Langmuir **1985**, *1*, 673–678 673

A Quantitative Theory of Negative Adsorption of Nonelectrolytes Caused by Repulsive van der Waals Forces

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Received June 6, 1984. In Final Form: April 1, 1985

It is known that sucrose raises the surface tension of water; it is negatively adsorbed at the air/water interface. We have analyzed this phenomenon from the point of view that the solute molecules are repelled from the interface because of the existence of a repulsive van der Waals force. The theoretical treatment employs the Lifshitz theory of forces, together with the thermodynamic theory of interfacial distances. Our calculation has yielded a quantitative prediction of the increase in surface tension of water as a function of solute concentration, which agrees well with experimental observations. It also predicts the concentration gradient of solute molecules in the region below the surface.

Introduction

It is a familiar fact of surface science that electrolyte solutes in water cause an increase in surface tension above that of the pure solvent. It is not so well-known that certain nonelectrolytes also cause an increase in surface tension. For both types of solutes, the change in surface tension is certainly due to negative adsorption.

Wagner[1] and Onsager and Samaras[2] have developed the theory of the effect of electrostatic forces on ions at and near an air/water interface. The electrostatic "image force" causes a net repulsion to act on the ions, so that they are excluded from the interfacial region. Onsager and Samaras were able to make predictions of the phenomenon which were in a fair agreement with experimental observations.

The negative adsorption of nonelectrolytes such as sucrose at the air/water interface suggests that a repulsive force should be inferred, acting on the solute molecules.

Initial attempts to treat the case of nonelectrolyte solutions were made by Buff and Goel.[3] They applied their calculations to the case of aqueous amino acids. The surface excess quantity was distributed between two parameters, $\bar{\alpha}$ and $\bar{\beta}$, where the former designated the surface activity of the fatty acid portion of the amino acids. The numerical magnitude of $\bar{\alpha}$ was derived utilizing the empirical relation between the surface tension decrease and the chain length of the lower fatty acids, known as Traube's rule. (The surface tension of aqueous fatty acid solutions is a linear function of the solute concentration in the Henry's law region. Traube's rule[4] states that the proportionality factor between the decrease in surface tension and solute concentration is, in turn, a linear function of the chain length of the fatty acids.) The second parameter was assigned to the effect arising from an inverse cubic interaction law. This law was derived from an analytical solution of the electrostatic problem of multipoles embedded in a spherical cavity. Although Buff and Goel took into account the effects due to multipole interactions, they showed that the dipolar contribution constituted the dominant term in the net cavity image potential. Later, Clay, Goel, and Buff,[5] in a more detailed treatment, considered the effects of finite solute size, anisotropy, and also the diffuse nature of the interface.

The approximate mathematical expression for the image potential of a randomly oriented dipole, obtained by Buff and Goel, was

$$w(z) = \frac{\mu^2 \phi_1}{12 \epsilon_m z^3} \tag{1}$$

where μ is the dipole moment of the solute molecule, ϵ_m is the dielectric constant of water, z is the distance of the dipole from the air/water interface, and ϕ_1 is a dimensionless correction factor, which ranges from 1 to 2.23. Since $\mu^2/3kT$ has the dimensions of the static dipolar polarizability, we can rearrange eq 1 in a convenient form, such as

$$w(z) = \frac{kT\phi_1}{4z^3}\left(\frac{\alpha}{\epsilon_m}\right) \tag{2}$$

where k is Boltzmann constant, T is absolute temperature, and α is the dipole polarizability of the solute molecule in a vacuum.

We note, however, that the electrostatic behavior of a solute molecule that is due to the presence of the phase boundary (liquid/vapor or liquid/air) cannot be accounted for merely by the polarizability of the solute. The solute molecule replaces an equal volume of solvent, which (in the absence of solute) had a self-energy due to the surrounding solvent and to the *absence* of solvent on the other side of the phase boundary. Thus, it is more correct to employ an "excess" polarizability, α^*, rather than α which is given by $\mu^2/3kT$.

So, in the limit of a continuum approximation, one would expect that $w(z)$ should be zero when the solute has the same dipole moment and dielectric constant as the solvent. Also, $w(z)$ should be negative if the dipolar polarizability of the solute is less than that of the solvent.

Unfortunately, these two expectations cannot be derived from eq 1 and 2. In order to elucidate the limits of validity of eq 2, we will now focus our attention on an improved expression for the self-energy of the solute molecule, as derived by Imura and Okano.[6] Israelachvili,[7] following the procedure of previous authors, has shown that the electrodynamic self-energy of a randomly orienting solute molecule, at a distance z from the air/water interface, can be expressed as

$$g(z) = -\frac{kT}{2z^3}\sum_{n=0}^{\infty}{}' \frac{\alpha^*_s(i\omega_n)}{\epsilon m(i\omega_n)}\left[\frac{\epsilon_j(i\omega_n) - \epsilon_m(i\omega_n)}{\epsilon_j(i\omega_n) + \epsilon_m(i\omega_n)}\right] \tag{3}$$

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where $\alpha^*_s(i\omega_n)$ is the excess polarizability of the solute molecule and $\epsilon_j(i\omega_n)$ and $\epsilon_m(i\omega_n)$ are respectively the dielectric permeability of air and of water; these functions are evaluated along the complex frequency axis, $i\omega_n$.[7] The prime in the sum indicates that the zero frequency term is given half-weight in the summation. The zero frequency term in eq 3 originates from the orientation and the induction contributions to the multipole image interaction.[7] Since the static dielectric constant of air is unity and that of water is about 80, $\epsilon_m >> \epsilon_j$, and we can obtain a simplified, approximate expression for $g(z)_{n=0}$ from eq (3), as follows:

$$g(z)_{n=0} = \frac{kT}{4z^3}\left(\frac{\alpha^*_s}{\epsilon_m}\right) \tag{4}$$

where α^*_s is now the excess static polarizability of the solute, the dominant term of which is due to the dipolar contribution, for a polar solute.

It is worthwhile to note the similarity of form, between eq 4 and 2. Equation 4 is, however, significantly different from eq 2, since, in the derivation of eq 3, and hence of eq 4, the concept of *excess* polarizability was invoked. Equation 4 potentially can predict that $g(z)_{n=0}$ can be zero, negative or positive, depending upon the sign of α^*_s.

An approximate expression for α^*_s has been given by McLachlan,[8] as follows:

$$\alpha^*_s = \epsilon_m\left(\frac{\epsilon_s - \epsilon_m}{\epsilon_s + 2\epsilon_m}\right)r^3 \tag{5}$$

where, ϵ_s is the dielectric constant of the solute and r is the radius of the solute, in the spherical approximation. From eq 4 and 5, it is clear that if $\epsilon_s < \epsilon_m$, α^*_s will be negative, and it will be positive when $\epsilon_s > \epsilon_m$. The values of the static dielectric constants for most water-soluble nonelectrolytes are generally smaller than that of water, and, hence, in view of eq 4 and 5, one would expect a positive adsorption of the solutes, but Buff and Goel's equation will only predict a negative adsorption.

The complete, exact treatment of positive and negative adsorption of dipolar nonelectrolytes in aqueous solution is far more complicated than has been believed to be the case, mainly because no general, quantitative theory exists that can properly account for the effects due to short-range forces, especially hydrogen bonding. The assumptions of electromagnetic theory, from the earliest "image force" treatment to the sophisticated Lifshitz approach[9] require that the distances considered be large compared to the distance between centers of charge. This directly excludes hydrogen bonds from the treatment. Moreover, hydrogen bonds are known to be partially covalent in character. The inclusion of hydrogen bonding in the continuum treatment of surface phenomena, e.g., using dipole–dipole (Keesom) interaction as a surrogate,[10] has allowed hydrogen bonding to be included as a contributor to Hamaker coefficients[10,11] and hence to a widely used treatment of surface tension.[12-14] But the inherently short-range and directional character of hydrogen bonds is mathematically incompatible with the inherently long-range character of electromagnetic (London, Debye, or Keesom) interactions. Therefore, it is justified, or indeed necessary, to introduce a sharp dichotomy of short-range (SR) interactions vs. long-range interactions. The latter can be treated by the methods of London[15,16] and Lifshitz;[9] we refer to them, elsewhere,[17,18] as "LW".

In principle, if the enthalpy of hydration of a solute is known, the contribution of the H-bond interaction to the net surface excess quantity can be estimated by using a step-function Boltzmann equation for the concentration profile. Fowkes[19] has put forth the idea that the H-bond interaction is a subset of acid/base interaction, and proposed the use of Drago's empirical acid/base parameters[20] in obtaining a quantitative estimate of the H-bond interaction. Drago's table of these parameters is, unfortunately, far from complete, and hence the Drago-Fowkes approach cannot be followed at the present time.

If we encounter a situation where the solute is strongly hydrated, so that the energy of hydration is much larger than the average kinetic energy, then we can simplify the picture by assuming that at least the first monolayer of water at the interface will be devoid of solute. This assumption points directly to a negative adsorption of the solute. But it does not, in general, account for the magnitude of the negative adsorption. The profile of solute concentration as a function of distance from the surface is needed. For example, it would be possible to envision a case where the profile of concentration vs. distance could have a maximum just below the surface layer, even though the very last layer was solute-depleted. Such a distribution would be rare, because it would require the combining of low polarizability of the solute with a strong tendency toward hydrogen bonding to water. In principle, we can calculate the contribution due to electrodynamic forces by using the expression for the self-energy of the solute, following Israelachvili's approach.[7] There is, however, an immediate difficulty: it is not very clear as to what should be the best mathematical form for $\alpha^*_s(i\omega_n)$ as a function of dielectric permeabilities of the solute and the solvent. For example, we note that eq 5 is only an approximation. Fortunately, there is a better approach, since, in principle, it is feasible to arrive at an expression for the self-energy of the solute in a solvent phase by using the Lifshitz theory of forces. Approaches similar to that described below have been used by other workers in related fields.[21-23]

We will now develop an expression for the self energy of the solute, using the Lifshitz theory of flat-plate interaction. This procedure, coupled with Gibbsian thermodynamics of interfacial distances, will then be applied to calculate the increase in the surface tension of sucrose solution as a function of solute concentration. This result will in turn be compared with the available experimental data. Toward the end of this paper, some relevant numerical calculations will be made for the self-energy of the solute, utilizing Israelachvili's approach, and these will be compared with the result obtained by the Lifshitz theory.

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Theory

In order to calculate the free energy (self-energy) of an electrically neutral molecule (1) in medium (3) at a distance, z, from the interface between fluids 2 and 3, we will use the Lifshitz theory of electromagnetic interactions across a phase boundary. According to this theory,[9] the free energy of interaction between two semiinfinite parallel slabs, j and k, through a medium, m, of thickness, l, is expressed as

$$G(l) = -\frac{kT}{8\pi l^2}\sum_{n=0}^{\infty}{}'\left[\frac{\epsilon_j(i\omega_n) - \epsilon_m(i\omega_n)}{\epsilon_j(i\omega_n) + \epsilon_m(i\omega_n)}\right]\left[\frac{\epsilon_k(i\omega_n) - \epsilon_m(i\omega_n)}{\epsilon_k(i\omega_n) + \epsilon_m(i\omega_n)}\right] \quad (6)$$

where ϵ_j, ϵ_k, and ϵ_m are, respectively, the dielectric permeabilities of the phases j, k, and m along the complex frequency axis, $i\omega_n$;[9,24] i.e.,

$$\epsilon = \epsilon(i\omega_n) = 1 + \frac{2}{\pi}\int_0^{\infty}\frac{\omega\epsilon''(\omega)}{(\omega^2 + \omega_n^2)}\,d\omega \quad (7)$$

where $\epsilon''(\omega)$ is the loss component of the frequency-dependent dielectric function, $\epsilon(\omega) = \epsilon'(\omega) + i\epsilon''(\omega)$, $\omega_n = 4\pi^2 nkT/h$, h = Planck's constant, and n = quantum number of the relevant oscillation. The prime on the summation sign indicates that the $n = 0$ term is given half-weight in the sum. It will be shown below, the eq 26, how ϵ_j, ϵ_k, and ϵ_m are to be evaluated.

Since we are interested in the aqueous solution/air interface, we will use a notation in which the medium 2 or j is air, medium 3 or m is water, and medium k is the solution.

We will assume, first, that the solution is dilute, so that as far as mutual interaction of the solute molecules is concerned, the rarified medium approximation can be applied. That is to say, the sucrose molecules do not interact with each other, and in their interaction with water, the water can be treated as a continuum.[22] We note that Onsager and Samaras[2] and also Buff and Goel,[3] in their theory of the negative adsorption of solutes, treated water as a continuum.

Second, we will use a preliminary model in which the concentration of the solute molecules is practically zero from the air/water interface down to a depth l, and is constant throughout the rest of the solution phase, i.e., from $z = l$ to $z = \infty$ (see Figure 1). We do this in order to calculate the self-energy of a sucrose molecule as a function of its distance from the air/water interface. (At the conclusion of this section, we will make some calculations that have a bearing on the validity of the model.)

It is to be noted that, in this procedure, the interaction of the water molecules *in the solution*, with air, *through a water film*, is set equal to zero. As a result, we need to calculate the energy of interaction of only the solute molecules in the solution phase, with air, through a film of water of thickness of l.

Let us now assume that the interaction energy with the air phase, of a single solute molecule in the solution, at a distance z from the air/water interface, is represented approximately by

$$G(z) = -a/|z|^{\nu} \quad (8)$$

Since $G(z)$ cannot be infinite, this applies in the region that extends from some small distance from the physical interface, e.g., one molecular diameter, to the region where the solute concentration has its bulk value, $c_s(b)$.

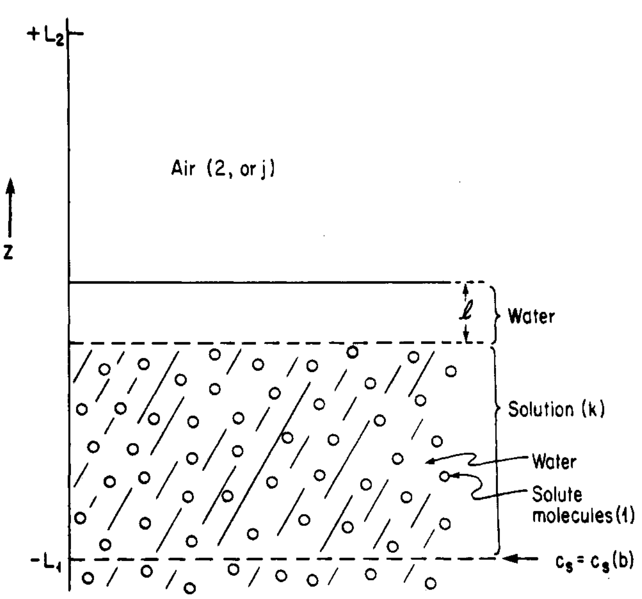

Figure 1.

If N_s denotes the number of solute molecules per unit volume, then the total energy of interaction of all solute molecules in unit volume of the solution phase, with air, through a water film of thickness l (see Figure 1) is

$$G(l) = -N_s\int_l^{\infty}\frac{a}{|z|^{\nu}}\,dz = -\frac{N_s a}{(\nu - 1)l^{\nu-1}} \quad (9)$$

This $G(l)$ is the same as the $G(l)$ in eq 6. Hence, it may be deduced that the power of z in eq 8 is equal to 3. This will be exact when $l >> r$, where r is the molecular radius of the solute. The coefficient a is given by

$$a = \frac{kT}{4\pi N_s}\sum_{n=0}^{\infty}{}'\left[\frac{\epsilon_j - \epsilon_m}{\epsilon_j + \epsilon_m}\right]\left[\frac{\epsilon_k - \epsilon_m}{\epsilon_k + \epsilon_m}\right] \quad (10)$$

It is possible to evaluate the coefficient, a, in eq 8, if we know the loss component of the dielectric permeabilities of water and of the solute in pure phases as a function of frequency. Expressing N_s in terms of volume fraction, ϕ_s, and the volume $(4\pi r^3/3)$ of a single solute molecule treated as a sphere, eq 10 can be simplified to

$$a = \frac{kT}{3\phi_s}r^3\sum_{n=0}^{\infty}{}'\left[\frac{\epsilon_j - \epsilon_m}{\epsilon_j + \epsilon_m}\right]\left[\frac{\epsilon_k - \epsilon_m}{\epsilon_k + \epsilon_m}\right] \quad (11)$$

If the coefficient a in eq 8 is negative, the solute particle will be repelled from the interface, and negative adsorption will prevail.

The concentration of the solute in an aqueous medium at a distance z from the liquid/vapor interface may then be expressed in terms of Boltzmann's equation, relative to the concentration $c_s(b)$ in the bulk:

$$c_s(z) = c_s(b)\exp[-G(z)/kT] \quad (12)$$

See Figure 2, the line representing $c_s(z)$.

At constant temperature, the Gibbs adsorption equation[25], may be written in the form[26]

$$d\gamma = -\sum\Gamma_i^{(\beta)}\,d\mu_i \quad (13)$$

where μ_i is the chemical potential and $\Gamma_i^{(\beta)}$ is the Gibbsian surface excess of component i with respect to a surface

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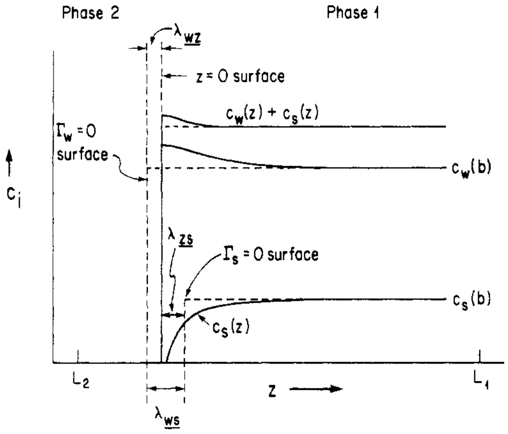

Figure 2. Schematic concentration profiles. Subscripts w refers to water and s to sucrose. Dashed lines indicate Gibbs construction for dividing surfaces: $\Gamma_s = 0$ surface, $\Gamma_w = 0$ surface, and $z = 0$ surface.

defined by an arbitrary criterion $\hat{\beta}$. (We will, for clarity, employ symbols with a circumflex to denote dividing surfaces. $\hat{\beta}$ designates a dividing surface for which the criterion that identifies it has not yet been specified.) We will employ, for the criterion $\hat{\beta}$, the $z = 0$ surface, i.e., a surface that is assumed to coincide with the geometric surface, which demarcates the liquid phase from the vapor phase, and denote it by the superscript $(\hat{z})$ or, in Figures 2 and 3, by underlining. We may now write

$$d\gamma = -\sum \Gamma_i^{(\hat{z})}\, d\mu_i \tag{14}$$

$\Gamma_i^{(\hat{z})}$ can be expressed in the form[26]

$$\Gamma_i^{(\hat{z})} = \int_{-L_1}^{z=0} [c_i(z) - c_i(b_1)]\, dz + \int_{z=0}^{L_2} [c_i(z) - c_i(b_2)]\, dz \tag{15}$$

where the integration is carried out over a path normal to the interface, from a location at $-L_1$, deep within bulk phase 1, to a location L_2, deep within bulk phase 2 (see Figure 2). $c_i(z)$ is the concentration of component i at elevation z and $c_i(b_1)$ and $c_i(b_2)$ are bulk concentrations of i in phases 1 and 2, respectively. Since medium 2 is air, the concentration of both water and sucrose may be taken as effectively zero in that phase, so that the second integral vanishes. Then eq 15 can be written

$$\Gamma_i^{(\hat{z})} = \int_0^{L_1} [c_i(z) - c_i(b)]\, dz \tag{16}$$

where we have dropped the subscript 1 on b.

The concentration c_i of the ith component in an ideal solution can be expressed in terms of the volume fraction ϕ_i:

$$c_i = \phi_i \rho_i / M_i \tag{17}$$

where ρ_i and M_i are, respectively, the density and molecular weight of that component in its pure state. Equation 15 can be used with eq 29, below, to relate the surface excesses, $\Gamma_w^{(\hat{z})}$ and $\Gamma_s^{(\hat{z})}$, to each other.

It has been shown[26] that the distance between the Gibbs dividing surfaces for $\Gamma_w = 0$ and for $\Gamma_s = 0$ is $\lambda_{\hat{w}\hat{s}}$. If the solute is negatively adsorbed, the $z = 0$ surface lies between the $\Gamma_w = 0$ and $\Gamma_s = 0$ surfaces (see Figure 2).

The surface excesses of water and of solute with respect to the $z = 0$ surface can now be expressed as

$$\Gamma_w^{(\hat{z})} = \lambda_{\hat{w}\hat{z}} c_w(b) = \frac{\rho_w}{M_w} \int_0^{L_1} [\phi_w(z) - \phi_w(b)]\, dz \tag{18a}$$

and

$$\Gamma_s^{(\hat{z})} = \lambda_{\hat{z}\hat{s}} c_s(b) = \frac{\rho_s}{M_s} \int_0^{L_1} [\phi(z) - \phi_s(b)]\, dz \tag{18b}$$

where $\lambda_{\hat{w}\hat{z}}$ and $\lambda_{\hat{z}\hat{s}}$ are the Gibbsian distance parameters[26] for water and solute, respectively, relative to the $z = 0$ surface, and L_1 is large compared to the thickness of the interfacial region, i.e., effectively infinity (see Figure 2):

$$\lambda_{\hat{w}\hat{s}} = \lambda_{\hat{z}\hat{s}} + \lambda_{\hat{w}\hat{z}} \tag{19}$$

$\lambda_{\hat{w}\hat{s}}$ the last section, we will evaluate $\lambda_{\hat{w}\hat{s}}$ from experimental data. $\lambda_{\hat{w}\hat{s}}$ is of considerably more operational significance than $\lambda_{\hat{w}\hat{z}}$ or $\lambda_{\hat{z}\hat{s}}$. Since $\phi_w = (1 - \phi_s)$, eq 15, 18a, and 18b can be combined to obtain

$$\lambda_{\hat{w}\hat{z}} = -[\phi_s/\phi_w]\lambda_{\hat{z}\hat{s}} \tag{20}$$

$\lambda_{\hat{z}\hat{s}}$, which is equal to $\Gamma_s^{(\hat{z})}/c_s(b)$, is given by

$$\lambda_{\hat{z}\hat{s}} = \frac{\Gamma_s^{(\hat{z})}}{c_s(b)} = \int_0^{L_1} \left[\frac{c_s^{(z)}}{c_s(b)} - 1 \right] dz \tag{21}$$

Through the employment of eq 12, eq 21 simplifies to

$$\lambda_{\hat{z}\hat{x}} = \int_0^{L_1} \left[\exp\left(-\frac{G(z)}{kT} \right) - 1 \right] dz \tag{22}$$

The chemical potential, μ_i, can be written in terms of the mole fraction, x_i, of the ith component as

$$\mu_i = \mu_i^\circ + RT \ln x_i \tag{23}$$

where μ_i° is the standard chemical potential of the ith component and x_i is the mole fraction of i.

Substituting eq 23 into eq 14 and using eq 19 and 20 yields

$$d\gamma = -\lambda_{\hat{z}\hat{s}} RT[N/V_w]\, dx_s \tag{24}$$

where $N = N_w + N_s$ is the total number of moles and V_w is the volume of pure water in the solution. Integrating eq 24, we obtain

$$\Delta\gamma = \gamma - \gamma_0 = -\lambda_{\hat{z}\hat{s}} RT \int_0^{x_s} (N/V_w)\, dx_s \tag{25}$$

Application to Sucrose Solutions

In order to estimate $G(z)$, the free energy of interaction, our first task is to find a suitable representation of the dielectric permeability, $\epsilon_j(i\omega_n)$. An expression for $\epsilon_j(i\omega_n)$ which Ninham and Parsegian[27] developed from eq 7 can be used:

$$\epsilon_j(i\omega_n) = 1 + \frac{(\epsilon_\infty - \epsilon_0)}{1 + \left[\dfrac{\omega_n}{\omega_{MW}}\right]} + \frac{(\epsilon_0 - n_0^2)}{1 + \left[\dfrac{\omega_n}{\omega_{IR}}\right]^2} + \frac{(n_0^2 - 1)}{1 + \left[\dfrac{\omega_n}{\omega_{UV}}\right]^2} \tag{26}$$

where ϵ_∞ = zero frequency dielectric constant, ϵ_0 = dielectric constant in the microwave range at the high frequency limit, n_0 = refractive index in the optical region, and ω_{MW}, ω_{IR}, and ω_{UV} are the characteristic absorption frequencies in the microwave, infrared, and ultraviolet regions, respectively. For sucrose there is a small, insignificant infrared relaxation. The dielectric constant of sucrose in the microwave region is about 3.3,[28] which is not significantly different from the square of the refractive index (n_0^2 =

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Table I. Dielectric and Optical Properties of the Substances Employed

				characteristic frequencies			
material	ϵ_∞	ϵ_0	n_0	$\omega_{MW} \times 10^{-11}$, rad/s	$\omega_{IR} \times 10^{-14}$, rad/s	$\omega_{UV} \times 10^{-16}$, rad/s	ref
water	80.1	5.2	1.332	1.06	5.66	1.9	31
sucrose		3.3	1.5376			2.3	32

2.38) in the optical region. The infrared term is small enough that neglecting it will not cause significant error in the numerical computation of the coefficient a. (For further details on this subject, see ref 29.)

In order to calculate a in eq 8, we have decomposed the sum, eq 11, into two terms, as follows:

$$a_{n=0} = \frac{kT}{6\phi_s} r^3 \left[\frac{\epsilon_j - \epsilon_m}{\epsilon_j + \epsilon_m} \right] \left[\frac{\epsilon_k - \epsilon_m}{\epsilon_k + \epsilon_m} \right] \tag{27a}$$

and

$$a_{n>0} = \frac{kT}{3\phi_s} r^3 \sum_{n=1}^{\infty} \left[\frac{\epsilon_j - \epsilon_m}{\epsilon_j + \epsilon_m} \right] \left[\frac{\epsilon_k - \epsilon_m}{\epsilon_k + \epsilon_m} \right] \tag{27b}$$

When j refers to air, ϵ_j will be taken as unity. To calculate $a_{n=0}$, we have used the available data[30] for the static dielectric constant of sucrose solutions. $a_{n=0}$, which was independent of ϕ_s, was found to be equal to $0.055kTr^3$.

In order to carry out the summation in eq 27b, we have expressed the dielectric permeability of the solution, ϵ_k, in terms of ϵ_w and ϵ_s, via the Lorentz–Lorenz equation, in the form

$$\frac{\epsilon_k - 1}{\epsilon_k + 2} = \phi_w \left[\frac{\epsilon_w - 1}{\epsilon_w + 2} \right] + \phi_s \left[\frac{\epsilon_s - 1}{\epsilon_s + 2} \right] \tag{28}$$

$a_{n>0}$ was calculated by using eq 26–28 in conjunction with the dielectric data of Table I. The value of $a_{n>0}$ was thus found to be $-1.06kTr^3$. The value of a $(=a_{n=0} + a_{n>0})$ may now be estimated as $-kTr^3$.

At this point, for the sake of comparison, we will recalculate the value of the coefficient a, using eq 3. Substituting the expression of α^*_s from eq 5 into eq 3, one immediately arrives at the following expression:

$$g(z) = -\frac{kTr^3}{2z^3} \sideset{}{'}\sum_{n=0}^{\infty} \frac{[\epsilon_s(i\omega_n) - \epsilon_m(i\omega_n)][\epsilon_j(i\omega_n) - \epsilon_m(i\omega_n)]}{[\epsilon_s(i\omega_n) + 2\epsilon_m(i\omega_n)][\epsilon_j(i\omega_n) + \epsilon_m(i\omega_n)]} \tag{3a}$$

The coefficient a now can be expressed as

$$a = \frac{kTr^3}{2} \sideset{}{'}\sum_{n=0}^{\infty} \frac{[\epsilon_s(i\omega_n) - \epsilon_m(i\omega_n)][\epsilon_j(i\omega_n) - \epsilon_m(i\omega_n)]}{[\epsilon_s(i\omega_n) + 2\epsilon_m(i\omega_n)][\epsilon_j(i\omega_n) + \epsilon_m(i\omega_n)]} \tag{11a}$$

Equation 11a is formally similar to eq 11. It can, however, be noted that, in eq 11a, the dielectric permeability of the solute $\epsilon_s(i\omega_n)$ appears explicitly, whereas, in eq 11, the contribution of the solute is implicit in the dielectric permeability of the solution, $\epsilon_k(i\omega_n)$.

Using the Ninham and Parsegian representation (eq 26) for the dielectric permeabilities of all the species involved, and the parameters in Table I, we have calculated the values of $a_{n=0}$ and $a_{n>0}$ from eq 11a. The values of $a_{n=0}$ and $a_{n>0}$ were thus found to be $0.126kTr^3$ and $-1.113kTr^3$, respectively. This gives the value of net a $(=a_{n=0} + a_{n>0})$ to be $-0.986kTr^3$, which is indeed very close to the value obtained by Lifshitz theory (eq 11).

The fact that the net coefficient a is negative indicates that sucrose will be repelled by the air/water interface, and negative adsorption will prevail.

Quantitative Results and Discussion

On the basis of the above discussion, the Boltzmann expression, eq 12, can be simplified to

$$c_s(z) = c_s(\mathrm{b}) \exp[-(r/z)^3] \tag{29}$$

In order to calculate the Gibbsian distance parameter, $\lambda_{\hat{z}\hat{s}}$, we have decomposed the integral, eq 21, into two parts and let L go to infinity:

$$\lambda_{\hat{z}\hat{s}} = \int_0^{\delta} \left[\frac{c_s(z)}{c_s(\mathrm{b})} - 1 \right] \mathrm{d}z + \int_{\delta}^{\infty} \left[\frac{c_s(z)}{c_s(\mathrm{b})} - 1 \right] \mathrm{d}z \tag{32}$$

where δ is a distance of the order of the diameter of a water molecule.

In the region $0 < z < \delta$, eq 29 does not apply. At such short distances, short-range interactions which do not obey the Lifshitz theory become important. Since sucrose molecules interact with the surrounding water molecules through formation of hydrogen bonds, the sucrose molecules are, effectively, solvated. The energy of formation of a hydrogen bond is in the range of 3–5 kcal/mol. Desolvating a sucrose molecule by removal of all the water molecules that would lie between it and the gas phase would require at least 3 times this energy, depending on orientation of the sucrose molecule. So the energy requirement will be about 15–25 times kT at room temperature, and the Boltzmann probability of finding a sucrose molecule in the region, $z < \delta$, will be in the range 2×10^{-7} to 1×10^{-11}. Even if the energy to detach a water molecule were only 1.35 kcal (or 4 kcal for three molecules) the Boltzmann factor would be 10^{-3}; and this would correspond to effectively total exclusion of water from that region.

In the region, $\delta < z < \infty$, the Boltzmann relation (eq 29) will be applicable. So we can rewrite eq 30 as

$$\lambda_{\hat{z}\hat{s}} = -\delta + \int_{\delta}^{\infty} [e^{-(r/z)^3} - 1] \, \mathrm{d}z \qquad 31$$

The diameter δ for water, as estimated from the density and molecular weight data, is about 3.5 Å. The diameter, $2r$, for sucrose, is about 8.0 Å.

In order to estimate $\lambda_{\hat{z}\hat{s}}$, the integral in eq 31 was evaluated by expanding the exponential in a power series and integrating term by term until a satisfactory convergence was observed. This led to an estimate of $\lambda_{\hat{z}\hat{s}}$, the Gibbsian distance parameter of sucrose in water, of 5.5 Å.

For sucrose solutions, N/V_w as a function of x_s was found to be linear. Data were taken from ref 28, to obtain the equation

$$N/V_w = 0.0555 + 0.05954x_s \tag{34}$$

where N and V_w are expressed in mol and cm^3, respectively. With the use of eq 32, eq 25 becomes

$$\Delta\gamma = -\lambda_{\hat{z}\hat{s}} RT(0.0555x_s + 0.02977{x_s}^2) \tag{33}$$

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[30] Harned, H. S.; Owen, B. B. "The Physical Chemistry of Electrolyte Solutions", 2nd ed.; Reinhold: New York, 1950; ACS Monogr. No. 95, p 188.

[31] Parsegian, V. A.; Ninham, B. W. *J. Colloid Interface Sci.* **1971**, *37*, 332.

[32] Nir, S. *Progr. Surf. Sci.* **1977**, *8*, 1–58.

Table II. Change of the Surface Tension of Water as a Function of Sucrose Concentration

concentration of sucrose, wt%	$\Delta\gamma_{\text{calcd}}$, dyn/cm	$\Delta\gamma_{\text{exptl}}$, dyn/cm ref 19
10	0.45	0.5
20	1.0	1.0
30	1.64	1.4
40	2.6	2.1
55	4.6	3.7

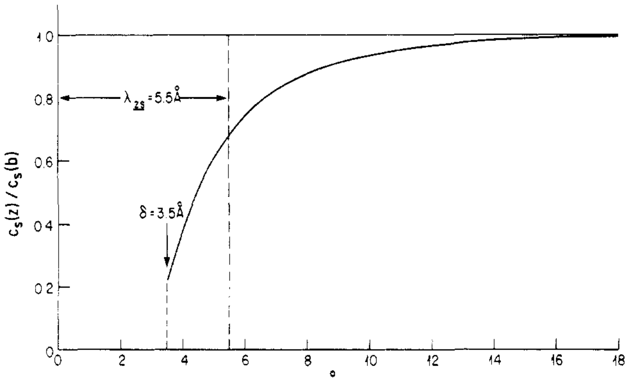

Figure 3. Calculated dimensionless distribution of sucrose as a function of distance from the $z = 0$ surface.

At this stage, we can compute $\Delta\gamma$ as a function of solute concentration. The results are shown in Table II, where they are compared with the experimental values. The agreement with experiment is excellent, for the lower concentrations. At higher concentrations of sucrose, the theory overpredicts the value of $\Delta\gamma$ by about 0.5–0.9 dyn/cm; this is not a high level of disagreement.

Figure 3 shows the calculated relative concentration of sucrose vs. distance from the $z = 0$ surface. As already noted, the model breaks down for distances less than about 3.5 Å. The smooth curve in Figure 3 describes average, not instantaneous, composition, of course. It is interesting that the sucrose concentration reaches about 90% of the bulk concentration at a distance of about 8 Å, or the diameter of a sucrose molecule (treated as a sphere) from the $z = 0$ surface. If we assume that the region of total exclusion of sucrose is 3.5 Å thick, we can see from Figure 3 that this region accounts for no more than about 60% of the negative adsorption.

Discussion

The discrepancy between the experimental and theoretical values of $\Delta\gamma$ at higher concentrations is probably due to a number of factors which were not included in the approximation of this theory:

(1) The interactions of solute molecules among themselves were neglected. In a more realistic approximation, three- and many-body effects will come into the picture, especially at high concentrations.

(2) The electromagnetic interaction may be screened because of the diffuse nature of the distribution of sucrose from the interface to the bulk. This fact was neglected in the approximation employed.

(3) We have used a continuum model for water, which will break down when $z \rightarrow r_w$, the radius of the water molecule. This breakdown will be pronounced, at the higher concentrations of solute.

(4) We have assumed that the solute molecule is isotropic, which is not exact for sucrose.

(5) Better spectroscopic data are needed, and also a better representation of $\epsilon(i\omega_n)$, for the actual calculations.

With refinements such as these, it should be possible to improve upon these computations that we have made.

Conclusion

The important conclusion of this paper is that the elevated surface tension of sucrose solutions, due to the negative adsorption of solute molecules at the air/solution interface, is a manifestation of the short-range forces between sucrose and water and the electrodynamic repulsion of the (hydrated) solute molecules from the surface. The negative adsorption can be predicted nearly quantitatively by means of the Lifshitz theory.

In spite of the simplifications employed, the results that we have obtained are in excellent agreement with experiments, except at high concentrations. This agreement encourages us to feel that the theory is probably correct.

Acknowledgment. We thank the NSF for support of this work under Grant CPE 79-18245.

Registry No. H_2O, 7732-18-5; sucrose, 57-50-1.