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A Generalized Scale of Free Energy of Excess Adsorption of Solute and Absolute Composition of the Interfacial Phase[†]

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Moles of a surfactant ($\Gamma_2{}^1$) absorbed per unit area of the solid−liquid interface estimated analytically from the difference of the solute molality in the bulk phase before and after adsorption have been quantitatively related to the absolute compositions Δn_1 and Δn_2 of the solvent and solute forming the inhomogeneous surface phase in contact with the bulk phase of homogeneous composition. By use of isopiestic experiments, negative values of $\Gamma_2{}^1$ for the adsorption of inorganic salts onto a solid−liquid interface have been calculated in the same manner. From the linear plot of $\Gamma_2{}^1$ versus the ratio of the bulk mole fractions of the solute and solvent, values of Δn_1 and Δn_2 have been evaluated under a limited range of concentrations. For the adsorption of the surfactant and the inorganic salt respectively onto the fluid interface, $\Gamma_2{}^1$ values have been evaluated from the surface tension concentration data using the Gibbs adsorption equation. $\Gamma_2{}^1$ based on the arbitrary placement of the Gibbs dividing plane near the fluid interface is quantitatively related to the composition of the inhomogeneous surface phase. Also, the Gibbs equation for multicomponent solutions has been appropriately expressed in terms of a suitably derived coefficient m. Integrating the Gibbs adsorption equation for a multicomponent system, the standard free energy change, $\Delta G°$, per unit of surface area as a result of the maximum adsorption $\Gamma_2{}^m$ of the surfactant at fluid interfaces due to the change of the activity a_2 of the surfactant in the bulk from zero to unity have been calculated. A similar procedure has been followed for the calculation of $\Delta G°$ for the surfactant adsorption at solid−liquid interfaces using thermodynamically derived equations. $\Delta G°$ values for surfactant adsorption for all such systems are found to be negative. General expressions of $\Delta G°$ for negative adsorption of the salt on fluid and solid−liquid interfaces respectively have also been derived on thermodynamic grounds. $\Delta G°$ for all such systems are positive due to the excess spontaneous hydration of the interfacial phase in the presence of inorganic salt. Negative and positive values of $\Delta G°$ for excess surfactant and salt adsorption respectively have been discussed in light of a generalized scale of free energy of adsorption.

When adsorption of a solute occurs from a solution phase onto a solid−liquid or fluid interface, adsorbate molecules compete against solvent molecules of water to occupy its position in the interfacial region. As a result of this, relative adsorption of the solute may become positive, zero, or negative.[1] Kipling[1] reviewed early extensive works on adsorption from solution of nonelectrolytes at various types of solid−liquid interfaces. Composite adsorption isotherms[1,2] of completely miscible liquids by powdered solids have been presented by Kipling et al.,[1,2] Schay and coworkers,[3−5] and others, and many interesting conclusions on the physical nature of the process for relative adsorption have been made. A useful discussion on the different definitions and terminology of adsorption has been presented by Brown and Everett.[6]

Extensive reviews[7] on the adsorption of small molecules and ions, miscible liquid mixtures, and surfactants have been presented by Parfitt et al., Lane, Clunie et al., Hough et al., and Lyklema two decades ago.[7] Many features of adsorption of cationic and anionic surfactants by different types of powdered solid particles have been extensively studied in the last few decades as functions of various physicochemical parameters at bulk surfactant concentrations below and above the critical micelle concentration (cmc) and mechanisms for adsorption interactions on charged interfaces have been discussed elaborately by different workers.[7−23]

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Using the basic principles of chemical thermodynamics, Willard Gibbs[24] derived his elegant equation for adsorption or relative surface excess of a component from the bulk solution to the interface. In this treatment, the surface phase is separated by placement of the imaginary Gibbs dividing plane at an arbitrary position of the liquid column containing inhomogeneous surface phase. Subsequently the concept of the surface excess as well as basic ideas involved in the treatment of Gibbs have been critically examined by Guggenheim,[25] Hansen,[26] Motomura,[27] Fowkes,[28] Goodrich,[29] Rusanov,[30] Prigogine and Defay,[31] and Chattoraj,[32,33] and many alternative and quantitative proposals have been made. The surface excesses of cationic and anionic surfactants for multicomponent fluid systems have been calculated using appropriate forms of the Gibbs adsorption equations in both the presence and absence of excess neutral salt.[33−43]

Recently the increase of surface tension of water by the addition of inorganic salts has been related to the amounts of adsorbed water layer present at the interfacial region in contact with the bulk solution of electrolytes.[44−49] Attempts have been made to calculate extents of negative adsorption of electrolytes at different fluid interfaces using appropriate forms of the Gibbs adsorption equations. Using the Gibbs adsorption equation and analogous thermodynamic treatment, Matubayasi et al.[47,48] have measured temperature coefficients of the surface tension of water in the presence of different inorganic salts. Using the thermodynamic treatment of Motomura et al.,[49] they have calculated thermodynamic parameters related to surface formation. Negative adsorption of inorganic salts from aqueous solution to powdered solids,[50,51] proteins,[52] and lipids[53] have been measured recently using the isopiestic vapor pressure technique. Earlier, Lyklema[7] estimated negative adsorption of inorganic ions on a solid surface by using an electrochemical technique.

On the basis of the Traube's[54] rule, Langmuir,[56] was able to calculate the standard free energy change per CH_2 group for the transfer of a homologous series of fatty acids from the solution onto the air−water interface. Ward[57] discussed different conformational and orientation factors of the adsorbed solute molecules in the light of the validity of Traube's rule. On the basis of the concept of monolayer adsorption of gases on solid interface, Langmuir[55,56] presented his equation for adsorption of a surface-active solute in a most convenient form. Following this concept, Langmuir equations for solute adsorption at solid−liquid and fluid interfaces for fixed and mobile monolayers[58−60] at the interfacial region have been derived. By use of these equations in linear form, the free energy of adsorption of surface-active solutes expressed in kilojules per mole of solute transferred from the bulk to the surface have been determined by many workers.[58−60] An important limitation of the determination of the free energy of adsorption by the Langmuir approach lies in the fact that the experimental data are expected to fit a linear form of the Langmuir equations for fixed and mobile neutral monolayers only. The Langmuir equation is not strictly valid for the charged monolayer and modified equations, for it has been found to obey experimental data only with limited success.[33,61] Further, for the negative adsorption of a solute, the Langmuir equation cannot be used for the calculation of free energy of adsorption.

When the adsorption of solute such as dyes on a solid−liquid surface fit the linear plot of the Langmuir equation, standard free energies of adsorption[8] and related thermodynamic parameters can be evaluated. Everett et al.[62] have extended the Langmuir treatment by incorporating the concept of surface activity coefficient. Attempts have also been made to calculate free energy of adsorption from the ratio of the concentrations of the solute present in the bulk phase and interfacial phase of certain assumed thickness.[63,64]

On the basis of thermodynamics, Bull[65,66] has used an integrated form of the Gibbs adsorption equation for the

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calculation of the standard free energy of proteins adsorbed at the glass–water interface. Rosen[67] has used a similar approach for the calculation of the standard free energy of adsorption of surface-active solutes at different types of fluid interfaces.

In the present paper, using the relevant data on the relative adsorption of solute and solvent on various types of solid–liquid and fluid interfaces, we shall make an attempt to quantitatively relate the surface excesses of solute and solvent with the absolute compositions of the solute and solvent present in the inhomogeneous interfacial phase. Chattoraj et al. have presented the experimental data used in the present treatment in the last three decades. For the fluid interface, an attempt will be made to derive a unique relation between the absolute compositions of interfacial phase and the Gibbs surface excess quantities based the placement of the imaginary Gibbs dividing plane near the interfacial region. Attempt will also be made to calculate the standard free energy change for the adsorption of surfactants and inorganic salts respectively from the bulk aqueous solution onto the fluid interface using the integrated forms of the Gibbs adsorption equations for multicomponent solution. Attempt will also be made to develop a thermodynamic scale for the free energy of adsorption for comparison of relative positive and negative affinities of solute for different fluid surfaces. We shall also extend this thermodynamic treatment for the calculation of the standard free energy change for the adsorption of the solute at a solid–liquid interface.

Adsorption at a Solid–Liquid Interface

For the actual measurement of the extent of relative adsorption of a surface-active solute by a solution depletion method,[68,69] a definite amount (ω_1) of an aqueous solvent containing a surfactant of molal concentration $m_2{}^t$ is taken in a stoppered bottle. A definite weight (ω_s) of a powdered solid of known specific surface area is added to this solution, and the system in the stoppered bottle is shaken for 24 h or more when a state of adsorption equilibrium is reached. On standing for 6 h or more, the particles settle down and the solution from the top has been centrifuged. The equilibrium molal concentration (m_2) of the surfactant is estimated by a suitable analytical technique. Moles $\Gamma_2{}^1$ of a solute adsorbed per square meter (or kg) of the solid particles can be calculated using eq 1.

$$\Gamma_2{}^1 = \frac{W_1{}^t(m_2{}^t - m_2)}{1000} \tag{1}$$

$W_1{}^t$ (equal to $\omega_1/\omega_{s.A}$) in this equation stands for the weight of the solvent in grams per square meter (or per kg) of the solid surface. A stands for the specific surface area of the solid determined from a separate experiment. We shall refer to components 1 and 2 as solvent and solute present in the system, respectively. The superscript in $\Gamma_2{}^1$ indicates that the uptake of the solvent by the solid powder is arbitrarily taken as zero.

For the dilute solution of a surfactant having strong affinity for the surface, $m_2{}^t$ and m_2 may be conveniently replaced by $C_2{}^t$ and C_2 of the surfactant before and after adsorption, respectively. Equation 1 will now assume the form

$$\Gamma_2{}^1 = \frac{V^t(C_2{}^t - C_2)}{1000} \tag{2}$$

Here V^t, equal to $W_1{}^t$, stands for the total volume of the dilute solution in milliliters associated per square meter (or per kilogram) of the powdered solid.

In eq 1, $m_2{}^t$, m_2, and $W_1{}^t$ all expressed in cgs units can be replaced by $1000n_2{}^t/M_1n_1{}^t$, $1000n_2/M_1n_2$, and $n_1{}^tM_1$, respectively. Here $n_2{}^t$ and n_2 are moles of solute in the bulk phase before and after adsorption. Similarly $n_1{}^t$ and n_1 are moles of solvent in bulk before and after adsorption. Putting all these in eq 1

$$\Gamma_2{}^1 = n_2{}^t - n_1{}^t\frac{n_2}{n_1} \tag{3}$$

Also

$$\frac{n_2}{n_1} = \frac{X_2}{X_1} = \frac{m_2}{55.5} \approx \frac{C_2}{55.5} \tag{4}$$

Here X_1 and X_2 represent the mole fractions of the solvent and the solute, respectively, present in the free bulk (supernate) phase at adsorption equilibrium. Equation 3 can be also written in the form

$$n_1{}^t - n_2{}^t\frac{n_1}{n_2} = -\Gamma_2{}^1\frac{n_1}{n_2} = \Gamma_1{}^2 \tag{5}$$

The left-hand expression has been put as $\Gamma_1{}^2$, the relative surface excess of solvent per unit area (or per kg) of the powdered solid. Combining eq 4 with relations 3 and 5, we can write

$$\Gamma_2{}^1 = n_2{}^t - n_1{}^t\frac{X_2}{X_1} \tag{6}$$

$$\Gamma_1{}^2 = n_1{}^t - n_2{}^t\frac{X_1}{X_2} \tag{7}$$

and

$$\Gamma_1{}^2X_2 + \Gamma_2{}^1X_1 = 0 \tag{8}$$

Relation 8 indicates that the values of $\Gamma_2{}^1$ and $\Gamma_1{}^2$ are not independent but are related to each other. If at a fixed value of X_2/X_1 (or $m_2/55.5$), the value of $\Gamma_2{}^1$ determined from an experiment is positive and the value of $\Gamma_1{}^2$ becomes fixed and negative in sign or vice versa. For the adsorption of a binary mixture of completely soluble liquids, this equation has been derived and used by Schay et al.[3–5] and others[1] for the study adsorption on the surface of different solid powders. They have also shown that $\Gamma_1{}^2X_2$ and $\Gamma_2{}^1X_1$ are equal to the extents of apparent adsorption $\Gamma_1{}^n$ and $\Gamma_2{}^n$ of components 1 and 2, respectively. The apparent adsorption of a component can be defined in terms of the mole fraction difference of a component in the mixture measured before and after adsorption by solid. For dilute solution, X_1 tends to unity so that $\Gamma_2{}^n \cong \Gamma_2{}^1$.

Interfacial Phase

Let us now assume that the surface of a dry solid is separated from a binary solution at adsorption equilibrium. The solute present in the solution may be nonelec-

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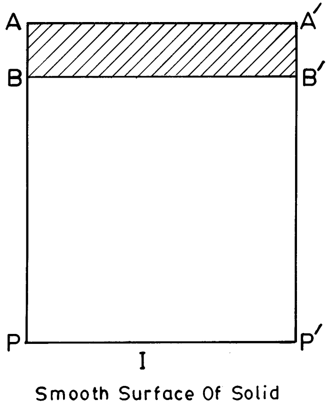

Figure 1. Solid−liquid systems with a highly polished surface plane.

trolyte or electrolyte. If the surface of a thin solid plate is highly polished, the surface plane AA′ of unit area will be smooth (Figure 1) and it is attached with the inhomogeneous surface phase AA′ BB′. The inhomogeneous surface phase may be imagined to be separated from the homogeneous bulk phase by plane BB′. Both the surface phase AA′BB′ and the bulk phase BB′PP′ contain binary solvent component 1 and solute component 2, respectively. We now assume that the bulk phase composed of n_1 and n_2 moles of solvent and solute components respectively may be divided into k number of layers parallel to AA′ so that

$$n_1 = n_1^a + n_1^b + n_1^c + \ldots n_1^k \tag{9}$$

$$n_2 = n_2^a + n_2^b + n_2^c + \ldots n_2^k \tag{10}$$

Here a, b, c, ..., k are assigned for each of these thin bulk layers. Since the composition of the bulk phase is uniform and homogeneous

$$\frac{n_2}{n_1} = \frac{n_2^a}{n_1^a} = \frac{n_2^b}{n_1^b} = \ldots = \frac{n_2^k}{n_1^k} \tag{11}$$

In contrast to the uniformly homogeneous nature of the bulk phase, the surface phase AA′BB′ containing Δn_1 and Δn_2 moles of solvent and solute, respectively, must be inhomogeneous because of the presence of the unbalanced interfacial forces present in this region. If this inhomogeneous region is imagined to be made of σ number of microscopically homogeneous layers α, β, γ, ..., σ, then

$$\Delta n_1 = \Delta n_1^\alpha + \Delta n_1^\beta + \ldots \Delta n_1^\sigma \tag{12}$$

$$\Delta n_2 = \Delta n_2^\alpha + \Delta n_2^\beta + \ldots \Delta n_2^\sigma \tag{13}$$

Δn_1^σ and Δn_2^σ moles of components 1 and 2 are present in the σth layer and so on.

Since overall surface phase is inhomogeneous

$$\frac{\Delta n_2}{\Delta n_1} \neq \frac{\Delta n_2^\alpha}{\Delta n_1^\alpha} \neq \frac{\Delta n_2^\beta}{\Delta n_1^\beta} \neq \ldots \neq \frac{\Delta n_2^\sigma}{\Delta n_1^\sigma} \tag{14}$$

Further, due to the existence of interfacial forces operative in the surface phase AA′BB′, $\Delta n_2/\Delta n_1$ (and also $\Delta n_2^\sigma/\Delta n_1^\sigma$) will not be equal to the ratio n_2/n_1 valid for the homogeneous bulk phase (except at the surface azeotropic state). Degree of inhomogenity of the surface region will be further enhanced if the polished surface plane is replaced by mildly rough or extensively rough solid surface of unit surface area. This roughness will affect significantly the number of k and σ layers in the bulk and surface phases, but eqs 9 to 13 will remain valid for each system even in this altered situation.

We shall now write eqs 15 and 16 for the whole system

$$n_1^t = \Delta n_1 + n_1 \tag{15}$$

$$n_2^t = \Delta n_2 + n_2 \tag{16}$$

Combining relations 9, 10, 15, and 16

$$n_1^t = \Delta n_1 + \sum_{k=a}^{k} n_1^k \tag{17}$$

$$n_2^t = \Delta n_2 + \sum_{k=a}^{k} n_2^k \tag{18}$$

Inserting these values of n_1^t and n_2^t in eq 3

$$\Gamma_2^1 = \left(\Delta n_2 - \Delta n_1 \frac{n_2}{n_1}\right) + \sum_{k=a}^{k} \left(n_2^k - n_1^k \frac{n_2}{n_1}\right) \tag{19}$$

According to eq 11, $(n_2/n_1)n_1^k$ is equal to n_2^k so that relation finally assumes the form

$$\begin{aligned} \Gamma_2^1 &= \Delta n_2 - \Delta n_1 \frac{n_2}{n_1} \\ &= \Delta n_2 - \Delta n_1 \frac{X_2}{X_1} \end{aligned} \tag{20}$$

valid only for the inhomogeneous surface phase in contact with the bulk phase. In the absence of the surface phase, Δn_1, Δn_2, and Γ_2^1 will be zero. At a surface azeotropic state occurring at a critical value of m_2, different values of Δn_1^σ and Δn_2^σ for different surface layers will be different but sum total values $\Delta n_2/\Delta n_1$ will be equal to n_2/n_1 only at a particular value of m_2.

Similarly it can be shown that

$$\begin{aligned} \Gamma_1^2 &= \Delta n_1 - \Delta n_2 \frac{n_1}{n_2} \\ &= \Delta n_1 - \Delta n_2 \frac{X_1}{X_2} \end{aligned} \tag{21}$$

For many binary liquid mixtures, Schay et al.[3−5] assumed that the surface phase is a monolayer formed by the adsorption of two liquid components. Introducing this monolayer concept in the composite adsorption equations, these workers have evaluated individual amounts of liquid components present per unit area of the adsorbed layer. Kipling et al.[1] have indicated that the general assumption of the monolayer model is arbitrary and incorrect for many systems. Such a monolayer model for the interfacial phase has not been included in the present treatment and the only assumption is that the surface phase is inhomogeneous and the bulk phase is homogeneous. It will be shown later on that such division is fully consistent with the concept of the Gibbs surface excess used for the adsorption of a solute at a fluid interface.

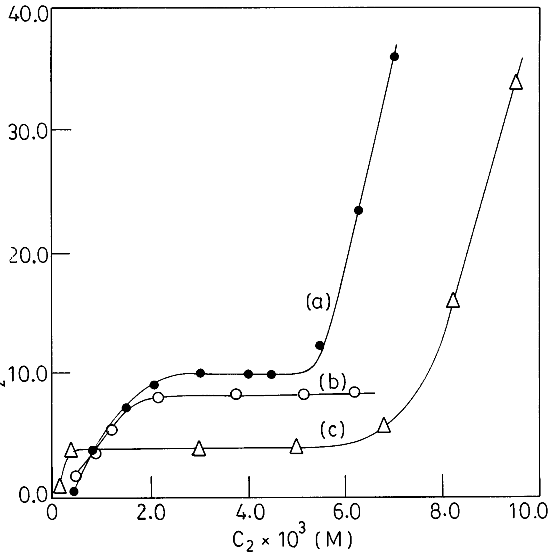

Figure 2. Plot of Γ_2^1 vs C_2 for adsorption of SDS at alumina surface:[16] (a) pH 6.0, $\mu = 0.125$, 36 °C; (b) pH 6.0, $\mu = 0.0625$, 28 °C; (c) pH 4.0, $\mu = 0.125$, 28 °C.

Equation 20 can be written in the form

$$\Gamma_2^1 = \Delta n_2\left(1 - \frac{n_2/n_1}{\Delta n_2/\Delta n_1}\right) = \Delta n_2\left(1 - \frac{m_2}{m_2^s}\right) \tag{22}$$

provided we are allowed to write the average molality m_2^s of the inhomogeneous surface phase be equal to $55.5\Delta n_2/\Delta n_1$. The plot shown in Figure 2 for the adsorption of SDS from aqueous solution onto the rigid and solid alumina[68] surface indicates that the value of Γ_2^1 defined by eq 20 or 22 increases with the increase of C_2 (i.e., m_2) since Δn_2 in these cases will increase and subsequently Δn_1 decrease due to the desorption of water from the interface. In all cases of surfactant adsorption whenever, $m_2^s \gg m_2$, Γ_2^1 is close to Δn_2. With increase of C_2 to a critical value C_2^m, the adsorbed water layer is completely displaced ($\Delta n_1 = 0$) with the formation of a monolayer of SDS saturating the interfacial phase. With further increase of C_2 from C_2^m, Γ_2^m (i.e., Δn_2) remains constant since Δn_1 is zero. Values of Δn_2 representing the composition of the interfacial phase of this type (when $\Delta n_1 = 0$) are presented in Table 1 for many solid−liquid systems.[68,69] When $C_2 \gg C_2^m$, Γ_2^1 for many of these systems (see Figure 2) sharply increases without reaching any limiting value as a result of the formation of multilayers of surfactant forming the interfacial phase in the complete absence of solvent ($\Delta n_1 = 0$).

In Figure 3, the isotherms for the adsorption of CTAB, MTAB, and DTAB on strongly hydrophilic surfaces of dry cellulose powder[70] are shown. The cellulose powder is made of flexible chains of glucose residues containing a large number of hydrophilic groups. We note with interest that for CTAB, Γ_2^1 is positive at low values of C_2 but it increases with the increase of C_2 until it attains a maximum value $(\Gamma_2^m)_{ap}$ at a critical value of surfactant concentration C_2^m (see Table 2). Unlike an alumina surface, the value of Δn_1 at this condition is also significantly higher than zero near the cmc of the surfactant. With further increase of C_2 above C_2^m, both Δn_2 and Δn_1 remain fixed so that Γ_2^1 in eq 20 decreases linearly with the increase of C_2. For dilute solutions, $C_2/55.5$ may be taken to be equal to X_2/X_1. Thus above $C_2 > C_2^m$, Γ_2^1 sharply decreases to zero (at the surface azeotropic state) and then its value becomes negative since Δn_2 is less than Δn_1 ($C_2/55.5$). It has been shown also in Figure 3 that Γ_2^1 varies linearly with increase of C_2 so that using eq 20 (after putting X_2/X_1 equal to $C_2/55.5$), values of Δn_2 and Δn_1 for adsorbed solute and solvent in moles per kilogram of cellulose can be evaluated. The values of Γ_2^1 for all values of C_2 (or m_2) for DTAB are negative (see Figure 3). But the plot of $-\Gamma_2^1$ versus C_2 is linear with zero intercept and negative slope so that absolute values of Δn_1 and Δn_2 for this system can also be evaluated using eq 20. At very high values of C_2, $-\Gamma_2^1$ vs C_2 plot deviates from linearity since Δn_1 and Δn_2 do not remain constant but change with further increase of C_2. Isotherms for adsorption of CTAB onto cellulose in the presence of excess urea are similar with the isotherm of CTAB on alumina possibly as a result of increase of hydrophobicity of cellulose powder in the presence of urea. Values of Δn_1 and Δn_2 for adsorption of CTAB on cellulose surface are found to depend on temperature and nature of inorganic salts used during adsorption measurements (see Table 2). The hydration of cellulose in the presence of CTAB indicated by Δn_1 in this table depends on the nature of cations and anions present in the excess neutral salt. Adsorption of many types of cationic, anionic, and nonionic surfactants on rigid and flexible (soft) surfaces[68−70] has been studied and features of the isotherms are found to be similar as those presented in Figures 2 and 3.

Adsorption of Electrolytes at Solid−Liquid Interfaces

Several workers[50−53,33] have determined the excess hydration of powdered solids in the presence of various inorganic electrolytes using an isopiestic vapor pressure technique. In the simple experimental arrangement for this, a definite weight of dry powdered solid like alumina, silica, etc. is taken in a weighing bottle. The bottle containing the sample also contains definite weight of salt solution containing a known amount of electrolyte. The sample bottle (with its lid open) is allowed to float on the reference aqueous solution of the same salt contained in a desiccator. The desiccator is then closed and evacuated so that an exchange of water vapor between the reference solution and sample will take place until a state of vapor pressure equilibrium is attained. The total water content in the sample system is determined by weighing so that molality m_2^t of the salt in solution associated with the dry powder[50,51] is calculated. The molality of the reference salt solution is determined accurately, and this may be taken to be equal to m_2 after neglecting the insignificant contribution of hydrated powder to equilibrium vapor pressure. Thus, using measured values of m_2^t, m_2, and weight of the powder, ω_s, the value of Γ_2^1 for a salt can be calculated as function of m_2 using directly eq 1. The results of a few cases are shown in Figure 4. Values of Γ_2^1 in these figures are positive at low values of m_2, but at higher concentrations, their values are all negative. At intermediate values of m_2 equal to m_2^{azeo}, Γ_2^1 becomes zero at an azeotropic state.[33] As in the case of surfactant adsorption by cellulose, a plot of Γ_2^1 against m_2 is found to be linear in a wide range of concentrations, so that values of Δn_1 and Δn_2 for various salts can be evaluated. Some of these values are presented in Table 3. Δn_1 and Δn_2 representing absolute amounts of the salt and solvent present in the interfacial phase of the solid−liquid system are all positive (or close to zero). Unlike Γ_2^1 and Γ_1^2, values

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(70) Biswas, S. C.; Chattoraj, D. K. *Langmuir* **1997**, *13*, 4505.

Table 1. $\Delta G°$ for Adsorption of Surfactants at Solid−Liquid Interfaces, pH 6.0, 28 °C, $\mu = 0.25$, $\Delta n_1 = 0$, $\Delta n_2 = \Gamma_2{}^m$

solid	surfactants	$\Gamma_2{}^m \times 10^6$, mol m^{-2}	$-\Delta G° \times 10^6$, kJ m^{-2}	$-\Delta G_B°$, kJ mol^{-1}	$-\Delta G_{hi}° \times 10^6$ kJ m^{-2}
BaSO$_4$	SDS	0.320	9.60	30.0	32.9
silica	SDS	0.290	8.38	28.9	102
alumina	SDS	6.80	189	27.8	
charcoal	SDS	0.491	16.7	34.0	401
BaSO$_4$	CTAB	2.22	81.7	36.8	
alumina	CTAB	3.12	112	35.8	
charcoal	CTAB	0.280	112	40.0	79.3

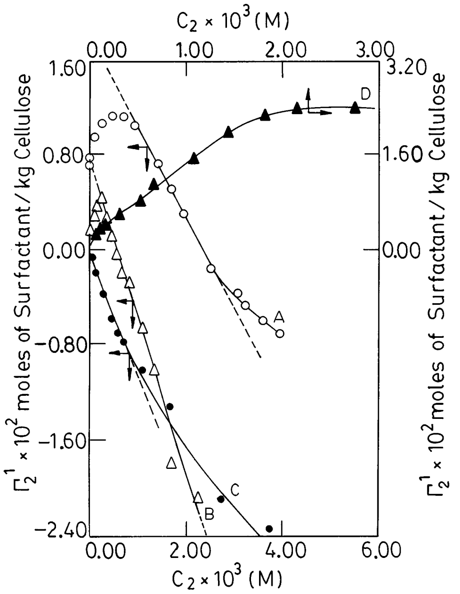

Figure 3. Plot of $\Gamma_2{}^1$ vs C_2 for adsorption of cationic surfactants at the cellulose−water interface[18] pH, 6.0, $\mu = 0.1$, 30 °C: (A) CTAB; (B) MTAB; (C) DTAB; (D) CTAB in 8 M urea.

of Δn_1 and Δn_2 representing the composition of the interfacial phase never become negative.

Adsorption at Fluid Interfaces

For the adsorption of a solute at a liquid interface, the value of $C_2{}^t - C_2$ in eq 2 is difficult to measure directly since the area of the fluid surface available for measurement is relatively small. However, $\Gamma_2{}^1$ for such systems can be calculated using the Gibbs adsorption equation[24] derived rigorously on thermodynamic grounds. In this elegant approach of Gibbs, a liquid column containing several components, 1, 2, 3, ..., i, has been considered in which two bulk phases, α and β, are separated from each other by a boundary region of unit surface area. The boundary region is inhomogeneous and difficult to define. The bulk phases α and β contain i number of components. Gibbs considered side by side an idealized column in which two phases are separated by a mathematical plane. By arbitrary placement of this ideal plane at a fixed position of the inhomogeneous surface phase, Gibbs deduced his elegant eq 23 on rigorous thermodynamic grounds

$$-\mathrm{d}\gamma = \Gamma_2{}^1\, \mathrm{d}\mu_2 + \Gamma_3{}^1\, \mathrm{d}\mu_3 + ...\ \Gamma_i{}^1\, \mathrm{d}\mu_i \qquad (23)$$

Here $\Gamma_2{}^1$, $\Gamma_3{}^1$, ..., $\Gamma_i{}^1$ stand for the surface excesses (or relative adsorption) of components 2, 3, ..., i with reference to the surface excess of component 1 equal to zero by suitable placement of the dividing plane within the inhomogeneous surface phase. The superscript of Γ_i represents this condition when $\Gamma_1{}^1 = 0$. Also μ_i represents the chemical potential of the ith component in the liquid column.

By placement of the dividing plane to another fixed position within the inhomogeneous surface phase, $\Gamma_2{}^2$ can be made arbitrarily zero, so the Gibbs equation now in different form reads,[24,33]

$$-\mathrm{d}\gamma = \Gamma_1{}^2\, \mathrm{d}\mu_1 + \Gamma_3{}^2\, \mathrm{d}\mu_3 + ...,\ \Gamma_i{}^2\, \mathrm{d}\mu_i \qquad (24)$$

Defay and Prigogine[31] have further extended the thermodynamic treatment for the ideal liquid column imagined by Gibbs using the Gibbs−Duhem equations. They have also combined their derived equation with the mass balance equation used by Gibbs for the total amount of ith component present in the system and finally derived quantitatively the relation (25) for the absorption of ith solute at the air−water interface or that of an electrolyte adsorbed at an oil−water interface

$$\Gamma_i{}^1 = n_i{}^t - n_1{}^t \frac{n_i}{n_1} \qquad (25)$$

For binary solution, $i = 2$ so that eq 25, valid for a fluid interface, becomes the same as eq 3 obtained directly for the adsorption occurring at a solid−liquid interface. Exactly following similar arguments, we can divide the fluid system into inhomogeneous surface phase and homogeneous bulk phase so that the mass balance equations (15 and 16) will be valid on the same argument followed in deriving relations 9 to 14. Combining relations 15 and 16 with relation 25 in a similar manner and putting $i = 2$, we obtain for the fluid interface, relations 20 and 21.

$$\Gamma_2{}^1 = \Delta n_2 - \Delta n_1 \frac{X_2}{X_1} \qquad (20)$$

and

$$\Gamma_1{}^2 = \Delta n_1 - \Delta n_2 \frac{X_1}{X_2} \qquad (21)$$

From the thermodynamic treatment of Gibbs, $\Gamma_2{}^1$ (and $\Gamma_1{}^2$) occurring in the Gibbs equation (23) or its extension by Defay et al.[31] in the form (25) represents moles of solute component per unit area for the fixation of the imaginary Gibbs dividing plane at a specific position so that the surface excess of solvent ($\Gamma_1{}^1$) becomes zero. As pointed out by Guggenheim[25] and Good[71] for such imaginary placement of the dividing plane, the physical picture of the surface phase becomes abstract. But by just combining eq 25 with mass balance equations 15 and 16, we obtain relations 20 and 21 in which the physical concept of $\Gamma_2{}^1$ for the surface phase in terms of Δn_1, Δn_2, and bulk mole ratio compositions is perfectly clear. For the first time, surprisingly the Gibbs surface excess becomes quantitatively related to the actual compositions Δn_1 and Δn_2 of inhomogeneous surface phase.

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(71) Good, R. J. *J. Colloid Interface Sci.* **1986**, *110*, 299.

Table 2. $\Delta G°$, Δn_1, and Δn_2 for Adsorption at Cellulose−Water Interfaces, $\mu = 0.15$ and pH 6.0

					(high) concentrated	
surfactants	$(\Gamma_2^m)_{ap} \times 10^2$, mol kg^{-1}	$-\Delta G° \times 10^2$, kJ kg^{-1}	$-\Delta G_B°$, kJ kg^{-1}	$+\Delta G_{hi}° \times 10^2$, kJ kg^{-1}	$\Delta n_1 \times 10^2$, mol kg^{-1}	$\Delta n_2 \times 10^2$, mol kg^{-1}
CTAB (30 °C)	1.12	36.3	32.4	159	0.230	1.42
MTAB (30 °C)	0.425	14.7	34.7	133	0.113	0.70
DTAB (30 °C)	-			62.7	6.29	0
CTAB (37 °C)	0.845	27.2	32.2	188	0.191	1.18
CTAB (37 °C), 6 M urea	2.29	76.9	33.6			
CTAB (37 °C), 2 M LiCl	1.09	38.2	35.0	473	17.4	4.07
CTAB (37 °C), 2 M NaCl	1.26	45.2	35.9	165	5.52	1.27
CTAB (37 °C), 2 M KCl	1.60	55.0	34.4	248	9.15	2.41
CTAB (37 °C), 0.667 M Na_2SO_4	0.816	29.3	35.9	214	13.1	1.18

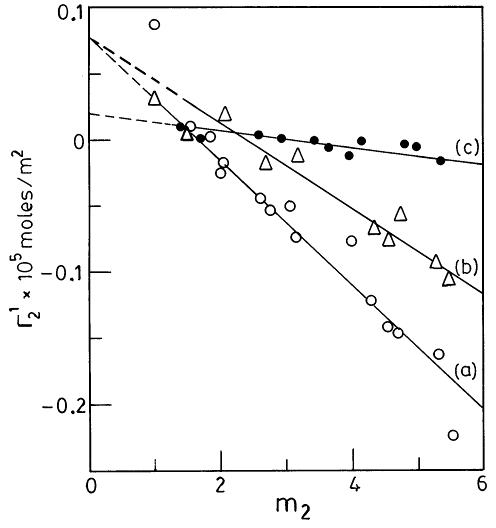

Figure 4. Plot of Γ_2^1 vs m_2 for hydration of different solid surfaces[16] in the presence of NaCl at 25 °C: (a) alumina; (b) $BaSO_4$; (c) silica.

Table 3. Δn_1 and Δn_2 for Negative Adsorption of Inorganic Salts at Solid−Water Interfaces at 25 °C

	$10^4\Delta n_1$, mol m^{-2}			$10^4\Delta n_2$, mol m^{-2}		
electrolytes	alumina	silica	$BaSO_4$	alumina	silica	$BaSO_4$
LiCl	3.74	8.60	13.1	0.077	0.200	0.725
NaCl	4.42	1.50	3.75	0.165	0.070	0.200
KCl	4.47	7.65	1.38	0.133	0.307	0.050
CsCl	5.32	5.79	6.50	0.260	0.046	0.025
RbCl	2.09	9.02	6.25	0.010	0.094	0.250
NaBr	2.55	5.33	2.13	0.088	0.280	0.150
NaI	2.43	2.72	12.5	0.066	0.132	0.138
$CaCl_2$	2.74	5.45	8.63	0.122	0.234	0.325
Na_2SO_4	4.67	9.02	26.4	0.0792	0.209	0.350

For two component systems containing nonionic surface-active solute, eqs 23 and 24 can be written in the form

$$-\mathrm{d}\gamma = \Gamma_2^{\,1}\,\mathrm{d}\mu_2 \tag{26}$$

or

$$-\mathrm{d}\gamma = \Gamma_1^{\,2}\,\mathrm{d}\mu_1 \tag{27}$$

From combinations of these two equations, an exactly similar equation (8) derived for a solid−liquid interface has been obtained by Guggenheim and Adam[72] for adsorption at a fluid interface. Also for such binary system

$$\mathrm{d}\gamma = -RT\,\Gamma_2^{\,1}\,\mathrm{d}\ln a_2 \tag{28}$$

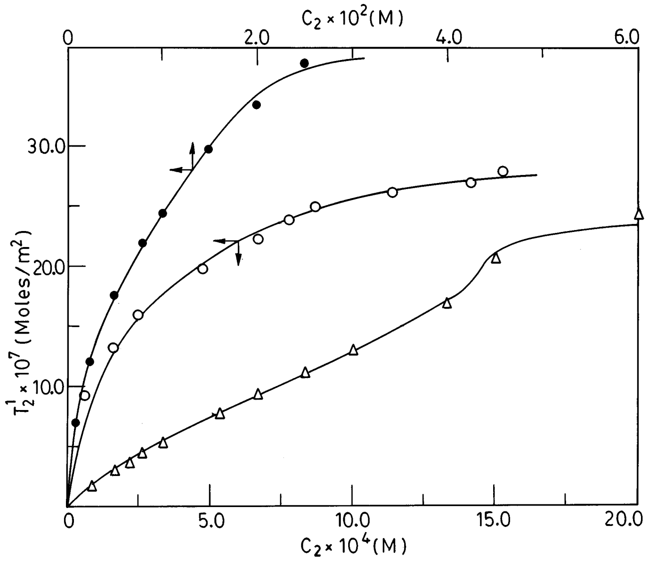

Figure 5. Plot of Γ_2^1 vs C_2 at 30 °C: (○) sodium sebacete in presence of 1 M NaCl, pH 11.0; (△) sodium sebecete (no salt), pH 11.0; (●) sebacic acid, pH 2.0.

Table 4. Values of Δn_1 and Δn_2 from Aqueous Mixtures of Organic Compounds

liquid system	$10^6\Delta n_2$, mol m^{-2}	$10^6\Delta n_1$, mol m^{-2}
1. pyridine + H_2O	3.72	0.20
2. formic acid + H_2O	3.87	0.38
3. methyl alcohol + H_2O	6.89	0.44
4. ethyl alcohol + H_2O	6.60	1.91
5. propyl alcohol + H_2O	5.98	4.35
6. acetone + H_2O	3.40	5.00
7. gylcerol + H_2O	0.89	0.69

For dilute solutions, the activity a_2 may be replaced by molar concentration C_2 of the solute so that Γ_2^1 for a solute can easily be estimated using a γ−ln C_2 plot. In Figure 5, values of Γ_2^1 for sebacic acid at the heptane−water interface have been plotted against C_2 at pH 2.0. Γ_2^1 increases with the increase of C_2 until it reaches the state of maximum adsorption due to monolayer saturation. For concentrated solutions of binary liquid mixtures, Γ_2^1 values for different values of a_2 (equal to f_2X_2) have been calculated using eq 28. Here f_2 stands for the activity coefficient of the component in the binary solution. From the linear plot of Γ_2^1 against X_2/X_1 (or plot of Γ_1^2 against X_1/X_2) in wide ranges of solution composition, the values of Δn_1 and Δn_2 representing the compositions of the inhomogeneous surface phases of a few fluid systems have been evaluated (see Table 4) for aqueous mixture of few organic substances[74] using eqs 20 and 21.

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(72) Guggenheim, E. A.; Adam, N. K. *Proc. R. Soc. London, Ser. A* **1933**, *139*, 218.

(73) Chattoraj, D. K. *Indian J. Chem.* **1968**, *6*, 309.

(74) Chattoraj, D. K.; Moulik, S. P. *Indian J. Chem.* **1977**, *15A*, 73.

Many surfactants such as SDS, CTAB, and sodium salts of octanoic and sebacic acids are organic electrolytes which lower the boundary tension (γ) of water significantly. Lowering of γ with the surfactants becomes more in the presence of excess neutral salt such as NaCl.

For anionic surfactant RNa_Z dissociating completely into R^{Z-} anions of valency Z and Na^+ cation in the presence of NaCl, the Gibbs equations will be written in the form[33−37]

$$-d\gamma = RT[\Gamma_{R-}\, d\ln C_{R-} + \Gamma_{Na}{}^{+}\, d\ln C_{Na+} + \Gamma_{Cl-}\, d\ln C_{Cl-}] \qquad (29)$$

C_{R-}, which is equal to C_2, stands for concentration of the organic electrolyte and C_{Cl-}, which is equal to C_3, represents the concentration of the inorganic electrolyte. The experimental design is such that γ is decreased with the increase in the concentration of RNa_Z (or R^{Z-}) keeping the NaCl concentration (C_{Cl-}) constant.

Equation 29, which is valid for dilute solutions, now assumes the form[33−37]

$$-d\gamma = mRT\, \Gamma_{R^-}\, d\ln C_R$$

or

$$-d\gamma = mRT\, \Gamma_2{}^1\, d\ln C_2 \qquad (30)$$

where

$$m = 1 + \frac{Z}{1 + \dfrac{C_{Cl^-}}{ZC_R} f(\psi)} \qquad (31)$$

Here $f(\psi)$ is the function of the surface potential whose value depends on the models of the electrical double layer.[33−37] For the Helmholtz double layer, its value may be taken as unity. Values of m for different values of C_{Cl^-}/C_{R^-} for the adsorption of uni-univalent electrolyte, polyelectrolyte, micelles, nonelectrolyte, and electrolyte mixtures have been derived rigorously for dilute as well as concentrated solutions. Complex expressions of m for weak organic electrolyte undergoing hydrolysis at pH 7.0 with or without excess neutral salt have been derived.[73]

From eq 31, we note that for C_{Cl^-} equal to zero, m becomes equal to $1 + Z$ in the absence of salt hydrolysis. For SDS or CTAB, m will be equal 2. For sodium sebacete, its value is taken as 3 at pH 11.0 where hydrolysis is negligibly small and concentration of NaOH is also small compared to C_{R-}. Using appropriate values of m in eq 37, the adsorption of sodium sebacete monolayers is compared in Figure 5 at pH 11.0. Values of m for adsorption of SDS and CTAB at the oil−water interface have been evaluated from direct experiments.[43]

In Table 5, values of $\Gamma_2{}^m$ equal to Δn_2 have been presented for various organic electrolytes adsorbed at different types of fluid interfaces. The values of Δn_2 are all positive those of Δn_1 are zero.

Table 5. $\Delta G°$ for Adsorption of Surfactants at 30 °C, $\Delta n_1 = 0$ and $\Delta n_2 = \Gamma_2{}^m$

surfactants	interface	$\Gamma_2{}^m \times 10^6$, mol m^{-2}	$-\Delta G° \times 10^6$, kJ m^{-2}	$-\Delta G_B°$, kJ mol^{-1}
without salt	A/W	4.30	200	46.5
DTAB	H/W	1.67	130	78.1
DTAB	NB/W	1.90	95.5	50.3
CPCL	A/W	22.4	1260	57.6
CPCL	H/W	9.79	596	65.4
SDS	A/W	36.5	1660	45.5
SDS	H/W	17.4	846	48.6
SDS	NB/W	18.0	928	51.5
in presence of 1 M NaCl				
DTAB	A/W	6.15	195	31.5
DTAB	H/W	4.15	213	51.3
DTAB	NB/W	3.39	110	32.4
CPCL	A/W	22.4	798	35.6
CPCL	H/W	11.7	451	38.6
CPCL	NB/W	9.92	251	25.3
SDS	A/W	5.65	217	38.5
SDS	H/W	9.59	413	43.1
SDS	NB/W	5.00	164	32.7

Negative Adsorption of Salts at a Fluid Interface

It is well-known that the addition of an inorganic salt to water increases the boundary tension of water so that $d\gamma/d\ln a_2$ at a given value of a_2 becomes positive. $\Gamma_2{}^1$ calculated from the Gibbs adsorption equations (23) may be written as[31,33]

$$\begin{aligned} -d\gamma &= \Gamma_2{}^1\, d\mu_2 \\ &= \Gamma_2{}^1(\upsilon_+\, d\mu_+ + \upsilon_-\, d\mu_-) \\ &= RT\, \Gamma_2{}^1(\upsilon_+ + \upsilon_-)\, d\ln f_\pm X_\pm \\ &= RTm\Gamma_2{}^1\, d\ln f_\pm X_\pm \end{aligned} \qquad (32)$$

Here m is equal to $\upsilon_+ + \upsilon_-$ where υ_+ and υ_- represent the valency of cations and anions, respectively. Also $f_\pm$ and $X_\pm$ stand for mean activity coefficient and mean mole fraction of the electrolyte, respectively. At a given mole fraction of an electrolyte, values of $f_\pm$ and $X_\pm$ in the rational scale can be evaluated using appropriate standard tables. Values of $\Gamma_2{}^1$ in all cases for different salts at air−water and oil−water interfaces are found to be all negative so that according to relation 32, excess adsorption of water solvent is positive.[44,45,77] Also plots of $-\Gamma_2{}^1$ against X_2/X_1 are observed for many electrolyte systems to be linear in wide ranges of concentration (Figure 6) so that values of Δn_1 and Δn_2 have been evaluated for these systems using eq 20. These values presented in Table 6 are all positive or zero but never negative since they represent the absolute composition of the inhomogeneous interfacial phase.

Free Energy of Adsorption at Fluid Interface

In eq 30 for the fluid interface, γ stands for the free energy due to the formation of unit area of the fluid surface. The standard free energy change $\Delta G°$ for the adsorption of the surfactant due to the change of a_2 (or C_2) in the bulk phase from zero to unity can be obtained from the

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(75) Ghosh, L. N.; Das, K. P.; Chattoraj, D. K. *Indian J. Chem.* **1987**, *26A*, 807.

(76) Chattoraj, D. K.; Ghosh, L. N.; Mahapatra, P. K. In *Surfactants in Solution*; Mittal, K. L., Shah, D. O., Ed.; Plenum Press: New York, 1992; Vol. 11, p 277.

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(78) Lyklema, J. In ref 7, p 243.

(79) Eskilsson, K.; Leal, C.; Lindman, B.; Miguel, M.; Nylander, T. *Langmuir* **2001**, *17*, 1666.

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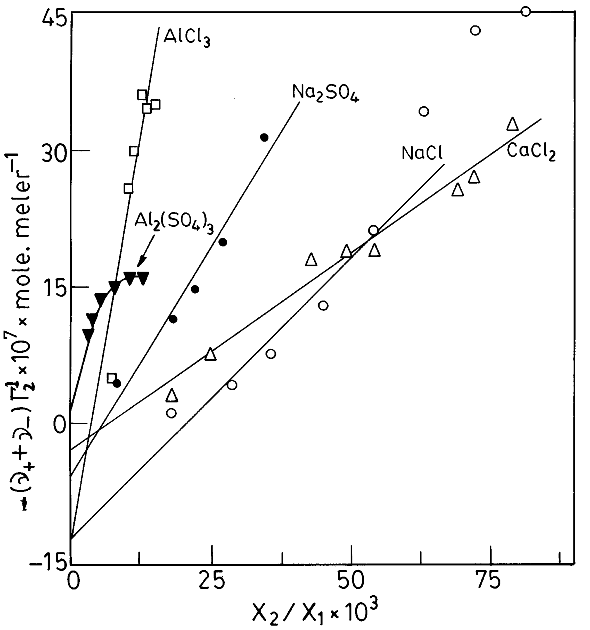

Figure 6. Plot of Γ_2^1 $(\upsilon_+ + \upsilon_-)$ of electrolytes against X_2/X_1 of electrolytes at the benzene−water interface at 30 °C.

Table 6. Δn_1 and Δn_2 for Negative Adsorption of Inorganic Salts at Fluid Interfaces at 30 °C

	$10^5\Delta n_1$, mol m^{-2}				$10^5\Delta n_2$, mol m^{-2}			
electrolytes	A/W	B/W	T/W	NB/W	A/W	B/W	T/W	NB/W
NaCl	2.37	5.12			0.034	0.12		
$CaCl_2$	5.80	4.24			0.077	0.03		
Na_2SO_4	13.5	10.0	20.3	17.0	0.16	0.058	0	0.058
$AlCl_3$		36.8				0.145		
$Al_2(SO_4)_3$	8.40			1.70	0	0	0	0
LiCl	2.56		3.3		0	0.021	0.021	
KCl	2.52				0			
NaBr	1.53				0			
$MgCl_2$	2.22				0			
$MgSO_4$	26.3				0			

integration of eq 30 so that

$$\begin{aligned}\Delta G^\circ &= \int_1^2 \mathrm{d}\gamma = -mRT \int_{\mathrm{o}}^{a_2=1} \frac{\Gamma_2^{\ 1}}{a_2}\,\mathrm{d}a_2 \\ &= -mRT\left[\int_{\mathrm{o}}^{a_2{}^m} \frac{\Gamma_2^{\ 1}}{a_2}\,\mathrm{d}a_2 - \Gamma_2^{\ m}\ln a_2^{\ m}\right] \\ &= \Delta G_{\mathrm{ad}} + \Delta G_{\mathrm{dil}}\end{aligned} \tag{33}$$

The integral term in eq 33 multiplied by mRT represents the free energy change ($\Delta G_{\mathrm{ad}}°$) due to the saturation of the surface by adsorption when a_2 is altered from zero to $a_2{}^m$ and the boundary tension of the interface is altered from γ_{o} to γ_{m}, its minimum value.

The second term in the brackets of eq 33 multiplied by mRT represents the free energy change ($\Delta G_{\mathrm{dil}}°$) due to the change of the bulk activity of the solute from $a_2{}^m$ to its value at the standard state of unit activity. This includes the hypothetical assumption that $\Gamma_2{}^m$ remains constant when a_2 is altered from $a_2{}^m$ to unity. Equation 33 has been earlier deduced by Bull[65,66] for the calculation of the free energy of adsorption of a protein at the glass−water interface using the molar scale of activity.

Equations 30 and 33 may be combined together for the adsorption in the fluid system so that

$$\begin{aligned}\Delta G^\circ &= \int_0^{\gamma_{\min}} \mathrm{d}\gamma + mRT\,\Gamma_2^{\ m}\ln a_2^{\ m} \\ &= -\Pi_m + mRT\,\Gamma_2^{\ m}\ln a_2^{\ m}\end{aligned} \tag{34}$$

Here Π_{m} stands for $\gamma_0 - \gamma_{\min}$.

Ghosh et al.[75] have measured lowering of boundary tension at air−water (A/W), heptane−water (H/W), and nitrobenzene−water (NB/W) interfaces as functions of increasing concentrations of sodium dodecyl sulfate (SDS), cetylpyridinium chloride (CPCL), and dodecyltrimethylammonium bromide (DTAB), respectively, both in the presence and in the absence of excess NaCl. Values of $\Gamma_2{}^1$ for different values of C_2 (or a_2) have been evaluated using eq 30. Values Π_{m}, $\Gamma_2{}^m$, and $C_2{}^m$ (equal to $55.5X_2{}^m$ for dilute solutions) can be evaluated from the experimental data so that values of $\Delta G°$ for different systems have been evaluated appropriately using eq 34. These are included in Table 5.

$\Delta G°$ for different surface-active agents presented in Table 5 represents the change in the surface free energy when the surface is saturated and the solute activity in the bulk phase is altered from zero to unity. The standard free energy change, $\Delta G_{\mathrm{B}}°$, for the transfer of 1 mol of the surfactant from the bulk solution to an interface can be calculated using eq 35

$$\Delta G_{\mathrm{B}}^\circ = \frac{\Delta G^\circ}{\Gamma_2^{\ m}} \tag{35}$$

This equation has been first used by Bull[65,66] in molality scale for the excess adsorption of surfactant at an interface. Values of $\Delta G_{\mathrm{B}}°$ in mole fraction scale for different fluid systems can be written in the form

$$\Delta G^\circ = \Gamma_2^{\ m}\Delta G_{\mathrm{B}}^\circ \tag{36}$$

$\Delta G°$ is thus composed of the maximum packing factor $\Gamma_2{}^m$ of the surfactant molecules at the interface multiplied by the factor of the free energy of transfer per mole of surfactant from the bulk to the interface.

For long-chain cationic and anionic surfactants, values of $\Delta G°$ in Figure 6 are found (see Table 5) to increase with the increase of $\Gamma_2{}^m$ both with and without excess neutral salt, respectively. $\Gamma_2{}^m$ represents maximum affinities for the ionic surfactants for air−water, heptane−water, and nitrobenzene−water interfaces. The first two surfaces are hydrophobic, but the NB/W interface is hydrophilic in nature. The hydrophobic tail part of the surfactant contains a different number of CH_2 groups, and the hydrophilic headgroup may be cationic or anionic in nature. Even at the state of maximum adsorption, the orientations of the molecules at these interfaces are widely different from each other. In plots of $-\Delta G°$ against $\Gamma_2{}^m$ in Figure 6 are found to be nonlinear in nature both in the absence and in the presence of excess salt. $\Delta G°$ obtained from the integration of the Gibbs equation includes free energy changes due to the chemical interaction, electrostatic repulsion, and attraction in the interfacial double layer, molecular orientations at different interfaces, hydrophobic interaction, interfacial hydration, etc. Because of these effects, magnitudes of $-\Delta G°$ as well as $\Gamma_2{}^m$ (also calculated using the Gibbs adsorption equation) will be different for different systems. If the effects of the sum total of these factors both on $-\Delta G°$ and on $\Gamma_2{}^m$ are close to each other, then $\Delta G_{\mathrm{B}}°$ (equal to $\Delta G°/\Gamma_2{}^m$) will also be very close to each other for many systems, and in that case a plot of $-\Delta G°$ against $\Gamma_2{}^m$ would have been linear. On the other hand, if these effects on $\Delta G°$ and $\Gamma_2{}^m$ significantly differ

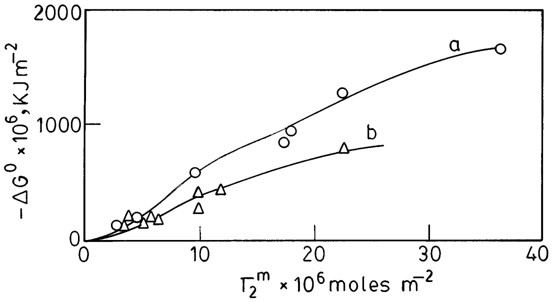

Figure 7. Plot of $-\Delta G^\circ$ vs $\Gamma_2{}^m$ for the fluid interface: (a) DTAB, CPCL, SDS at A/W, H/W, NB/W interfaces, 30 °C; (b) DTAB, CPCL, SDS at A/W, H/W, NB/W interfaces in presence of 1 M NaCl at 30 °C.

Table 7. ΔG° for Negative Adsorption of Inorganic Salts at Fluid Interfaces[a] at 30 °C

	$10^4 \times \Delta G^\circ$, kJ m^{-2}			
electrolytes	A/W	B/W	T/W	NB/W
NaCl	1.07	180	0.655	0.245
$CaCl_2$	1.45	0.378	0.286	0.590
Na_2SO_4	2.60	5.40	4.00	5.24
$AlCl_3$	0.316	4.10	0.653	0.243
$Al_2(SO_4)_3$	0.689	2.00	0.651	
LiCl	1.35			

[a] Key: air−water (A/W); benzene−water (B/W), toluene−water (T/W); nitrobenzene−water (NB/W).

from each other, then ΔG° will vary with $\Gamma_2{}^m$ in nonlinear fashion and $\Delta G_B{}^\circ$ for such systems will widely differ from each other (see Figure 7 and Table 5).

We also note with interest that at a given value of $\Gamma_2{}^m$ in Figure 7, ΔG° in the presence of salt is significantly less than that in the absence of salt as a result of the large decrease in the electrostatic free energy due to the significant decrease of the thickness of the interfacial double layer.

The apparent standard free energy change, $\Delta G_{ap}{}^\circ$, for the solution of an inorganic salt at a given value of the mean mole fraction $X_\pm$ in the rational scale can be calculated from eq 37 derived from the integrated form of eq 32. Equation 37 is very similar to eq 33 already derived for the positive adsorption of a surfactant from the bulk solution to a fluid surface

$$\Delta G_{ap}{}^\circ = -mRT\left[\int_0^{X_\pm} \frac{\Gamma_2{}^1}{X_\pm f_\pm}\, dX_\pm f_\pm - \Gamma_2{}^1 \ln f_\pm X_\pm\right] \quad (37)$$

combining eq 32 with eq 37, relation 38 will be obtained.

$$\Delta G_{ap}{}^\circ = -\Pi + m\Gamma_2{}^1 RT \ln f_\pm X_\pm \quad (38)$$

Unlike ΔG°, $\Delta G_{ap}{}^\circ$ depends on the value of $f_\pm X_\pm$ (or X_2). Also its value at a given value of $X_\pm$ is a positive quantity.

Ghosh et al.[76] have extensively measured surface and interfacial tensions of various types of oil−water interfaces as functions of increasing concentrations of inorganic salts. Positive values of $\Delta G_{ap}{}^\circ$ calculated from the experimental data using eq 38 are observed to increase with increase of $1/X_\pm{}^{1/2}$ linearly when $X_\pm$ values are high (see Figure 8). From the extrapolation of $\Delta G_{ap}{}^\circ$ at $(1/X_\pm)^{1/2}$ (or $X_\pm$) equal to unity, ΔG° values for different electrolyte systems are calculated. Values of this standard free energy change at unit activity have been evaluated from the experimental data. These are presented in Table 7. We may point out that the negative values of ΔG° for the adsorption of surfactants at a fluid interface (see Table 5) and positive values of ΔG° for adsorption of electrolytes at a liquid interface (Table 6) both refer to the same standard state of unit activity of the solute in the bulk phase so that these values of ΔG° for different systems are comparable in terms of relative affinities of a solute for an interface.

Table 8. ΔG° for Negative Adsorption of Inorganic Salts at Solid−Water Interfaces at 25 °C

	$10^4 \times \Delta G^\circ$, kJ m^{-2}		
salt	alumina	silica	$BaSO_4$
LiCl	7.38	17.1	135
NaCl	9.66	3.11	68.8
KCl	13.2	20.1	2.75
CsCl	1.88	22.1	232
RbCl	7.52	32.8	143
NaBr	5.37	7.46	25.0
NaI	5.91	3.44	563
$CaCl_2$	0.87	2.87	45
Na_2SO_4	29.4	59.0	170

The excess standard free energy change for the solvent adsorption (hydration) $\Delta G_{hy}{}^\circ$ per unit surface area can be obtained also from the integration of eqs 26 and 27

$$\begin{aligned}\Delta G_{hy}{}^\circ &= \int_1^2 d\gamma = -\int_0^{X_1=1} \Gamma_1{}^2\, d\mu_1 \\ &= -\int_0^{X_1=1} \Gamma_2{}^1\, d\mu_2 = -\int_{X_2=1}^{X_2=0} \Gamma_2{}^1\, d\mu_2 \quad (39) \\ &= +\int_0^{X_2=1} \Gamma_2{}^1\, d\mu_2 = -\Delta G^\circ\end{aligned}$$

Thus only by multiplying values of $+\Delta G^\circ$ by -1 we can estimate $\Delta G_{hy}{}^\circ$, and signs for these for electrolyte solutions will be negative indicating the spontaneous nature of excess hydration of the fluid surface in the presence of salts.

ΔG° for Adsorption at a Solid−Liquid Interface

We have already shown from our mathematical analysis that $\Gamma_2{}^1$ directly determined for the solid−liquid interface is the same as that deduced from the Gibbs adsorption equation using liquid−gas and liquid−liquid systems. Further, the inhomogeneous surface phase AA′BB′ in contact with a highly polished solid surface of unit area (see Figure 1) is composed of Δn_1 and Δn_2 moles of solvent and solute, respectively, so that using the Gibbs−Duhem equation, we can write

$$\left(\sum_1^\sigma \Delta n_1{}^\sigma\right) d\mu_1 + \left(\sum_1^\sigma \Delta n_2{}^\sigma\right) d\mu_2 + A\, d\gamma_{SL} = 0 \quad (40)$$

or

$$\Delta n_1\, d\mu_1 + \Delta n_2\, d\mu_2 + A\, d\gamma_{SL} = 0 \quad (41)$$

A standing for the area of the polished interface is taken as unity. γ_{SL} stands for the free energy per unit area of the solid−liquid interface.

Using the Gibbs−Duhem equation for the bulk phase BB′PP′, one can write eq 42

$$n_1\, d\mu_1 + n_2\, d\mu_2 = 0 \quad (42)$$

combining conveniently eqs 41 and 42, we can write

$$\begin{aligned}d\gamma_{SL} &= -\left(\Delta n_2 - \Delta n_1 \frac{n_2}{n_1}\right) d \ln a_2 \\ &= -\Gamma_2{}^1\, d\mu_2\end{aligned} \quad (43)$$

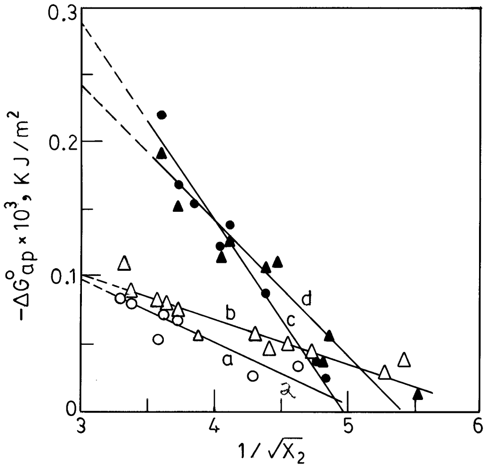

Figure 8. Plot of $\Delta G_{ap}°$ vs $1/X_2^{1/2}$ for hydration of solid surfaces[16] in the presence of different electrolytes ($X_\pm = X_2$): (a) silica (NaCl); (b) alumina (CsCl); (c) silica (KCl); (D) alumina (KCl).

so that the standard free energy change $\Delta G°$ per unit surface area of solid can be expressed by eq 44

$$\Delta G° = \int_1^2 d\gamma_{SL} = -RT\int_0^1 \Gamma_2{}^1 \,d \ln a_2 = -RT\left[\int_0^{\Gamma_2{}^m} \Gamma_2{}^1 \,d \ln a_2 - \Gamma_2{}^m \ln a_2{}^m\right] \quad (44)$$

As in the case of the fluid system, for the adsorption of the ionic surfactant in the presence and absence of excess neutral salt, eq 44 will assume the form

$$\Delta G° = -mRT\left[\int_0^{\Gamma_2{}^m} \Gamma_2{}^1 \,d \ln a_2 - \Gamma_2{}^m \ln a_2{}^m\right] \quad (45)$$

Although eq 45 for the solid−liquid system is similar to eq 33 for the fluid system, there is one significant operational difference between them. For the fluid system, γ is measurable from accurate experiments whereas for the solid−liquid system, it cannot be computed directly from experiment. However, unlike the fluid system, $\Gamma_2{}^1$ for the solid−liquid system is directly measurable for various values of C_2 (or X_2). The integrated expression of the right side of eq 45 for solid−liquid system will be same as that shown on the right side of eq 33 for the fluid system for the estimation of $\Delta G°$ in both cases. The integral in this equation can be graphically evaluated from the measured values of $\Gamma_2{}^1$, $\Gamma_2{}^m$, a$_2$, and $a_2{}^m$ (in mole fraction scale) for solid−liquid systems. Since in all types of measurements for such a system ionic strength is always very high, m in eq 45 may be taken as unity for all practical purposes.

From the analogy with eq 37 valid for the fluid interface for the negative adsorption of an inorganic salt at a solid−liquid interface, we can write the relation for the apparent free energy change $\Delta G_{ap}°$ for the negative adsorption of the inorganic electrolyte thus

$$\Delta G_{ap}° = -(\nu_+ + \nu_-)RT\left[\int_0^{X_\pm} \Gamma_2{}^1 \,d \ln a_\pm + \Gamma_2{}^1 \ln f_\pm X_\pm\right] \quad (46)$$

At a given value of X$_\pm$, $\Gamma_2{}^1$, $f_\pm$, the value of $\Delta G_{ap}°$ for the negative adsorption of salt onto the solid−liquid adsorption can be calculated using eq 46. From the plot of the values of $\Delta G_{ap}°$ against $1/X_\pm{}^{1/2}$ (see Figure 8), the extrapolated value of $\Delta G_{ap}°$, values of the standard free energy change, $\Delta G°$, at $X_\pm = 1$ for various systems can be evaluated. These are included in Table 8.

Values of $\Delta G°$ for the adsorption saturation of different surfaces by SDS and CTAB, respectively, calculated in this manner with use of eq 44 are shown in Table 1. A similar approach has been followed for the calculation of $\Delta G°$ at $\Gamma_2{}^1$ equal to $\Gamma_2{}^m$ for the adsorption of CTAB on the cellulose surface (Table 2).

Values of $\Delta G°$ for the adsorption of CTAB and SDS on various types of rigid solid−liquid interfaces always refer to the standard state of unit solute activity in bulk so that these values are comparable to each other. Further, $-\Delta G°$ is observed to increase linearly[68,69] with the increase in the value of $\Gamma_2{}^m$ so that the average value of the slope representing $\Delta G_B°$ according to eq 5 is 33 kJ mol^{-1}. The reason for such constancy in the value of $\Delta G_B°$ for different systems under different physicochemical conditions has already been discussed.

For the adsorption of SDS on alumina and other surfaces, $\Gamma_2{}^1$ at very high values of a_2 ($a_2 \gg a_2{}^m$) exceeds $\Gamma_2{}^m$ considerably without reaching a limiting value. For such system undergoing multilayer adsorption, the apparent standard free energy change $\Delta G_{ap}°$ at measured fixed values of $\Gamma_2{}^1$, a_2, and Π, respectively, can be calculated using the equation

$$\Delta G_{ap}° = -mRT\left[\int_0^{\Gamma_2{}^1} \frac{\Gamma_2{}^1}{a_2} \,da_2 - \Gamma_2{}^1 \ln a_2\right] \quad (47)$$

From the plot of $\Delta G_{ap}°$ for such multilayer systems against $1/X_2{}^{1/2}$, the value of the standard free energy change $\Delta G_{hi}°$ can be evaluated from the extrapolation of the value of $\Delta G_{ap}°$ to $1/X_2{}^{1/2}$ (or X_2) equal to unity. Values of $\Delta G_{hi}°$ for few systems are included in Table 1. The difference $\Delta G_{hi}° - \Delta G°$ represents $\Delta G_{co}°$, the free energy change due to the cooperative interaction occurring at the solid−liquid interface.

In the case of adsorption of CTAB on cellulose,[70] $\Gamma_2{}^1$ decreases sharply from the value of $\Gamma_2{}^m$ when C$_2$ exceeds the cmc value of the surfactant, and finally it attains the negative value when the X_2 value is large using eq 47, $\Delta G_{ap}°$ for various values of C_2 (or X_2) can be evaluated at these higher concentration ranges. The negative value of $\Delta G_{ap}°$ decreases sharply with increase of X_2 until its value becomes positive. From the plot of $\Delta G_{ap}°$ against $1/X_2{}^{1/2}$, positive extrapolated values of $\Delta G°$ at $X_2 = 1$ can be obtained in the similar manner. In Table 2 some of these positive values obtained due to the excess hydration of cellulose in the presence of CTAB have been included.

Discussion and Conclusion

In the present treatment, we have considered selected experimental data for the extents of positive or negative adsorption of ionic surfactants and inorganic salts from the aqueous solution onto surfaces of various types. At the solid−liquid interface, calculation of $\Gamma_2{}^1$ based on eq 1 involves the assumption that the concentration of the solvent component before and after adsorption remains unchanged. At the fluid interface, $\Gamma_2{}^1$ calculated on the basis of the Gibbs adsorption eq 30 involves the assumption that $\Gamma_1{}^1$ is zero by suitable and arbitrary placement of the Gibbs dividing plane within the fluid system. Both of these assumptions are not correct quantitatively from the physical point of view since both solute and solvent may be present in the inhomogeneous surface phase.

It has been pointed out that the composition of homogeneous bulk phase should be different from that of the inhomogeneous surface phase except at the azeotropic state when overall compositions become the same for both phases. Assuming this picture for the system, eq 1 for the solid−liquid system may be converted to the form (20) or its complementary form (21). These two equations indicate quantitatively relations between Γ_2^1 (or Γ_1^2) with actual amounts Δn_1 and Δn_2 of the solvent and the solute, respectively, present in the inhomogeneous surface phase in contact with homogeneous bulk phase of uniform mole ratio composition n_2/n_1. Equation 20 presents a clear physical picture of the interfacial phase and it also explains the exact conditions for the evaluation of positive, negative, or zero values of Γ_2^1 for different solid−liquid systems under different physicochemical conditions. Under limited experimental conditions, plots of Γ_2^1 vs n_2/n_1 (or X_2/X_1) are found to be linear so that using eq 20 the values of two unknown quantities Δn_1 and Δn_2 of the inhomogeneous surface phase can be estimated (see Tables 1−3) for positive adsorption of surfactants and negative adsorption of inorganic salt, respectively. In the nonlinear region of the plot, a second equation relating Δn_1 and Δn_2 may be developed using some model. Such an additional independent relation may be obtained if the surface phase is assumed to be a monolayer.[3−5,74] Recently few physical techniques[79−82] are available for direct measurement of Δn_2, so that inserting this in eq 20, the value of Δn_1 may be calculated. Values of Δn_1 and Δn_2 in Tables 1−3 are all positive or zero but never negative.

We have also shown that positive values of Γ_2^1 for an ionic surfactant adsorbed at a fluid interface can be calculated from the surface tension−concentration data using eq 30. Here the value of the coefficient m should be obtained from the design of the boundary tension experiment, ratio of the concentration of the surfactant and neutral salts, nature of the electrical double layer, etc. For inorganic salt, Γ_2^1 can be also calculated from $\gamma - a_2$ data using eq 32. The Gibbs surface excess Γ_2^1 thus correctly evaluated for the solute component is shown to be related to the actual composition Δn_1 and Δn_2 of the inhomogeneous surface phase by eq 20. The physical picture of the Gibbs surface excess (based on the arbitrary fixation of the dividing plane) in terms of the composition of the inhomogeneous surface phase has thus been established directly. From the linear plot of Γ_2^1 against X_2/X_1 for the adsorption of organic solutes, surfactants, and inorganic salts at fluid interfaces, values of Δn_1 and Δn_2 for different systems under limited ranges of composition have been evaluated (see Tables 4−6). From the use of boundary tension concentration data. Like solid−liquid systems, absolute values of Δn_1 and Δn_2 for the fluid system also are positive or close to zero but never negative in sign.

We have also shown that using the Gibbs adsorption equations appropriately in integrated forms the standard free energy changes $\Delta G°$ for the positive adsorption of surfactants and negative adsorption of inorganic salts respectively at fluid interfaces can be evaluated from the experimental values of Π for different values of a_2. From the plot of Π against a_2, the maximum value of Π (equal to Π_m) at a critical value of $a_2{}^m$ should be known for the case of surfactant adsorption.

For the adsorption of inorganic salt, $\Delta G°$ can be obtained from the extrapolation of the values of $\Delta G_{ap}°$ at $X_\pm$ equal to unity. $\Delta G°$ for surfactant adsorption is negative, and that for inorganic salt is positive. Multiplying $\Delta G°$ by −1, the standard free energy change $\Delta G_{hy}°$ for excess adsorption of solvent at the fluid interface can be obtained.

All values of $-\Delta G°$ can be arranged in increasing order of their magnitude so that a thermodynamic scale for relative affinities (or maximum free energy decrease) of adsorption of surfactants at different fluid surfaces can be compared. Values of $-\Delta G°$ all with reference to the unit activity of the solute in the bulk phase are strictly comparable in this free energy scale. The magnitude of positive values of $\Delta G°$ may be arranged in increasing order for various systems so as to form the positive side of the thermodynamic scale all referred to unit activity of the salt in the bulk phase. Increase in the value of $\Delta G°$ increases negative affinity of the inorganic salt for the surface or positive affinity of the solvent for the interface under specified physicochemical condition. In this manner, the complete thermodynamic scale of the free surface energy change for positive and negative adsorption of a solute component 2 from the bulk to a fluid surface can be framed for the comparison of their maximum affinities for the interface.

We have also seen that $\Delta G_B°$ equal to $\Delta G°/\Gamma_2{}^m$ is defined in the unit of kilojoules per mole of surfactant transferred from the bulk to the interface. When the hydrophobic tail of the adsorbed surfactant is long and hydrophilic headgroups are ionic, the surfactants at the interface may assume different types of orientations so that $\Delta G°$ increases with increase of $\Gamma_2{}^m$ in a nonlinear manner (see Figure 5) in agreement with the scale of thermodynamics. For short chain fatty acids in a homologous series, $\Gamma_2{}^m$ values for the oil−water interface in the maximum state of packing are quite close to each other, so that both $\Delta G°$ and $\Delta G_B°$ according to eq 36 will increase with increase of CH_2 groups of the fatty acid as expected from the Traube's rule.[54]

The free energy change $\Delta G_L°$ due to the adsorption of short chain fatty acids at an oil−water interface calculated from the Langmuir equation modified by Haydon and Taylor[58] have been compared critically with $\Delta G_B°$ calculated[59,69] on the basis of the Gibbs adsorption equation as discussed in the present paper. $\Delta G_B°$ for butyric, valeric, caproic, and caprylic acids are 18.4, 22.7, 25.1, and 33.7 kJ mol^{-1}, whereas corresponding values of $\Delta G_L°$ are 16.4, 19.4, 22.8, and 31.7 kJ mol^{-1}, respectively. $\Delta G_L°$ values in all cases are less than $\Delta G_B°$ and their difference is 2−3 kJ mol^{-1}. In the treatment of Langmuir, $\Delta G_L°$ is related to only chemical interaction of the surfactant with a surface whereas in the treatment of Bull based on the Gibbs equation $\Delta G_B°$ includes all types of adsorbate−adsorbent interaction occurring at the inhomogeneous interfacial phase.[69] Unlike $\Delta G_L°$ based on the linear plot of the Langmuir equation, no such linear plot is needed for the calculation of $\Delta G_B°$ and further the approach can be used for ionized monolayers, negative adsorption, etc. most conveniently.

Using eqs 44 and 46 valid for the positive adsorption of surfactants and negative adsorption of inorganic salts on the solid−liquid interfaces, respectively, values of $\Delta G°$ have been calculated. $\Delta G°$ values presented in Tables 1 and 2 are found to increase almost proportionately with the increase of $\Gamma_2{}^m$ so that according to eq 38, $\Delta G_B°$ (equal to $\Delta G°/\Gamma_2{}^m$) for different systems are quite close to each other. As pointed out earlier, various factors are affecting $\Delta G°$ and $\Gamma_2{}^m$ to a similar extent so that the ratios of $\Delta G°/\Gamma_2{}^m$ (equal to $\Delta G_B°$) do not differ from each other significantly. Unlike $\Delta G°$, $\Delta G_B°$ cannot be used to compare the relative affinities for adsorbate−adsorbent interaction. This can only be achieved by comparing $\Delta G°$, the free energy change per unit surface area. $\Delta G°$ is equal to free energy change per mole of adsorbed surfactant multiplied by the moles of surface-active sites available per unit surface area.

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It may be pointed out that biopolymers such as proteins, nucleic acids, and polysachharides possess a colloidal dimension, but unlike suspended solids, they dissolve in the aqueous solvent without formation of any physical surface. These polymers termed as biocolloids are able to bind surfactants under specific physicochemical conditions. The equation for the calculation of the excess binding (Γ_2^1) of a surfactant to biocolloid is similar to eqs 1 and 2 used for the adsorption of the surface-active agent at the solid−liquid interface. It has been shown[83−89] that moles of absolute binding (Δn_1 and Δn_2) of solvent and solute, respectively, to 1 kg (or 1 mol) of biopolymer can be equated to Γ_2^1 by using eq 20 derived on thermodynamic grounds for a single-phase system. Also following a similar argument for the one-phase system, a standard free energy change for binding saturation of surfactant to 1 kg (or 1 mol) of biocolloid can be estimated using a similar eq 45 derived elsewhere.[83−89] With isopiestic experiments, negative binding $-\Gamma_2^1$ for various inorganic electrolytes to 1 kg (or 1 mol) of biopolymer forming aqueous solution or hydrated gel have been calculated for soluble proteins, starch, and carboxymethyl cellulose using eq 1. Also using equation similar to relation 46 derived elsewhere,[84−88] a standard free energy change $\Delta G°$ for binding interaction to the biocolloids per kilogram (or per mole) can be calculated. A universal scale of free energy change due to positive and negative binding of solute to 1 kg of biocolloid have been similarly proposed in which the bulk solute activity is unity in all cases.[84,85]

From all these discussions, the following may be concluded:

(a) The surface excesses Γ_2^1 and $\Gamma'_1{}^2$ for solid−liquid and fluid interfaces in contact with the bulk solution of solvent and surface active solute or inorganic salt, respectively, can be determined using analytical, isopiestic, or boundary tension experiments. Γ_2^1 and $\Gamma'_1{}^2$ are not independent but are related to each other by eq 8.

(b) Integrating the Gibbs equations for adsorption of surfactant and neutral salt, respectively, negative or positive values of the standard free energy $\Delta G°$ for the adsorption of surfactants or salt in kilojoules per unit surface area have been estimated for change of the bulk activity of the solute from zero to unity. A universal scale for $\Delta G°$ has been proposed to compare affinities of solute (surfactant or neutral salt) for a surface. An equation for $\Delta G°$ for solid−liquid interface has been derived, and a generalized free energy scale has similarly been proposed for adsorption phenomena occurring at a solid−liquid interface.

(c) The experimentally measured quantities Γ_2^1 and $\Gamma'_1{}^2$ for relative adsorption are based on the following assumptions: (i) only one component is adsorbed and other components are not involved in the adsorption process at solid−liquid interfaces; (ii) alternatively such an assumption is indirectly involved in the derivation of the Gibbs adsorption equation by putting Γ_1^1 or Γ_2^2 equal to zero by arbitrary placement of the Gibbs dividing plane in the surface region. In both cases, it has been shown that eq 20 or 21 remains valid. Equation 20 relating the Gibbs surface excess Γ_2^1 based on the placement of the Gibbs dividing plane arbitrarily is shown to be linearly related to the actual composition (Δn_1 and Δn_2) of the inhomogeneous surface phase first imagined to exist by Guggenheim.

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