

An electrostatic-surface stability interpretation of the “hydrophobic” force inferred to occur between mica plates in solutions of soluble surfactants

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We analyse the data on the “hydrophobic” forces between mica surfaces immersed in solutions of the surfactant CTAB. For the particular regime where these “attractive” forces are not directly seen but are only inferred to exist because of a deviation from expected repulsive forces, we find that there is a strong correlation between the surface electrostatic potential that appears to be the source of electrostatic repulsion and the force at collapse that is used to infer the hypothetical attractive hydrophobic interaction. A simple phenomenological model is presented that takes note of this previously neglected internal correlation. From this model we suggest that, at least in the case of CTAB, the collapse is probably not due to the balance between electrostatic and Van der Waals or “hydrophobic” attractive forces; it is due rather to a shift in the balance between the inter- and intra-surface forces that govern surfactant deposition. Such a view, based on the critical desorption or rearrangement of lipids or other solutes, is consonant with recent reports that the earlier experimental results of Pashley and Israelachvili are not reproduced when one uses purified CTAB. Recognition of solute desorption and adsorption might provide a key to the puzzling data where very long-range net attractive forces are observed but where these forces change with the activity of solutes in the intervening solution.

1. Introduction

Recent interest in the long-range attraction between “hydrophobic” surfaces has been based on two kinds of measurement. Early observations [1] at separations between 1 and 10 nm never showed a net attractive force. Rather, a long-range exponentially decaying attraction was inferred from the collapse of surfaces brought together against a repulsive force, which was taken to be due to the electrostatic double layers emanating from mica surfaces rendered non-polar by the adsorption of soluble CTAB surfactant from the solution. The difference between an extrapolated electrostatic double layer repulsion and the net-zero force when surfaces collapsed together was ascribed to “hydrophobic” attraction. This inferred attraction was said to decay exponentially with a 1 nm decay length [1].

Later measurements, between mica surfaces rendered non-polar by chemical modification or by coating with relatively insoluble surfactants, often show net attractive forces [2,3]. Aside from their

qualitatively exponential decay, attractive forces measured in these various preparations vary greatly with a range and decay rate that almost seem to increase monotonically with the year in which the measurement is made. Most recently [3], forces are reported to occur to separations of 300 nm with exponential decay constants of 42 to 62 nm. Exponential decay is approximately preserved with addition of NaBr [3], or MgSO_4 [4] salt but the coefficient of the force is clearly suppressed even at 10^{-2} M activities. It is worth noting here that the salt-activity sensitivity of interacting-surface energies is *prima facie* evidence of a Gibbs surface excess or depletion of solute from the surface.

Later soluble-surfactant measurements, however, with purified CTAB [5] were so different from the early studies that it was “not possible to obtain an accurate estimate of the magnitude of this (hydrophobic) force”, but collapse of the repulsive force suggested to the authors the action of an attractive component reaching to 20 nm and unpublished data suggested to them an attractive force with a 2.5 nm

decay length in the range 5 to 20 nm. The difference between these later CTAB results and the earlier "CTAB" results might provide a useful clue, that forces reflect adsorption and desorption of solute such as CTAB and what might be with CTAB in impure preparations. Indeed, surfactant adsorption, particularly with reference to the point of surfactant micellization, seems to be a central feature of thinking about the nature of the interacting surfaces [5].

There is no reason a priori why there should be a fundamental connection between the soluble-surfactant results, where attractive forces are only inferred, and the net-attractive-force data, where there is such a plethora of force coefficients and decay lengths [2-4]. The basis of any such connection appears to be the idea that non-polar surfaces perturb water solvent and that the interactions observed are in some sense "hydrophobic forces".

Yet it is increasingly difficult to see how solvent perturbation can be extending literally hundreds of nanometers. For the very reason of range, electrostatically based theories [6,7] seem to fail [4] even though electrostatic forces generally appear to be of longer range than hydration forces. Even between strongly hydrating polar surfaces where they have been detected and systematically measured, repulsive hydration forces seem to exert themselves only out to separations of up to 2 or 3 nm [8-13].

In this paper, then, we return to the soluble-surfactant studies in order to re-examine this part of the literature from the perspective of solute adsorption. We do not try at the same time to examine the longer range forces to which the CTAB data are only problematically related. The results though might provide a clue to thinking about solute-dependent net-attractive forces in the other preparations. In particular, we suggest here that the conundrum of at least this 0 to 10 nm "attractive" force might be explained by more careful consideration of the remarkably powerful electrostatic repulsion seen between surfaces that are taken to be non-polar. Why, e.g., should such surfaces take on reported electrostatic potentials of the order of 100 mV (a best fit from classical DLVO theory) [1]. As a corollary, we suggest that adsorption and desorption of (often unidentified) solutes can be the central factor even in the net attraction that is called "hydrophobic".

In this way of thinking CTA^+ or other, unidenti-

fied ions, though soluble in water, accumulate on the bare charged mica surface because this lowers the electrostatic energy of the surface. They, however, appear to accumulate only up to a point where the lowering of the electrostatic energy on adsorption is compensated by the increase in the "chemical" adsorption energy, part of which is certainly due to the creation of the high-energy hydrophobic coverage of the mica surface. Pushing the two surfaces toward each other raises the electrostatic energy, adding to the system's ability to compensate the unfavorable "chemical" adsorption energy and therefore displacing the surface charge (as well as the surface potential) towards smaller values. (It is also possible that at high enough surfactant concentrations a full monolayer forms on the mica surface. Additional surfactant can deposit on such a fully formed monolayer to lower the energy of the non-polar moieties forming a high-energy hydrocarbon/water interface; deposition will charge the surface, rather than discharge it, to the point where the electrostatic cost of further charging balances the favorable non-electrostatic energy of adsorption to cover the non-polar layer. The fact that potentials can be either positive or negative [5] suggests that one be open to both possibilities.)

Under applied force between repelling surfaces there can exist a critical intersurface separation where the energy required to remain charged exceeds the charge-carrying capacity of the apposed surfaces. The result: discharge and collapse of the two surfaces. In this scenario, there is no significant attractive force, only a marked deviation from an expected repulsive force whose properties should be the real focus of inquiry.

Central to this line of thought is a simple, previously neglected, empirical correlation within the experimental parameters extracted from the data in refs. [2] and [4]:

(a) Take the square of the surface potentials ϕ_∞ . To a first approximation (which we shall use formally in the next section), this is a measure of the self-energy of an isolated surface. To similar approximation, the electrostatic repulsion, at separations where the superposition ansatz is valid, between like charged surfaces goes also as ϕ_∞^2 .

(b) Next take the maximum work $(F/R)_{\text{max}}$, a measure of the maximum work applied to the sur-

faces before they collapse. (It is the deviation of this quantity from the extrapolated electrostatic double layer repulsion that was used in ref. [1] to “measure” an attractive force. It is often forgotten that this quantity, the force between two oppositely curved surfaces, is in fact an energy, the integral of forces at all distances from the minimum separation to infinite separation.)

(c) Take the ratio ϕ_∞^2 divided by $(F/R)_{\max}$ (table 1), a quantity with units of length.

As can be seen in table 1a the ratio $\phi_\infty^2 / (F/R)_{\max}$ is nearly constant for all data sets where these parameters are given in ref. [1]. Note that this ratio varies by some 15% while the maximum force $(F/R)_{\max}$ and surface potential ϕ_∞ vary by some two orders of magnitude!

Data with the purified CTAB, ref. [5], table 1b, show almost as good a correlation, with a rms deviation of 24%.

If the surface energy were purely electrostatic, then

it might be better to test for the constancy of the ratio $\kappa\phi_\infty^2 / (F/R)_{\max}$. This expression treats ϕ_∞ more literally as an electrostatic rather than as a general measure of surface energy. In that case, the pure CTAB data give an even better correlation with an rms standard deviation of 20%.

We suggest, though, that such a literal interpretation of the fitted ϕ_∞ is inappropriate given the very limited information available on the interacting surfaces. Because there is this limited experimental information and because there has been virtually no systematic variation of solution parameters such as pH, CTAB concentration, salt concentration and salt type, it is difficult to to more than to look for general properties of charged surfaces of adsorbed salt and amphiphile. We can see the suggested behavior realized in a simple model based on a generalization of surface regulation models introduced in refs. [6,7] and much earlier in ref. [14].

Table 1
Parameter values for different force curves in the cases of (a) mica–impure CTAB experiment [1] and (b) mica–recrystallized CTAB experiments [5]. $(F/R)_{a=a_t}$ is a measure of the interaction energy at the collapse point $2a_t$. κ^{-1} is the Debye length and ϕ_∞ the value of the surface potential at infinite separation. The last column is the ratio between the square of the surface potential and the maximum measured repulsive force (related to the ratio between well depth and the collapse free energy which should be a constant, expressing the energy balance in our model eq. (13)).

$(F/R)_{a=a_t}$ (mN/m)	$2a_t$ (nm)	ϕ_∞ (mV)	κ^{-1} (nm)	$\phi_\infty^2 / (F/R)_{\max}$ ($\times 10^3$)	$\kappa\phi_\infty^2 / (F/R)_{\max}$ ($\times 10^2$)
(a) Data from ref. [1]					
0.10	8.0	20	7.7	4.0	
1.3	4.2	80	1.5	4.9	
2.8	5.6	105	10.5	3.9	
5.4	4.2	140	8.5	3.6	
9.2	3.8	200	2.3	4.3	
			average	4.14 ± 0.45 (11% std. dev.)	
(b) Data from ref. [5]					
0.584	6.9	−55	52	5.2	1.0
0.119	7.6	28	70	6.6	0.94
0.611	7.7	65	51	6.9	1.35
1.750	7.8	100/105	40.5	6.3	1.56
2.879	7.5	120	32	5.0	1.56
4.32	6.9	130	30	3.9	1.3
5.437	6.05	140	22	3.6	1.6
			average	5.4 ± 1.3 (24% std. dev.)	1.33 ± 0.27 (20% std. dev.)

The unit $(\text{mV})^2/(\text{mN/m})$ is equal to $1.11 \times 10^{-13} \text{ m}$ of $1.11 \times 10^{-11} \text{ cm}$, so that the ratios $\phi_\infty^2 / (F/R)_{\max}$ are, on average, $4.14 \times 10^3 \times 1.11 \times 10^{-11} \text{ cm} = 4.6 \text{ \AA}$ for the data of ref. [1] and $5.4 \times 10^3 \times 1.11 \times 10^{-11} \text{ cm} = 6 \text{ \AA}$ for the data of ref. [5]. The average of the ratio $\kappa\phi_\infty^2 / (F/R)_{\max}$ is dimensionless and equal to $1.33 \times 10^2 \times 1.11 \times 10^{-11} \text{ cm} / 10^{-7} \text{ cm} \approx 1.5 \times 10^{-2}$.

2. Analysis

Let us concentrate on a model system specified by two surfaces, immersed in a one-one electrolyte in equilibrium with a bulk reservoir, at a separation $2a$ located at $z = \pm a$ and extending in the (x, y) directions. In a previous publication [7] one of us has shown that the total free energy per unit surface area (\mathcal{F}) is given by

$$\mathcal{F} = \frac{1}{2} \epsilon \epsilon_0 \int [\nabla \phi(\mathbf{r})]^2 d^3\mathbf{r} - kT \int \rho[\phi(\mathbf{r})] d^3\mathbf{r} + \oint f[\phi(\mathbf{s})] d^2\mathbf{s}, \quad (1)$$

where ϵ is the dielectric permittivity of water, ϵ_0 the permittivity of free space, kT is the thermal energy, $\phi(\mathbf{r})$ is the local electrostatic potential at position \mathbf{r} , and \mathbf{s} is the two-dimensional position vector at the surface $\mathbf{s} = (x, y)$. The local charge density is given by

$$\rho[\phi(\mathbf{r})] = \sum_i \rho_{i0} \text{ch}[e_i \phi(\mathbf{r})/kT], \quad (2)$$

where ρ_{i0} is the concentration of the electrolyte in the bulk reservoir while e_i is the elementary charge. The first two terms (electrostatic field energy and the ionic osmotic pressure) are nothing but the standard expression for the mean-field free energy of a non-homogeneous electrolyte. The last term corresponds to the interaction of the charged species with the surfaces; its form depends on the nature of this interaction. (In the case of the amphiphile adsorption to a charged mica surface, it is $f(\phi)$ that contains the relevant information on the adsorption properties of the surface, i.e. $f = f\{\rho[\phi(z = \pm a)]\}$, pH, adsorption energy, etc.). The equilibrium profile of $\phi(\mathbf{r})$ is obtained by investigating the extrema of eq. (1). It can be shown that the Euler-Lagrange equations $\delta \mathcal{F}(\phi) = 0$ decouple into two terms of which the first one gives the standard Poisson-Boltzmann equation, and the second one is reduced to a statement about the charging equilibrium at the surfaces

$$-\epsilon \epsilon_0 \frac{\partial \phi(z = \pm a, \mathbf{s})}{\partial \mathbf{n}} = \sigma = \frac{\partial f[\phi(\mathbf{s})]}{\partial \phi}, \quad (3)$$

where σ is the surface charge density and \mathbf{n} the surface normal. The total free energy of the system per single surface can now be derived in the form

$$\mathcal{F} = f(\phi) - \int_0^\phi \sigma d\phi. \quad (4)$$

The total energy is therefore given by the sum of the "chemical" (adsorption) and electrostatic energy. It is straightforward to see that the charging equilibrium at the surface eq. (3) is given by the extremum of the total surface energy eq. (4) ($\partial \mathcal{F} / \partial \phi = 0$).

At this point it will be profitable to recast eq. (4) into a slightly different form. We shall add and subtract the electrostatic self-energy of a single surface at $2a \Rightarrow \infty$ obtaining

$$\mathcal{F} = f(\phi) - \int_0^\phi \sigma_\infty d\phi + \mathcal{F}_{\text{int}}(a), \quad (5)$$

where $\mathcal{F}_{\text{int}}(a)$ is the electrostatic interaction energy between the two surfaces that depends on the inter-surface separation $2a$.

A plausible model for the charging equilibrium of an electrified surface, where the adsorbing counter ion is a charged amphiphile, should give an equilibrium nonzero $\phi = \phi_\infty$ at $2a \Rightarrow \infty$ as inferred from experiments [1,5]. It should also provide a possibility of smaller surface potential states ($\phi < \phi_\infty$) that can be reached at the cost of additional energy, presumably provided by the compression of the surfaces. As a mathematically convenient but plausible ansatz, we take a ϕ^4 -model in the form

$$f(\phi) = -\frac{1}{2} \alpha \phi^2 + \frac{1}{4} b \phi^4, \quad (6)$$

that certainly satisfies all the requirements listed above. The first term in eq. (6) corresponds essentially to a nearest-neighbor interaction of a two-dimensional lattice gas [7] of adsorbing amphiphiles. It states that at high amphiphile coverage, where the non-electrostatic ("chemical") adsorption energy of the surface is most important, it becomes energetically more and more unfavorable for additional amphiphiles to adsorb. The second term in the above equation subsumes all the other surface interactions that favor crowding of the amphiphiles on the surface. (To be completely consistent, one should carry the expression for interaction energy between layers to terms of order ϕ^4 , but these are omitted for the present time with the expectation that they will be of short range.) It should be obvious that this ϕ^4 surface

ergy term is not to be confused with an interaction between surfaces decaying at half the Debye length.

We can now recast the total free energy into the form

$$\mathcal{F} = -\frac{1}{2}c\phi^2 + \frac{1}{4}b\phi^4 + \frac{1}{2}\Gamma(a)\phi^2, \quad (7)$$

where one can obtain to the lowest order

$$c = \alpha + \left. \frac{\partial \sigma_\infty}{\partial \phi} \right|_{\phi=0} \quad (8a)$$

$$\Gamma(a) = \left. \frac{\partial^2 \mathcal{F}_{\text{int}}(a)}{\partial \phi^2} \right|_{\phi=0} \quad (8b)$$

The sign of c therefore differentiates between the importance of electrostatic and non-electrostatic (e.g. hydrophobic, "chemical") energies on adsorption. For large enough separations where a superposition approximation makes sense, $\Gamma(a)$ has an approximately exponential behavior, viz.

$$\Gamma(a) \simeq \Gamma_0 e^{-2\kappa a},$$

where κ^{-1} is the Debye length. The charging equilibrium at the surface eq. (5) now leads to the following equilibrium solution for the surface potential

$$\phi = 0, \quad (9a)$$

$$\phi = \left(\frac{c - \Gamma(a)}{b} \right)^{1/2} \quad (9b)$$

At large separations where $\Gamma(a) \ll c$ the equilibrium value of the surface potential is $\phi(a \rightarrow \infty) = \phi_\infty = (c/b)^{1/2}$ and the system finds itself sitting in the energy well of depth

$$\mathcal{F}_{\text{well}}(a \rightarrow \infty) = -\frac{1}{4}c\phi_\infty^2.$$

At finite values of the intersurface separation the surface potential is always smaller than ϕ_∞ . On the other hand, at the surface separation $a = a_i$ where $c - \Gamma(a_i) = 0$ the solution eq. (9b) becomes unstable and a continuous transition to the state $\phi = 0$ is obtained, formally equivalent to a second-order phase transition in $\phi(a)$. At this separation the system discharges, its mean energy remaining constant and equal to $\mathcal{F}(a_i)$, and under an imposed external force collapses into the primary minimum (fig. 1). This "contact" necessarily involves deformation of mica to moot the meaning of radius R in F/R .

Returning now to the total free energy of the system we obtain

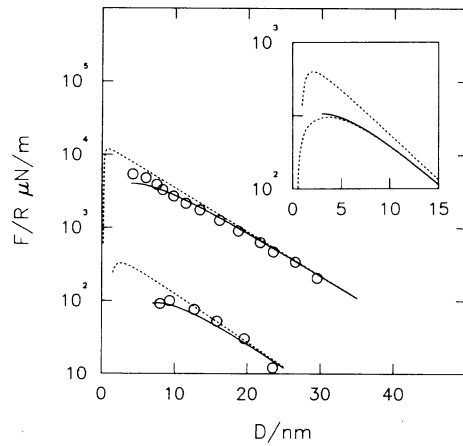


Fig. 1. An illustrative fit of eq. (11) to two mica-“CTAB” force curves [1]. The solid curves represent a fit of eq. (11) to two force curves with $\phi_\infty = 140$ mV (upper solid curve) and $\phi_\infty = 20$ mV (lower solid curve). The Debye lengths obtained from the fit, $\kappa^{-1} = 7$ nm (upper curve) and $\kappa^{-1} = 6.5$ nm (lower curve), are some 15% different from the quoted values [1]. This difference is due to the linearization approximation implicit in the fit. The dashed lines corresponds to the DLVO predictions with the Hamaker constant equal to $H = 2 \times 10^{-20}$ J [1]. The effective attraction, due to displacement of the charging equilibrium with separation, leads to the collapse at larger separations than the DLVO theory would predict. The inset represents the schematic drawing of the DLVO curve (upper dashed line), eq. (11) (solid line) and eq. (11) with the Van der Waals contribution (lower dashed line).

$$\Delta \mathcal{F} = \mathcal{F}(a) - \mathcal{F}(a \rightarrow \infty)$$

$$= \frac{1}{2}\Gamma(a)\phi_\infty^2 + \frac{1}{4}\Gamma(a)[\phi^2(a) - \phi_\infty^2]. \quad (10)$$

Since $\phi(a) \leq \phi_\infty$, clearly the second term in the above equation contributes an effective attraction to the otherwise repulsive interaction energy; this attraction is not of Van der Waals origin. This can be seen even more clearly if the above equation is rewritten in a more explicit form

$$\Delta \mathcal{F} \simeq \frac{1}{2}\Gamma_0\phi_\infty^2 e^{-2\kappa a} - \frac{1}{4} \frac{(\Gamma_0\phi_\infty)^2}{c} e^{-4\kappa a}. \quad (11)$$

It is instructive to investigate the magnitude of the total interaction at the point of the continuous transition from the $\phi \neq 0$ to the $\phi = 0$ state. As already stated, this point is located at a_i and we obtain

$$\Delta \mathcal{F}(a = a_i) = \frac{1}{4}c\phi_\infty^2. \quad (12)$$

The total energy that we had to put into the system to reach the collapse (transition) point is therefore exactly equal to the barrier height in the $\mathcal{F}(\phi)$ (at infinite separation), that separates the state of the lowest energy ($\phi = \phi_\infty$) from the state of zero potential (the discharged state). The statement that at the collapse point

$$\Delta\mathcal{F}(a=a_t) = |\mathcal{F}_{\text{well}}(a \rightarrow \infty)| \quad (13)$$

is nothing but the energy balance equation for this particular model system. Clearly, in order for the collapse to occur, the depth of the well should be smaller than the maximum interaction energy (the DLVO barrier). The energy balance eq. (13) shows that contrary to the viewpoint held by the standard DLVO theory, where collapse depends on the balance between repulsive and attractive forces acting between the surfaces, this model system, even in its mean-field form, leads to a collapsed state when the forces acting between the surfaces balance the forces acting within each surface.

So far our discussion has been based on a mean-field analysis. Fluctuations in the local electrostatic potential contribute an additional attractive term to the total free energy eq. (1) of a generalized Van der Waals type, as described in detail in ref. [7]. The effect of the fluctuations is to displace the collapse point. a_t is displaced towards larger values of a while the forces at $a < a_t$ become rapidly attractive. By using a variable spring stiffness in the surface force apparatus [2,4], it should be possible to detect these attractive forces.

3. Discussion

The above model, deliberately simplified and formalized to allow for analytical treatment, elucidates the connection between the intersurface forces that favor the discharged surface state (minimum electrostatic interaction energy) and the opposing intrasurface forces that by themselves prefer at least some amount of residual surface charge (as is clearly suggested by the mica⁻-CTA⁺ experiments). In the case of the ϕ^4 -model the repulsive pressure, exerted on the two charged surfaces when brought into close opposition, is turned, by way of the surface charging equilibrium eq. (3), into forces operating within the two

surfaces and acting to displace the surface charging equilibrium towards smaller values of the surface charge. The surfaces can counteract this tendency only up to a point where the interaction energy is less or equal to the total surface charging energy. At that point the equilibrium between the inter- and intra-surface forces cannot be maintained at any finite value of the intersurface separation and the surfaces jump into a primary minimum.

The usual thinking about constant-potential and constant-charge models, as if they were two extreme limits with any other surface behavior coming in between, is certainly not applicable to the model system presented above. Apparently a complex charging equilibrium at the surface due to the amphiphilic nature of the adsorbing cation can dramatically change double-layer behavior.

This scenario will vary with the particular model used for the surface charging equilibrium. There are, however, certain general characteristics that, we believe, are only weakly model dependent. Whenever the "chemical" part of the surface energy, $f(\phi)$, is soft enough (its second derivative in the range $\phi=0$ to $\phi=\phi_\infty$ should not be too large), the changes in the surface charging equilibrium will look like an effective attractive force acting to diminish the original Gouy-Chapman repulsion, as inferred from the value of the surface potential at large separations (ϕ_∞). Furthermore, at the point of collapse the energy balance of the form eq. (13) should be valid irrespective of the model and indeed the numerical data extracted from refs. [1,5] (see table 1) corroborate this conjecture to good accuracy. As for the presumed exponential dependence of the "hydrophobic attraction", the data can equally well be fitted to a power law dependence, that could even be due to the remaining Van der Waals-type forces superimposed on a greatly diminished (the system is close to a_t) repulsion.

Because desorption occurs under applied force, it can be much faster than characteristic times of diffusive solute equilibration with a surface. Still, the fact that measured forces change with [CTAB] concentration shows that there is some equilibration between surface and solution. These possibilities should be considered too in models of membrane fusion using CTAB/mica data that show CTAB concentration dependence [15].

For reasons given above, we have not considered

data where net attractive forces are observed [1,3]. Models of those forces that depend on ionic fluctuations and ionic screening [6,7] or on some single characteristic decay constant of water solvent [16] conflict with data showing very long decay distances that vary widely between different preparations [2,3,4].

While the CTAB data were thorough enough to allow some correlation to be extracted, the long-range attraction seems to show little internal correlation. For example, the forces between mica surfaces coated with polymerized ammonium surfactant vary strongly with ionic conditions, but the "pull-off force" is essentially the same in all three solutions used for measurement [3].

A lesson to take from the present analysis is the possibility of connecting measured forces with solute activities, and modification of the surface. Because measurements are between oppositely curved surfaces of radius R , the force F is actually a sum of interactions from the region of closest approach to infinite separation. That is, one measures the equivalent of a work or a free energy at each separation of the mica cylinders. Specifically

$$F/R = 2\pi E.$$

E is an energy per unit area, actually a work of bringing two parallel surfaces from infinite separation to the minimum separation between cylinders. From the standard method of the Gibbs adsorption isotherm, one knows that the change of surface energy with the activity of an adsorbing or desorbing species is proportional to the surface excess or deficit of that species.

One is then aware of the remarkable opportunity to compare F/R versus distance in different solutions of different solute concentration to measure the amount of solute associated with the surface as a function of separation. Through systematic measurements of this kind, it should finally be possible to discern which solution and surface properties create this puzzling "hydrophobic" interaction. But until such systematic studies – with simple solutes in well-defined well-buffered solutions – are available, further theorizing seems likely to be frustrating.

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