Gamma_{Cl^-}, \tag{34c}$$

and

$$Q_A = (1-\alpha^2)C - C_A + 2C_{H^+} = -(1-\alpha)^2 C + C_A + 2C_{OH^-}. \tag{34d}$$

No such system as that formed by neutralization of NaD by addition of HCl seems to have been dealt with experimentally. In the case of fatty acid, the formation of acid soap[22-24] would complicate the situation. Accordingly, we will not pursue this line further.

However, in the absence of added HCl and NaCl, *i.e.*, for $C_A = C_S = 0$, Eq. 34a yields

$$\Gamma_2 = \left(2 + \frac{(1-\alpha)^2 C}{(1-\alpha^2)C + 2C_{H^+}}\right)(\Gamma_{HD}+\Gamma_{D^-}) \tag{35}$$

Aqueous solutions of sodium carboxylate such as sodium laurate correspond to this system. Surface tension of such solutions has been measured by Powney.[25]

(III) $H_2O+NaD+NaOH+NaCl$

Equation 16 is now converted into a form of terms of neutral components, by the use of Eqs. 3 for NaD, NaOH, and NaCl, in such a way to leave the term of $d\mu_{Na^+}$ as a term of a single ion, which eventually vanishes by means of Eq. 17. As a result, we obtain

$$\begin{aligned}-d\gamma &= (\Gamma_{H_2O}+\Gamma_{H^+}+\Gamma_{HD})d\mu_{H_2O} + (\Gamma_{HD}+\Gamma_{D^-})d\mu_{NaD}\\ &\quad + (\Gamma_{Na^+}-\Gamma_{Cl^-}-\Gamma_{HD}-\Gamma_{D^-})d\mu_{NaOH}\\ &\quad + \Gamma_{Cl^-}d\mu_{NaCl}.\end{aligned} \tag{36}$$

Because of the condition imposed for the dividing plane, the coefficient of the first term must be zero:

$$\Gamma_{H_2O} + \Gamma_{H^+} + \Gamma_{HD} = 0. \tag{37}$$

The left-hand side of Eq. 37 comes from the fact that H_2O is consumed by reaction with D^- by the amount equal to that of HD formed, while H^+ remaining unaltered. Then Eq. 36 becomes

$$\begin{aligned}-d\gamma &= (\Gamma_{HD}+\Gamma_{D^-})d\mu_{NaD}\\ &\quad + (\Gamma_{Na^+}-\Gamma_{Cl^-}-\Gamma_{HD}-\Gamma_{D^-})d\mu_{NaOH}\\ &\quad + \Gamma_{Cl^-}d\mu_{NaCl},\end{aligned} \tag{38}$$

where $\Gamma_{HD}+\Gamma_{D^-}$ is the surface excess of NaD, $\Gamma_{Na^+}-\Gamma_{Cl^-}-\Gamma_{HD^-}-\Gamma_{D^-} = \Gamma_{OH^-}-\Gamma_{H^+}-\Gamma_{HD}$ is that of NaOH, and Γ_{Cl^-} is that of NaCl.

The chemical potentials of the three solutes are given by Eqs. 3, for which

$$\begin{aligned}C_{Na^+} &= C + C_B + C_S,\\ C_{Cl^-} &= C_S.\end{aligned} \tag{39}$$

After direct calculations we reach the equation in a form

$$-d\gamma = RT\{\Gamma_2 d\ln C + \Gamma_B d\ln C_B + \Gamma_3 d\ln C_S\}, \tag{40}$$

where

$$\begin{aligned}\Gamma_2 &= \left(1 - \frac{\alpha(1-\alpha)C}{P_B}\right)(\Gamma_{HD}+\Gamma_{D^-})\\ &\quad + \left(\frac{(1-\alpha)C}{P_B} + \frac{C}{C+C_B+C_S}\right)\Gamma_{Na^+} - \frac{(1-\alpha)C}{P_B}\Gamma_{Cl^-},\end{aligned} \tag{40a}$$

$$\begin{aligned}\Gamma_B &= -\frac{\alpha C_B}{P_B}(\Gamma_{HD}+\Gamma_{D^-})\\ &\quad + \left(\frac{C_B}{P_B} + \frac{C_B}{C+C_B+C_S}\right)\Gamma_{Na^+} - \frac{C_B}{P_B}\Gamma_{Cl^-},\end{aligned} \tag{40b}$$

$$\Gamma_3 = \frac{C_S}{C+C_B+C_S}\Gamma_{Na^+} + \Gamma_{Cl^-}, \tag{40c}$$

and

$$P_B = (1-\alpha^2)C + C_B + 2C_{H^+}. \tag{40d}$$

Solving Eqs. 40a, b, c, the surface excesses or the adsorbed amounts of the salt, either ionic or hydrolyzed, and Na$^+$ and Cl$^-$ are found to be

$$\Gamma_{HD} + \Gamma_{D^-} = \frac{1}{Z_B}\left\{(C+C_B+P_B+2C_S)\Gamma_2 - \frac{C}{C_B}[(1-\alpha)(C+C_B+2C_S)+P_B]\Gamma_B - \alpha C\Gamma_3\right\}, \tag{41a}$$

$$\Gamma_{Na^+} = \frac{C+C_B+C_S}{Z_B}\left\{\alpha\Gamma_2 - \frac{1}{C_B}[\alpha(1-\alpha)C-P_B]\Gamma_B+\Gamma_3\right\}, \tag{41b}$$

$$\Gamma_{Cl^-} = \frac{1}{Z_B}\left\{-\alpha C_S\Gamma_2 + \frac{C_S}{C_B}[\alpha(1-\alpha)C-P_B]\Gamma_B + [(1+\alpha^2)C+C_B+P_B+C_S]\Gamma_3\right\}, \tag{41c}$$

and

$$Z_B = 2C + 2C_B + 2C_S + 2C_{H^+}. \tag{41d}$$

These equations are applicable to the solutions of sodium carboxylate in the presence of NaOH, such as studied by Powney and Addison.[25] The effect of added K_2CO_3 on the surface tension of aqueous solutions of potassium laurate[26] may also be treated along the same line of consideration.[27]

In the absence of added NaOH and NaCl, *i.e.*, for $C_B=C_S=0$, again we can arrive at Eq. 35 from Eq. 40a.

Discussion

It was shown that the Gibbs adsorption equation for a plane surface of electrolyte solution can be represented either in terms of all species, both ionic and nonionic, present in the solution, as given by Eq. 1, or in terms of added neutral components, as shown by Eq. 4. The equivalence of both representations has not been well recognized so far, and the former representation has been preferred by most workers,[8–15,19,28] although the latter representation is more favorable and convenient for thermodynamic treatments. We have also followed the former.

To make the values of surface excess definite, a dividing plane has to be drawn at a definite position between two phases. The usual convention for dilute solutions is to set the plane in such a way as to extinguish the surface excess of added water component. As far as the solution of nonelectrolytes or strong electrolytes is concerned, this convention usually does not cause any confusion, irrespective of which kind of representation has been employed, because neither H$^+$ and OH$^-$ nor the ionization of water need be taken into account. However, once a weak electrolyte is involved, the choice of the representation comes to have a serious effect on the formal expression of convention. While the representation in terms of the neutral components does not require any novel expression for the surface excess of water, the representaion in terms of all species in the solution distinguishes unionized water, H_2O, from total added water, because the ionization of water itself must be taken into account. Consequently, the surface excess of added water component, which should be put to be zero, is expressed by the sum of the surface excesses of unionized water, H_2O, and of H$^+$ or OH$^-$ formed by the dissociation, in the absence of solutes. However, the significance of the setting of the dividing plane is nothing new but remains as usual, although the formal expression differs.

It is also noted that the measurements of surface tension on solutions containing a weak acid does not permit to estimate Γ_{HD} or Γ_{D^-} separately but only gives the values of $\Gamma_{HD}+\Gamma_{D^-}$. They are also limited in the evaluation of Γ_{H^+}, Γ_{OH^-} or even $\Gamma_{H^+}-\Gamma_{OH^-}$ and can give only the value of $\Gamma_{H^+}+\Gamma_{HD}-\Gamma_{OH^-}$.

For the rigorous treatment of experimental results, the postulate of ideal solution should be removed, but the introduction of the limiting expressions of the Debye-Hückel theory for activity coefficients of ions leads to explicit results with great difficulty, in general.

Appendix

For simplicity, we assume the concentrations of all species in the vapor phase to be negligible. In the solution phase the Gibbs-Duhem equation holds among chemical potentials of all species, and it can be written as

$$\sum_i C_i \mathrm{d}\mu_i = 0. \tag{A1}$$

By means of Eqs. 2 and 3 and the condition of electroneutrality among concentrations of ionic species, Eq. A1 can be rewritten

$$\sum_{\lambda=1}^{\nu} C_\lambda \mathrm{d}\mu_\lambda = 0. \tag{A2}$$

Equation A2 is the Gibbs-Duhem equation given in terms of all the neutral components added, and C_λ is actually expressed by an algebraic sum of C_i.

From Eq. A2 the variation of chemical potential of water component, 1, is represented by

$$\mathrm{d}\mu_1 \equiv \mathrm{d}\mu_{H_2O} = -\frac{1}{C_1}\sum_{\lambda=2}^{\nu} C_\lambda \mathrm{d}\mu_\lambda. \tag{A3}$$

Substituting Eq. A3 into Eq. 4, we have Eq. 5, in which

$$\Gamma_\lambda^{(1)} = \Gamma_\lambda - \frac{C_\lambda}{C_1}\Gamma_1. \tag{A4}$$

Equation A4 gives $\Gamma_1^{(1)}=0$, which is equivalent to set the dividing plane at the definite position.

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