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The Gibbs Adsorption Equation for Aqueous Solutions Containing a Weak Base

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The Gibbs adsorption isotherm for quaternary systems of water, weak base, HCl or NaOH, and NaCl including a vapor-solution interface is expressed in terms of variations of chemical potentials of neutral components added to make up the solution. Four systems are treated, and the Gibbs convention is introduced in such a way that the surface excess of added water is zero and the surface excesses of solute components are defined. Assuming that the activity coefficients of solute components are unity, the lowering of surface tension is given in terms of variations of total molar concentrations of weak base or its hydrochloride, HCl or NaOH, and NaCl, or of pH of the solution.

Recently[1,2] we have established a general method for applying the Gibbs adsorption isotherm to aqueous solutions containing two or three electrolytic solutes, either strong or weak. So far there has been no clear cognizance for an electrolyte solution containing two kinds of electrolytic solutes to be a multicomponent system, and, when the Gibbs adsorption isotherm has been applied to an aqueous solution of an ionic surfactant and a simple salt, the lowering of surface tension of the solution has been exclusively connected with the variation of surfactant concentration alone.[3-6] We have pointed out[1,2] that such an aqueous solution must be treated as a ternary system and the lowering of surface tension should be represented as a function of variations of concentration of simple salt as well as of surfactant concentration. The application of this method to aqueous solutions of a cationic surfactant has been exemplified previously[7,8] to derive the surface excesses of various ions on the solution.

When we are concerned with aqueous solution of a weak electrolyte such as an ionic-nonionic surfactant, in the presence of a strong acid or base and a simple salt, we have to treat the solution as a quaternary system, and the lowering of its surface tension should be related to the variations of concentrations of surfactant, acid or base, and simple salt. In a previous paper[9] we have applied the method to aqueous solution of a cationic-nonionic surfactant in the presence of HCl and NaCl, in which the lowering of surface tension is expressed as a function of variations of concentrations of surfactant and NaCl, as well as of degree of neutralization instead of concentration of HCl.

In the present paper we will give a general treatment of the Gibbs adsorption isotherm applied to aqueous solution containing a weak base, HCl or NaOH, and NaCl. Following four systems of added components are considered: (I) $H_2O+D+HCl+NaCl$, (II) $H_2O+D+NaOH+NaCl$, (III) $H_2O+DHCl+HCl+NaCl$, and (IV) $H_2O+DHCl+NaOH+NaCl$, where D is a weak base capable of combining with H^+ to form a cation DH^+. Final results will be given in the form as a function of variations of molar concentrations of added components, D or DHCl, HCl or NaOH, and NaCl, or alternatively, of molar concentrations of two components, D or DHCl, and NaCl, and pH of the solution. These equations enable us to derive the surface excesses of total base ($D+DH^+$), added HCl or NaOH, and NaCl from the derivatives of surface tension with respect to concentrations of added base (D) or its hydrochloride (DHCl), and of NaCl, as well as to concentration of added HCl or NaOH, or, alternatively, to pH of the solution.

Expressions in Terms of Chemical Potentials

A plane surface of aqueous solution formed by dissolving a weak base D or its hydrochloride DHCl, strong acid HCl or alkali NaOH, and NaCl into water will be treated with reference to its surface tension at constant temperature. The plane surface forms a vapor-solution interface. Since the weak base D combines with H^+ to form a cation DH^+ in water, or DH^+ dissociates into D and H^+ in water, and water itself consists of H_2O, H^+, and OH^-, the Gibbs adsorption isotherm for the vapor-solution interface can be written in terms of chemical potentials of species

$$-\mathrm{d}\gamma = \Gamma_{H_2O}\mathrm{d}\mu_{H_2O} + \Gamma_{D}\mathrm{d}\mu_{D} + \Gamma_{H^+}\mathrm{d}\mu_{H^+} + \Gamma_{DH^+}\mathrm{d}\mu_{DH^+} + \Gamma_{Na^+}\mathrm{d}\mu_{Na^+} + \Gamma_{OH^-}\mathrm{d}\mu_{OH^-} + \Gamma_{Cl^-}\mathrm{d}\mu_{Cl^-}, \tag{1}$$

where γ is the surface tension of solution, Γ_i and μ_i are the surface excess and chemical potential of species, i. Equation 1 is subject to several conditions of equilibrium and stoichiometry. Among them, water and the weak base are in ionization equilibrium, respectively, respresented by

$$\mu_{H_2O} = \mu_{H^+} + \mu_{OH^-}, \tag{2}$$

$$\mu_{DH^+} = \mu_{D} + \mu_{H^+}. \tag{3}$$

Furthermore, stoichiometric relations hold for strong electrolytes:

$$\mu_{DHCl} = \mu_{DH^+} + \mu_{Cl^-}, \tag{4}$$

$$\mu_{HCl} = \mu_{H^+} + \mu_{Cl^-}, \tag{5a}$$

$$\mu_{NaOH} = \mu_{Na^+} + \mu_{OH^-}, \tag{5b}$$

$$\mu_{NaCl} = \mu_{Na^+} + \mu_{Cl^-}. \tag{6}$$

Equations 2 and 3, together with the electroneutrality condition among surface excesses of ionic species

$$\Gamma_{H^+} + \Gamma_{DH^+} + \Gamma_{Na^+} = \Gamma_{OH^-} + \Gamma_{Cl^-}, \tag{7}$$

reduce the number of variables in Eq. 1 from 7 to 4. Individual cases will be demonstrated below, and Eq. 1 may be represented in terms of variations of chemical potentials of four added components, *i.e.*, H_2O, D or DHCl, HCl or NaOH, and NaCl.

Since the number of variances should be 3 for the quaternary system including an interface or two phases at constant temperature, the Gibbs convention must be introduced, so that the surface excess of solvent, *i.e.*, water, may vanish. The expression of the Gibbs convention for the individual cases is not necessarily given in a comprehensive form, but it proves to represent that the total surface excess of added water counted as moles of H_2O is zero.[10)]

Thus, Eq. 1 can be completely converted into a form consisting of independent variables alone, and the lowering of surface tension is given by variations of chemical potentials of added solute components.

Expressions in Terms of Solute Concentrations

When we express the chemical potentials of added components in terms of their molar concentrations, we can obtain the Gibbs adsorption isotherm in the form given by the variations of molar concentrations of added solutes. To do this in a tractable form, we make an assumption that the solution is ideal and the activity coefficients of added solute components are unity. Let the molar concentration of added D or DHCl be C, that of added HCl or NaOH be C_A or C_B, and that of NaCl be C_S, respectively. Then the chemical potentials are given by

$$\mu_D = \mu_D{}^\circ + RT\ln C_D \tag{8a}$$

$$\mu_{DHCl} = \mu^\circ_{DHCl} + RT\ln C_{DH^+}C_{Cl^-} \tag{8b}$$

$$\mu_{HCl} = \mu^\circ_{HCl} + RT\ln C_{H^+}C_{Cl^-} \tag{9a}$$

$$\mu_{NaOH} = \mu^\circ_{NaOH} + RT\ln C_{Na^+}C_{OH^-} \tag{9b}$$

$$\mu_{NaCl} = \mu^\circ_{NaCl} + RT\ln C_{Na^+}C_{Cl^-}, \tag{10}$$

where the superfix $\circ$ refers to the standard states.

There are several restrictions among the molar concentrations of species present in the solution, C_D, C_{DH^+}, C_{H^+}, C_{Na^+}, C_{OH^-}, and C_{Cl^-}. Concentrations of counter ion, C_{Cl^-} and coion, C_{Na^+}, for the surfactant ion are given by C_A or C_B and C_S. If the ionic product of water is defined by K_w, the molar concentrations of H^+ and OH^- are mutually dependent by means of Eq. 2, *i.e.*,

$$C_{H^+}C_{OH^-} = K_W. \tag{11}$$

If the degree of ionization or protonation is α, the molar concentrations of base, in unionized and ionized forms, are given by

$$C_D = (1-\alpha)C \text{ and } C_{DH^+} = \alpha C, \tag{12}$$

and the ionization equilibrium, Eq. 3, is defined by the ionization constant

$$\frac{1-\alpha}{\alpha}C_{H^+} = K. \tag{13}$$

There is the condition of electroneutrality in bulk

$$C_{H^+} + C_{DH^+} + C_{Na^+} = C_{OH^-} + C_{Cl^-}. \tag{14}$$

Then we can obtain C_{H^+} or α as a function of C and C_A or C_B for individual cases. For this purpose, however, we have to solve a cubic equation with respect to C_{H^+} or α, which is derived by substituting Eqs. 11, 12, and 13 into Eq. 14. For the derivation of the Gibbs adsorption equation it is not necessary to have C_{H^+} or α itself but to evaluate dC_{H^+} or $d\alpha$, and, consequently, we differentiate the cubic equation with respect to C and C_A or C_B and obtain dC_{H^+} or $d\alpha$ as a function of dC and dC_A or dC_B. The function includes α explicitly, and for numerical evaluation we have to calculate it from C, C_A, or C_B, and K and K_w by solving the cubic equation.

The final form of the Gibbs adsorption isotherm is written

$$-d\gamma = RT\{\Gamma_2 d\ln C + \Gamma_X d\ln C_X + \Gamma_3 d\ln C_S\}, \tag{15}$$

where X is A for HCl and B for NaOH. It should be noted, however, that values of Γ_A and Γ_B do not imply the surface excesses of HCl and NaOH, respectively. Values of Γ_2, Γ_X, and Γ_3 can be evaluated from the derivatives of surface tension with respect to molar concentrations of added components.

Alternatively, we are often interested in assigning pH of a solution rather than giving molar concentration of HCl or NaOH added. In such cases we must express α in terms of C_{H^+} from Eq. 13 and then C_A or C_B in terms of C_{H^+} and C from the cubic equation of C_{H^+} as mentioned above.

The lowering of surface tension is then given by

$$-d\gamma = RT\{\Gamma_c d\ln C + \Gamma_h d\ln C_{H^+} + \Gamma_3 d\ln C_S\}, \tag{16}$$

where Γ_c can be obtained from the derivative of surface tension at constant pH with respect to molar concentration of the weak base or its hydrochloride, and Γ_h can be evaluated from the variation of surface tension with pH. Γ_3 is identical with that in Eq. 15.

(I) $H_2O+D+HCl+NaCl$. This system was treated previously,[9)] and a modification of the derived equations was applied to surface tension of aqueous solutions of a nonionic-cationic surfactant at different degrees of neutralization. The Gibbs convention has the form

$$\Gamma_{H_2O} + \Gamma_{OH^-} = 0, \tag{17}$$

and the Gibbs adsorption isotherm can be written as

$$-d\gamma = (\Gamma_D+\Gamma_{DH^+})d\mu_D + (\Gamma_{Cl^-}-\Gamma_{Na^+})d\mu_{HCl} + \Gamma_{Na^+}d\mu_{NaCl}. \tag{18}$$

Concentrations of counterion and coion are given by

$$C_{Cl^-} = C_A + C_S \text{ and } C_{Na^+} = C_S. \tag{19}$$

For Eq. 15 we have

$$\Gamma_2 = \left(1+\frac{\alpha^2 C}{Q_A}\right)(\Gamma_D+\Gamma_{DH^+}) - \frac{\alpha C}{Q_A}(\Gamma_{Cl^-}-\Gamma_{Na^+}), \tag{20a}$$

$$\Gamma_A = -\frac{\alpha C_A}{Q_A}(\Gamma_D+\Gamma_{DH^+}) + \left(\frac{C_A}{Q_A}+\frac{C_A}{C_A+C_S}\right)\Gamma_{Cl^-} - \frac{C_A}{Q_A}\Gamma_{Na^+}, \tag{20b}$$

$$\Gamma_3 = \frac{C_S}{C_A+C_S}\Gamma_{Cl^-} + \Gamma_{Na^+}, \tag{20c}$$

where

$$Q_A = \alpha(2-\alpha)C - C_A + 2C_{H^+} \tag{20d}$$

$$= -\alpha^2 C + C_A + 2C_{OH^-}. \tag{20e}$$

Solving Eqs. 20a,b,c we have

$$\Gamma_D + \Gamma_{DH^+} = \frac{1}{H_A}\left\{(H_A-\alpha^2 C)\Gamma_2 + \frac{\alpha C}{C_A}(C_A+2C_S)\Gamma_A - \alpha C\Gamma_3\right\}, \tag{21a}$$

$$\Gamma_{\mathrm{Cl^-}} = \frac{C_\mathrm{A}+C_\mathrm{S}}{H_\mathrm{A}}\left\{\alpha\Gamma_2 + \frac{1}{C_\mathrm{A}}(H_\mathrm{A}-C_\mathrm{A}-2C_\mathrm{S})\Gamma_\mathrm{A} + \Gamma_3\right\}, \tag{21b}$$

$$\Gamma_{\mathrm{Na^+}} = \frac{1}{H_\mathrm{A}}\left\{-\alpha C_\mathrm{S}\Gamma_2 - \frac{C_\mathrm{S}}{C_\mathrm{A}}(H_\mathrm{A}-C_\mathrm{A}-2C_\mathrm{S})\Gamma_\mathrm{A} + (H_\mathrm{A}-C_\mathrm{S})\Gamma_3\right\}, \tag{21c}$$

where

$$H_\mathrm{A} = 2\alpha C + 2C_\mathrm{S} + 2C_{\mathrm{H^+}} \tag{21d}$$

$$= 2C_\mathrm{A} + 2C_\mathrm{S} + 2C_{\mathrm{OH^-}}. \tag{21e}$$

Similarly, for Eq. 16 we have

$$\Gamma_\mathrm{c} = \Gamma_\mathrm{D} + \Gamma_{\mathrm{DH^+}} + \frac{\alpha C}{C_\mathrm{A}+C_\mathrm{S}}\Gamma_{\mathrm{Cl^-}} \tag{22a}$$

$$\Gamma_\mathrm{h} = -\alpha(\Gamma_\mathrm{D}+\Gamma_{\mathrm{DH^+}}) + \left(1+\frac{Q_\mathrm{A}}{C_\mathrm{A}+C_\mathrm{S}}\right)\Gamma_{\mathrm{Cl^-}} - \Gamma_{\mathrm{Na^+}} \tag{22b}$$

and, solving Eqs. 22 and 20c, we have

$$\Gamma_\mathrm{D} + \Gamma_{\mathrm{DH^+}} = \frac{1}{H_\mathrm{A}}\left\{(H_\mathrm{A}-\alpha^2C)\Gamma_\mathrm{c} - \alpha C(\Gamma_\mathrm{h}+\Gamma_3)\right\} \tag{23a}$$

$$\Gamma_{\mathrm{Cl^-}} = \frac{C_\mathrm{A}+C_\mathrm{S}}{H_\mathrm{A}}\{\alpha\Gamma_\mathrm{c}+\Gamma_\mathrm{h}+\Gamma_3\}, \tag{23b}$$

$$\Gamma_{\mathrm{Na^+}} = \frac{1}{H_\mathrm{A}}\{-\alpha C_\mathrm{S}\Gamma_\mathrm{c} - C_\mathrm{S}\Gamma_\mathrm{h} + (H_\mathrm{A}-C_\mathrm{S})\Gamma_3\}. \tag{23c}$$

(II) $H_2O+D+NaOH+NaCl$. In order to suppress possible ionization of weak base dissolved in water, NaOH is added to the solution. In this case the Gibbs convention for the dividing surface is expressed by

$$\Gamma_{\mathrm{H_2O}} + \Gamma_{\mathrm{H^+}} + \Gamma_{\mathrm{DH^+}} = 0, \tag{24}$$

and the Gibbs adsorption isotherm has the form

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

Concentrations of counterion and coion are given by

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

For Eq. 15 we have

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

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

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

where

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

$$= -\alpha^2C - C_\mathrm{B} + 2C_{\mathrm{OH^-}}. \tag{27e}$$

Solving Eqs. 27a,b,c we have

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

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

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

where

$$H_\mathrm{B} = 2\alpha C + 2C_\mathrm{B} + 2C_\mathrm{S} + 2C_{\mathrm{H^+}} \tag{28d}$$

$$= 2C_\mathrm{S} + 2C_{\mathrm{OH^-}}. \tag{28e}$$

Similarly, for Eq. 16 we have

$$\Gamma_\mathrm{c} = \Gamma_\mathrm{D} + \Gamma_{\mathrm{DH^+}} - \frac{\alpha C}{C_\mathrm{B}+C_\mathrm{S}}\Gamma_{\mathrm{Na^+}}, \tag{29a}$$

$$\Gamma_\mathrm{h} = -\alpha(\Gamma_\mathrm{D}+\Gamma_{\mathrm{DH^+}}) + \Gamma_{\mathrm{Cl^-}} - \left(1+\frac{Q_\mathrm{B}}{C_\mathrm{B}+C_\mathrm{S}}\right)\Gamma_{\mathrm{Na^+}}, \tag{29b}$$

and, solving Eqs. 29 and 27c, we have

$$\Gamma_\mathrm{D} + \Gamma_{\mathrm{DH^+}} = \frac{1}{H_\mathrm{B}}\{(H_\mathrm{B}-\alpha^2C)\Gamma_\mathrm{c} - \alpha C(\Gamma_\mathrm{h}+\Gamma_3)\}, \tag{30a}$$

$$\Gamma_{\mathrm{Cl^-}} = \frac{1}{H_\mathrm{B}}\{\alpha C_\mathrm{S}\Gamma_\mathrm{c} + C_\mathrm{S}\Gamma_\mathrm{h} + (H_\mathrm{B}-C_\mathrm{S})\Gamma_3\}, \tag{30b}$$

$$\Gamma_{\mathrm{Na^+}} = \frac{C_\mathrm{B}+C_\mathrm{S}}{H_\mathrm{B}}\{-\alpha\Gamma_\mathrm{c}-\Gamma_\mathrm{h}+\Gamma_3\}. \tag{30c}$$

(III) $H_2O+DHCl+HCl+NaCl$. In order to suppress possible hydrolysis of hydrochloride of weak base, HCl is added to the solution. In this case the Gibbs convention is written as

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

and the Gibbs adsorption isotherm is given by

$$-\mathrm{d}\gamma = (\Gamma_\mathrm{D}+\Gamma_{\mathrm{DH^+}})\mathrm{d}\mu_{\mathrm{DHCl}} + (\Gamma_{\mathrm{Cl^-}}-\Gamma_\mathrm{D}-\Gamma_{\mathrm{DH^+}} - \Gamma_{\mathrm{Na^+}})\mathrm{d}\mu_{\mathrm{HCl}} + \Gamma_{\mathrm{Na^+}}\mathrm{d}\mu_{\mathrm{NaCl}}. \tag{32}$$

Concentrations of counterion and coion are

$$C_{\mathrm{Cl^-}} = C + C_\mathrm{A} + C_\mathrm{S} \text{ and } C_{\mathrm{Na^+}} = C_\mathrm{S}. \tag{33}$$

For Eq. 15 we have

$$\Gamma_2 = \left(1-\frac{\alpha(1-\alpha)C}{P_\mathrm{A}}\right)(\Gamma_\mathrm{D}+\Gamma_{\mathrm{DH^+}}) + \left(\frac{(1-\alpha)C}{P_\mathrm{A}}+\frac{C}{C+C_\mathrm{A}+C_\mathrm{S}}\right)\Gamma_{\mathrm{Cl^-}} - \frac{(1-\alpha)C}{P_\mathrm{A}}\Gamma_{\mathrm{Na^+}}, \tag{34a}$$

$$\Gamma_\mathrm{A} = -\frac{\alpha C_\mathrm{A}}{P_\mathrm{A}}(\Gamma_\mathrm{D}+\Gamma_{\mathrm{DH^+}}) + \left(\frac{C_\mathrm{A}}{P_\mathrm{A}}+\frac{C_\mathrm{A}}{C+C_\mathrm{A}+C_\mathrm{S}}\right)\Gamma_{\mathrm{Cl^-}} - \frac{C_\mathrm{A}}{P_\mathrm{A}}\Gamma_{\mathrm{Na^+}}, \tag{34b}$$

$$\Gamma_3 = \frac{C_\mathrm{S}}{C+C_\mathrm{A}+C_\mathrm{S}}\Gamma_{\mathrm{Cl^-}} + \Gamma_{\mathrm{Na^+}}, \tag{34c}$$

where

$$P_\mathrm{A} = -(1-\alpha)^2C - C_\mathrm{A} + 2C_{\mathrm{H^+}}, \tag{34d}$$

$$= (1-\alpha^2)C + C_\mathrm{A} + 2C_{\mathrm{OH^-}}. \tag{34e}$$

Solving Eqs. 34a,b,c, we have

$$\Gamma_\mathrm{D} + \Gamma_{\mathrm{DH^+}} = \frac{1}{Z_\mathrm{A}}\left\{(Z_\mathrm{A}-\alpha^2C)\Gamma_2 - \frac{C}{C_\mathrm{A}}[Z_\mathrm{A}-(1+\alpha)(\alpha C+C_\mathrm{S})-\alpha C_\mathrm{A}]\Gamma_\mathrm{A}-\alpha C\Gamma_3\right\}, \tag{35a}$$

$$\begin{aligned}\Gamma_{\mathrm{Cl^-}} = \frac{C+C_{\mathrm{A}}+C_{\mathrm{S}}}{Z_{\mathrm{A}}}\Big\{\alpha\Gamma_2 + \frac{1}{C_{\mathrm{A}}} \\ \times[Z_{\mathrm{A}}-(1+\alpha)C-C_{\mathrm{A}}-2C_{\mathrm{S}}]\Gamma_{\mathrm{A}} + \Gamma_3\Big\},\end{aligned} \tag{35b}$$

$$\begin{aligned}\Gamma_{\mathrm{Na^+}} = \frac{1}{Z_{\mathrm{A}}}\Big\{-\alpha C_{\mathrm{S}}\Gamma_2 - \frac{C_{\mathrm{S}}}{C_{\mathrm{A}}}[Z_{\mathrm{A}}-(1+\alpha)C-C_{\mathrm{A}} \\ -2C_{\mathrm{S}}]\Gamma_{\mathrm{A}}+(Z_{\mathrm{A}}-C_{\mathrm{S}})\Gamma_3\Big\},\end{aligned} \tag{35c}$$

where

$$Z_{\mathrm{A}} = 2\alpha C + 2C_{\mathrm{S}} + 2C_{\mathrm{H^+}} \tag{35d}$$

$$= 2C + 2C_{\mathrm{A}} + 2C_{\mathrm{S}} + 2C_{\mathrm{OH^-}}. \tag{35e}$$

Similarly, for Eq. 16 we have

$$\Gamma_{\mathrm{c}} = \Gamma_{\mathrm{D}} + \Gamma_{\mathrm{DH^+}} + \frac{\alpha C}{C+C_{\mathrm{A}}+C_{\mathrm{S}}}\Gamma_{\mathrm{Cl^-}}, \tag{36a}$$

$$\begin{aligned}\Gamma_{\mathrm{h}} = -\alpha(\Gamma_{\mathrm{D}}+\Gamma_{\mathrm{DH^+}}) \\ +\left(1+\frac{P_{\mathrm{A}}}{C+C_{\mathrm{A}}+C_{\mathrm{S}}}\right)\Gamma_{\mathrm{Cl^-}} - \Gamma_{\mathrm{Na^+}},\end{aligned} \tag{36b}$$

and, solving Eqs. 36 and 35c, we have

$$\Gamma_{\mathrm{D}} + \Gamma_{\mathrm{DH^+}} = \frac{1}{Z_{\mathrm{A}}}\{(Z_{\mathrm{A}}-\alpha^2C)\Gamma_{\mathrm{c}} - \alpha C(\Gamma_{\mathrm{h}}+\Gamma_3)\}, \tag{37a}$$

$$\Gamma_{\mathrm{Cl^-}} = \frac{C+C_{\mathrm{A}}+C_{\mathrm{S}}}{Z_{\mathrm{A}}}(\alpha\Gamma_{\mathrm{c}}+\Gamma_{\mathrm{h}}+\Gamma_3), \tag{37b}$$

$$\Gamma_{\mathrm{Na^+}} = \frac{1}{Z_{\mathrm{A}}}\{-\alpha C_{\mathrm{S}}\Gamma_{\mathrm{c}} - C_{\mathrm{S}}\Gamma_{\mathrm{h}} + (Z_{\mathrm{A}}-C_{\mathrm{S}})\Gamma_3\}. \tag{37c}$$

(IV) $H_2O+DHCl+NaOH+NaCl$. The Gibbs dividing surface is set in such a way that

$$\Gamma_{\mathrm{H_2O}} + \Gamma_{\mathrm{H^+}} - \Gamma_{\mathrm{D}} = 0, \tag{38}$$

and the Gibbs adsorption isotherm is written as

$$\begin{aligned}-\mathrm{d}\gamma = (\Gamma_{\mathrm{D}}+\Gamma_{\mathrm{DH^+}})\mathrm{d}\mu_{\mathrm{DHCl}} + (\Gamma_{\mathrm{D}}+\Gamma_{\mathrm{DH^+}}+\Gamma_{\mathrm{Na^+}} \\ -\Gamma_{\mathrm{Cl^-}})\mathrm{d}\mu_{\mathrm{NaOH}} + (\Gamma_{\mathrm{Cl^-}}-\Gamma_{\mathrm{D}}-\Gamma_{\mathrm{DH^+}})\mathrm{d}\mu_{\mathrm{NaCl}}.\end{aligned} \tag{39}$$

Concentrations of counterion and coion are given by

$$C_{\mathrm{Cl^-}} = C + C_{\mathrm{S}} \text{ and } C_{\mathrm{Na^+}} = C_{\mathrm{B}} + C_{\mathrm{S}}. \tag{40}$$

For Eq. 15 we have

$$\begin{aligned}\Gamma_2 = \left(1-\frac{\alpha(1-\alpha)C}{P_{\mathrm{B}}}\right)(\Gamma_{\mathrm{D}}+\Gamma_{\mathrm{DH^+}}) \\ +\left(\frac{(1-\alpha)C}{P_{\mathrm{B}}}+\frac{C}{C+C_{\mathrm{S}}}\right)\Gamma_{\mathrm{Cl^-}} - \frac{(1-\alpha)C}{P_{\mathrm{B}}}\Gamma_{\mathrm{Na^+}},\end{aligned} \tag{41a}$$

$$\begin{aligned}\Gamma_{\mathrm{B}} = \frac{\alpha C_{\mathrm{B}}}{P_{\mathrm{B}}}(\Gamma_{\mathrm{D}}+\Gamma_{\mathrm{DH^+}}) - \frac{C_{\mathrm{B}}}{P_{\mathrm{B}}}\Gamma_{\mathrm{Cl^-}} \\ +\left(\frac{C_{\mathrm{B}}}{P_{\mathrm{B}}}+\frac{C_{\mathrm{B}}}{C_{\mathrm{B}}+C_{\mathrm{S}}}\right)\Gamma_{\mathrm{Na^+}},\end{aligned} \tag{41b}$$

$$\Gamma_3 = \frac{C_{\mathrm{S}}}{C+C_{\mathrm{S}}}\Gamma_{\mathrm{Cl^-}} + \frac{C_{\mathrm{S}}}{C_{\mathrm{B}}+C_{\mathrm{S}}}\Gamma_{\mathrm{Na^+}}, \tag{41c}$$

where

$$P_{\mathrm{B}} = -(1-\alpha)^2C + C_{\mathrm{B}} + 2C_{\mathrm{H^+}} \tag{41d}$$

$$= (1-\alpha^2)C - C_{\mathrm{B}} + 2C_{\mathrm{OH^-}}. \tag{41e}$$

Solving Eqs. 41a,b,c we have

$$\begin{aligned}\Gamma_{\mathrm{D}} + \Gamma_{\mathrm{DH^+}} = \frac{1}{Z_{\mathrm{B}}}\Big\{(Z_{\mathrm{B}}-\alpha^2C)\Gamma_2 \\ + \frac{C}{C_{\mathrm{B}}}[Z_{\mathrm{B}}-(1+\alpha^2)C-\alpha C_{\mathrm{B}}-(1+\alpha)C_{\mathrm{S}}]\Gamma_{\mathrm{B}} \\ - \frac{C}{C_{\mathrm{S}}}[Z_{\mathrm{B}}-\alpha(1+\alpha)C-\alpha C_{\mathrm{S}}]\Gamma_3\Big\},\end{aligned} \tag{42a}$$

$$\begin{aligned}\Gamma_{\mathrm{Cl^-}} = \frac{C+C_{\mathrm{S}}}{Z_{\mathrm{B}}}\Big\{\alpha\Gamma_2 - \frac{1}{C_{\mathrm{B}}}[Z_{\mathrm{B}}-(1+\alpha)C-C_{\mathrm{B}}-2C_{\mathrm{S}}]\Gamma_{\mathrm{B}} \\ + \frac{1}{C_{\mathrm{S}}}[Z_{\mathrm{B}}-(1+\alpha)C+C_{\mathrm{S}}]\Gamma_3\Big\},\end{aligned} \tag{42b}$$

$$\begin{aligned}\Gamma_{\mathrm{Na^+}} = \frac{C_{\mathrm{B}}+C_{\mathrm{S}}}{Z_{\mathrm{B}}}\Big\{-\alpha\Gamma_2 \\ + \frac{1}{C_{\mathrm{B}}}[Z_{\mathrm{B}}-(1+\alpha)C-C_{\mathrm{B}}-2C_{\mathrm{S}}]\Gamma_{\mathrm{B}} \\ + \frac{1}{C_{\mathrm{S}}}[(1+\alpha)C+C_{\mathrm{S}}]\Gamma_3\Big\},\end{aligned} \tag{42c}$$

where

$$Z_{\mathrm{B}} = 2\alpha C + 2C_{\mathrm{B}} + 2C_{\mathrm{S}} + 2C_{\mathrm{H^+}}, \tag{42d}$$

$$= 2C + 2C_{\mathrm{S}} + 2C_{\mathrm{OH^-}}. \tag{42e}$$

Similarly, for Eq. 16 we have

$$\Gamma_{\mathrm{c}} = \Gamma_{\mathrm{D}} + \Gamma_{\mathrm{DH^+}} + \frac{C}{C+C_{\mathrm{S}}}\Gamma_{\mathrm{Cl^-}} + \frac{(1-\alpha)C}{C_{\mathrm{B}}+C_{\mathrm{S}}}\Gamma_{\mathrm{Na^+}}, \tag{43a}$$

$$\Gamma_{\mathrm{h}} = -\alpha(\Gamma_{\mathrm{D}}+\Gamma_{\mathrm{DH^+}}) + \Gamma_{\mathrm{Cl^-}} - \left(1+\frac{P_{\mathrm{B}}}{C_{\mathrm{B}}+C_{\mathrm{S}}}\right)\Gamma_{\mathrm{Na^+}} \tag{43b}$$

and, solving Eqs. 43 and 41c, we have

$$\begin{aligned}\Gamma_{\mathrm{D}} + \Gamma_{\mathrm{DH^+}} = \frac{1}{Z_{\mathrm{B}}}\Big\{(Z_{\mathrm{B}}-\alpha^2C)\Gamma_{\mathrm{c}} - \alpha C\Gamma_{\mathrm{h}} \\ - \frac{C}{C_{\mathrm{S}}}[Z_{\mathrm{B}}-\alpha(1+\alpha)C-\alpha C_{\mathrm{S}}]\Gamma_3\Big\},\end{aligned} \tag{44a}$$

$$\begin{aligned}\Gamma_{\mathrm{Cl^-}} = \frac{C+C_{\mathrm{S}}}{Z_{\mathrm{B}}}\Big\{\alpha\Gamma_{\mathrm{c}} + \Gamma_{\mathrm{h}} \\ + \frac{1}{C_{\mathrm{S}}}[Z_{\mathrm{B}}-(1+\alpha)C-C_{\mathrm{B}}]\Gamma_3\Big\},\end{aligned} \tag{44b}$$

$$\begin{aligned}\Gamma_{\mathrm{Na^+}} = \frac{C_{\mathrm{B}}+C_{\mathrm{S}}}{Z_{\mathrm{B}}}\Big\{-\alpha\Gamma_{\mathrm{c}} - \Gamma_{\mathrm{h}} \\ + \frac{1}{C_{\mathrm{S}}}[(1+\alpha)C+C_{\mathrm{S}}]\Gamma_3\Big\}.\end{aligned} \tag{44c}$$

Discussion

As was pointed out previously,[1,2] it has been shown that the Gibbs adsorption isotherm can be expressed in either of two forms, *i.e.*, in terms of variations of chemical potentials of constituents of two types, for an electrolyte solution. One is based on the ionic and nonionic species present in the solution, as given by Eq. 1, and the other is based on the neutral components added to make up the solution. The former expression is subject to various restrictions such as the ionic equilibria, Eqs. 2 and 3, and the stoichiometry, Eqs. 4—7, among different species, while the latter is free from such restrictions, except for setting the position of dividing surface. It was demonstrated that both expressions are equivalent and the dividing surface should be carefully drawn only after the latter expression has been obtained. The Gibbs convention is then expressed by Eq. 17, 24, 31, or 38, as is also illustrated in the expression for the Gibbs-Duhem equation.[10] As a result, the Gibbs adsorption isotherm is expressed in the form of Eqs. 18, 25, 32, or 39 by the variations of chemical potentials of all the solute components added and their surface excesses can be defined uniquely.

There has been a prevailing superstition that the Gibbs adsorption isotherm should be written down in terms of chemical potentials of ionic and nonionic species present in the solution, since Guggenheim[11] gave it exclusively in this expression. Furthermore, this expression has often lead to an erroneous expression for the Gibbs convention in the cases containing weak electrolytes or attending hydrolysis of salts, because the ionization of water itself has been overlooked.[3,11,12]

After introducing the correct Gibbs convention, we can proceed to convert the chemical potentials of solute components into their (molar) concentrations, by relying on some approximations. In the present work we have made an approximation that the activity coefficients of all the solute components are unity. Even in this approximation, the calculation is intricate. After a straightforward calculation, the lowering of surface tension is expressed in terms of variations of concentrations of added components, or of pH of solution, as given by Eq. 15 or 16. Then we can readily derive the surface excesses of three species, *i.e.*, $D+DH^+$, Cl^-, and Na^+, as functions of three experimentally measurable quantities, Γ_2, Γ_x, and Γ_3, or Γ_c, Γ_h, and Γ_3. For the actual calculation we may usually neglect C_{H^+} or C_{OH^-} in the final equations.

It is not possible to separate the surface excess of DH^+ from that of D, nor to derive the surface excesses of H^+ and OH^-, as far as only measurements of surface tension are performed.

As special cases we will now derive expressions for ternary systems without added HCl or NaOH. Two systems, (I) and (II), reduce to $H_2O+D+NaCl$, and we put $C_x=0$ and $\Gamma_{Cl^-}=\Gamma_{Na^+}$. Then we have

$$\Gamma_D + \Gamma_{DH^+} = \left(1-\frac{\alpha^2 C}{2C_{OH^-}}\right)\Gamma_2, \tag{45a}$$

$$\Gamma_{Cl^-} = \Gamma_{Na^+} = \frac{1}{2}\Gamma_3. \tag{45b}$$

Similarly, two other systems, (III) and (IV), reduce to $H_2O+DHCl+NaCl$, and we put $C_x=0$. Since the surface excess of total added hydrochloride should be equal to that of Cl^- not originating from added NaCl, we have $\Gamma_D+\Gamma_{DH^+}=\Gamma_{Cl^-}-\Gamma_{Na^+}$. Then we obtain

$$\Gamma_D + \Gamma_{DH^+} = \frac{P}{Y}\{(C+2C_S)\Gamma_2 - C\Gamma_3\} \tag{46a}$$

$$\Gamma_{Cl^-} = \frac{C+C_S}{Y}\{P\Gamma_2 + 2C_{H^+}\Gamma_3\} \tag{46b}$$

$$\Gamma_{Na^+} = \frac{1}{Y}\{C_S P\Gamma_2 + 2(C+C_S)C_{H^+}\Gamma_3\}, \tag{46c}$$

where

$$P = -(1-\alpha)^2 C + 2C_{H^+} = (1-\alpha^2)C + 2C_{OH^-} \tag{46d}$$

$$\begin{aligned} Y &= -(1-\alpha)^2 C^2 + 4(C+C_S)C_{H^+} \\ &= 2(1-\alpha^2)C(C+2C_S) + 4(C+C_S)C_{OH^-}. \end{aligned} \tag{46e}$$

Finally we will suggest that formal conversion is possible from the quaternary systems containing a weak base treated in this paper to those of a weak acid treated in a previous paper,[1] when $\Gamma_{HD}+\Gamma_{D^-}$ is substituted for $\Gamma_D+\Gamma_{DH^+}$, and Γ_{Cl^-} and Γ_{Na^+} are exchanged, in the equations cited below.

Equations, 20a,b,c, 21a,b,c, 22, and 23 hold for (I′) $H_2O+HD+NaOH+NaCl$, if C_A and C_{H^+} in Eqs. 20d and 21d are replaced by C_B and C_{OH^-}, respectively. Similarly, Eqs. 27a,b,c, 28a, b, c, 29, and 30 are valid for (II′) $H_2O+HD+HCl+NaCl$, if C_B and C_{H^+} in Eqs. 27d and 28d are replaced by C_A and C_{OH^-}, respectively.

Equations 34a,b,c, 35a,b,c 36, and 37 hold for (III′) $H_2O+NaD+NaOH+NaCl$, if C_A and C_{OH^-} in Eqs. 34e and 35e are replaced by C_B and C_{H^+}, respectively. Similarly, Eqs. 41a,b,c, 42a,b,c, 43, and 44 are valid for (IV′) $H_2O+NaD+HCl+NaCl$, if C_B and C_{OH^-} in Eqs. 41e and 42e are replaced by C_A and C_{H^+}, respectively.

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