# Comparison of light scattering of colloidal dispersions with direct force measurements between analogous macroscopic surfaces

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The equilibrium force laws (force vs distance) between two macroscopic surfactant-coated mica surfaces separated by organic liquids have been determined. The aim was to ascertain whether directly measured forces are able to be employed in the prediction of second virial coefficients as obtained from light scattering experiments on analogous colloidal suspensions (i.e., spherical particles coated with the same surfactant and dispersed in the same medium). The quantitative agreement between the two independent measurements was excellent. This suggests that the interaction energy per unit area, which governs the physical properties of a bulk colloidal system, is indeed, the same as the equilibrium interaction energy per unit area of two macroscopic surfaces, for the systems investigated here. Such a correlation has been tacitly assumed in the past, and it is the first time that this assumption has been confirmed experimentally for any system.

## INTRODUCTION

The interactions between colloidal particles is a subject of ongoing importance and current interest. These interactions may be expressed in terms of the potential of mean force $U(r)$, which is the work required to bring two colloidal particles from infinity to a separation $r$ under given solvent conditions. The potential governs most of the physical properties of a colloidal dispersion, such as the osmotic pressure and the occurrence of phase separation, i.e., colloid instability[1].

In recent years, great progress has been made in the ability to infer the interaction potential $U(r)$ from data obtained by means of various scattering techniques. A plethora of data now exist on the application of these techniques to both aqueous and nonaqueous colloidal systems.[2,3] These methods, however, assume some function description of the interaction, for instance, a square well potential, followed by the adjustment of certain parameters to fit the experimental scattering data. These parameters rely on the particular model adopted to theoretically describe the system in question. Hence the value of $U(r)$ finally attained is model dependent.

Our aim here was to investigate whether the interparticle forces which exist in continuum systems such as stable colloidal dispersions are able to be accessed quantitatively by means of direct force measurements between two macroscopic surfaces. A surface forces apparatus was used to directly determine the intermolecular forces acting between two macroscopic surfaces across a particular liquid medium. These results were then used to infer the thermodynamic properties, as measured by light scattering, of an analogous dilute colloidal system, i.e., colloidal particles with surface properties similar to the macroscopic surfaces, suspended in the same liquid across which the macroscopic surfaces act.

The surface forces apparatus (SFA) has been used previously to investigate repulsive electrostatic double layer forces in certain aqueous systems; the results were in accordance with those expected from the Derjaguin–Landau–Verwey–Overbeek (DLVO) theory.[4] The DLVO theory is usually employed in the prediction of colloidal interactions but, to date, SFA measurements have not been used to infer quantitative information about such forces in analogous colloidal systems. Other types of colloidal phenomena have also been studied by means of the SFA; for instance, polymer bridging forces in flocculation of colloids,[5] upper consulate temperatures in aqueous surfactant solutions,[6] etc. However, yet again, data on these systems have not been correlated quantitatively with the direct force measurements. The present investigation was begun with the idea of testing whether such correlations may be made for a particular case of interest.

The colloid system chosen for this study consisted of spherical calcium carbonate particles suspended in tetradecane. The particles were stabilized by an adsorbed monolayer of a randomly branched calcium alkylbenzene sulphonate surfactant (CaS). These colloidal particles have

been well characterized previously using small-angle neutron scattering[7] and are used as an acid-neutralizing aid in lubricating oils. Such a nonaqueous dispersion was considered ideal for the investigation attempted here since the interparticle interaction potential was expected to be simple, governed by attractive van der Waals forces and a hard core repulsion.

Additionally, thorough investigations of the CaS used to stabilize the colloids have been conducted already by two of us[8] using the SFA. The force vs distance profile of two mica surfaces each coated with a CaS monolayer interacting across liquid alkanes was found to be monotonically attractive down to a surface separation of about 15 Å. A smooth repulsion existed at smaller distances. Hence the absence of any short-range oscillatory forces[9] across CaS monolayers simplifies the direct measurements of the interaction forces and does not lead to any complications in the behavior and interpretation of the colloidal system.

This paper presents the measured forces between two adsorbed CaS monolayers across tetradecane and the effects that small amounts of dissolved octanol in the tetradecane has on the interactions. These results are used to infer the interactions between particles in the analogous colloidal system, i.e., calcium carbonate particles coated with a monolayer of CaS and suspended in tetradecane or a tetradecane/octanol mixture. The inferred results were then compared with the actual light-scattering data.

## EXPERIMENTAL SECTION

### Direct force measurements

#### *Materials*

The $n$-tetradecane (Sigma Chemical Company, $> 99\%$ pure) was further purified by distillation under pure, dry nitrogen. The 1-octanol (Fluka, puriss grade $> 99.5\%$ pure) was used as received. Both liquids were stored over $P_2O_5$ prior to use in order to scavenge any trace amounts of water.

The calcium alkylbenzene sulphonate surfactant (CaS) was supplied by Exxon Chemical Company. It is a randomly branched alkyl-chained surfactant with an average of 12 carbons per chain. Its head group is a calcium benzene sulphonate. The point of attachment of the alkyl chain to the ring is random. The CaS was purified by first dissolving a small amount (50 g) in dry heptane (50 ml) followed by addition of acetone (3×8 ml) with ultrasonication of the mixture between each addition. The supernatant was then decanted off and the precipitate, i.e., CaS, rotary evaporated in order to remove the remaining solvent.

#### *Surface preparation*

CaS monolayers were deposited onto the mica sheets by retraction from solution. This was performed by submerging each mica sheet into a solution of the surfactant for about 15 min. During this time, any water or organic impurities which adsorbed to the mica surface on exposure to air are displaced. Following this, the mica surfaces,

which are now expected to be clean,[10] are slowly drawn through the air/water interface where the surfactant resides. This procedure was repeated, after which the monolayer-covered surfaces were dipped in triply distilled water to remove any excess surfactant. The monolayer was considered to be properly bound to the mica when, on removal of the mica from the water, the water retracted easily from the surface indicating a fully dry, hydrophobic surface and hence a close-packed monolayer. Subsequently, the monolayer thickness was found to be about 15 Å (see below).

Pressure-area isotherms of a CaS monolayer at the air/water interface were typical of an all fluid monolayer when measured at 19 °C. The onset of the fluid phase was distinct and collapse of the monolayer occurred at the relatively low surface pressure of 34 mN m$^{-1}$.

### Force measurements and adsorbed monolayer characterization

Direct force measurements using the surface forces apparatus (SFA) is a well established technique which has been described in detail previously.[10] Briefly, two thin ( $\sim 1$ $\mu$m) backsilvered sheets of molecularly smooth mica are each glued to silica support disks of radius $\approx 1$ cm. A CaS monolayer is then deposited on each mica surface, as detailed above, and the mica surfaces are mounted as crossed cylinders inside the SFA. The lower disk is attached to a fixed double cantilever spring of known spring constant. The shortest distance $D$ between the surfaces is measured interferometrically with a resolution of about 1 Å. The force between the two surfaces is measured from the deflection of the double cantilever spring as the surfaces are moved towards or away from each other.

All experiments were executed with a macroscopic droplet of the liquid, which for the present study is tetradecane or a tetradecane/octanol mixture, injected between the surfaces. Before injection of the liquid and after mounting the surfaces, the inside of the SFA was dried by placing a receptacle of $P_2O_5$ inside the main chamber and continuously purging the system with pure, dry $N_2$ for 15–20 h. After injection of the liquid and during the course of the experiment, the $N_2$ flow was ceased but the $P_2O_5$ was kept inside the chamber to ensure that the experimental environment remained dry. The $P_2O_5$ was replaced by water at the end of an experiment. Thereby water was allowed to diffuse, via its vapor, into the system. Water is able to diffuse through a fluid hydrocarbon monolayer. This is not surprising since water has a finite solubility in bulk liquid hydrocarbons. Indeed, it is well documented that water permeates surfactant bilayers within seconds.[11,12] In the present experiments, about 12 h was allowed for the system to equilibrate with water.

An adhesion energy of $\gamma = 26$ mN m$^{-1}$ in an atmosphere of dry nitrogen was determined for two CaS monolayers adsorbed on mica. This result is very much as expected for a hydrocarbon surface across air. The interaction of the same monolayers across 2-methyloctadecane was monotonic with no evidence what-

soever of oscillatory forces.[8] The two monolayer surfaces came into a potential minimum at a surface separation $D = 15$ Å relative to the adhesive contact position in dry nitrogen. The surfaces could be forced closer in by the application of a positive pressure to $D = 2.5$ Å at which point there existed a hard-wall repulsion. It is important to state that this behavior was completely reversible and reproducible; the subsequent force vs distance profiles were unaltered when measured immediately after surface separation. This indicates that the monolayer retains its fluidity even when the surfactant molecules are physically adsorbed onto a rigid substrate since a solid or amorphous but frozen monolayer would not be as compressible and large compression of a solid monolayer usually results in irreversible damage to the monolayer.[13]

Equilibration of this system with water vapor resulted in an increase in magnitude of the attractive well by 2 orders of magnitude. Additionally, the surfaces now came easily to $D \approx 0$ Å and could be forced in to hard-wall mica/mica contact at $D = -29$ Å. This is further evidence of the fluidity of the monolayer which is enhanced by the presence of water. It also implies a monolayer thickness of approximately 15 Å, assuming that all the surfactant was pushed out from between the mica surfaces. This thickness is uniform within $\pm 1$ Å over a typical contact area of 100 $\mu m$,[2] as ascertained by the optical technique.

## Light scattering measurements

### Colloidal suspension

The colloidal particles consisted of a calcium carbonate core with an adsorbed monolayer of the same alkyl benzene sulphonate surfactant (CaS) used in the direct force measurements (see above). The synthesis procedures used to prepare the colloidal dispersion have been described fully by Markovic *et al.*[7]. The samples for scattering studies were prepared by dispersing known amounts of the concentrated material in tetradecane or the mixture of tetradecane and 1-octanol. The solvent quality and the drying procedure were the same as that for the direct force measurements. Finally, the suspension (5.5 wt%) was fractionated by ultracentrifugation for 2.5 h at the nominal acceleration of $10^5$ g (i.e., $10^7$ cm s$^{-2}$) in order to remove any colloidal aggregates.

### Characterization

The final calcium carbonate dispersion was found to be relatively monodisperse with less than 8% standard deviation in the particle radius, as determined by dynamic light scattering. Earlier small angle neutron scattering studies[7] of the same colloid showed that the particles were spherical with a particle radius of $50 \pm 5$ Å. Under the assumption that the adsorbed layer of surfactant formed a concentric shell around the $CaCO_3$ core, the neutron scattering data gave a monolayer thickness of $19 \pm 1$ Å.[7] This value is in good agreement with the 15 Å obtained from the SFA, as mentioned above. These dynamic scattering properties were observed to be stable over a period of months.

The molecular weight, $M$, of the colloid was obtained by ultracentrifuge studies of the sedimentation rate $v$ of the colloidal particles which is related to the centripital acceleration $f$ via Stokes' law

$$v = (M - M_0)f/(6\pi\eta R_h). \tag{1}$$

Here, the Stokes radius $R_h$ is the same hydrodynamic radius as measured by dynamic light scattering. The quantity $\eta$ is the known solvent viscosity. $M_0$ is the mass of the displaced fluid. To obtain this mass it is assumed that the solvent is displaced from the entire hydrodynamic volume $(4/3)\pi(R_h)^3$. The true displaced mass is probably slightly smaller than this. The resulting estimate was $M \approx 3 \times 10^5$ amu $\pm 15\%$.

## Light scattering

Light scattering measurements were performed using a Brookhaven Instruments light scattering goniometer (BI-200SM). The light source was a 30 mW He/Ne laser (Spectra Physics, Model 127). The sample cell was immersed in a toluene bath in order to match the refractive index of the cylindrical glass cell and so reduce background scattering from the cell. The light scattered from the well-defined scattering volume was collected by a photomultiplier (EMI 9863). Intensity measurements were accumulated automatically between the scattering angles $\theta$ of 45° and 90° for periods of 10 s.

## RESULTS AND DISCUSSION

Two media giving different interactions were studied. The "control" case medium was *n*-tetradecane. The "test" case medium was *n*-tetradecane with 7.5 wt % of dissolved 1-octanol. Octanol was chosen because it is completely miscible in tetradecane and can be used to modulate the interaction potential (see below).

In light of the ensuing comparison between direct force measurements on two isolated macroscopic surfaces and light scattering data on a bulk colloidal system, it should be stressed that the systems are analogous but not entirely identical. There is inevitably some difference between a monolayer of calcium alkylbenzene sulphonate surfactant (CaS) adsorbed on a mica substrate and that adsorbed on the colloidal calcium carbonate. However, we expect the two substrates to produce monolayers of comparable packing density since the two different determinations of monolayer thickness in either system gave comparable results, i.e., a minimum of 15 Å on mica and 19 Å on calcium carbonate. This density is controlled by the size of the polar head groups and the packing of the alkyl chains of the surfactant molecules. Additionally, the fluidity of the monolayer implies that curvature effects on the packing of the surfactant are minimal.

### Direct force measurements

Results of separate experiments on the interaction of two physisorbed calcium alkylbenzene sulphonate mono-
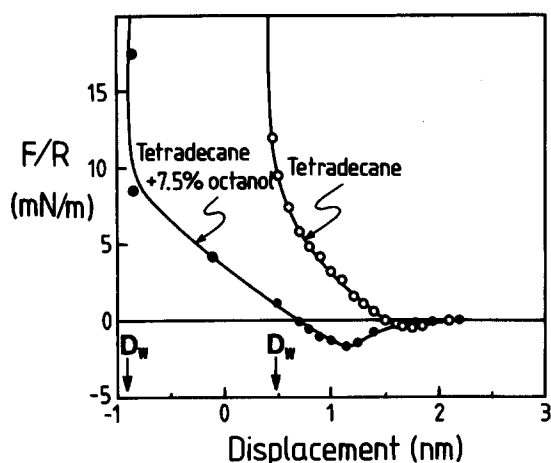
FIG. 1. Open circles: data of the scaled force $(F/R)$ versus distance $(D)$ profile obtained by direct force measurements for the interaction of two physisorbed CaS monolayers across pure tetradecane, i.e., the control case. Solid circles: scaled force $(F/R)$ vs distance $(D)$ data for the test case, i.e., tetradecane containing 7.5% dissolved octanol. Surface separations are measured relative to the position of the two monolayer-coated surfaces in contact in a dry nitrogen atmosphere (which defines $D = 0$). $D_w$ denotes the position of the hard-wall repulsion. The position of $D_w$ relative to contact in dry nitrogen is indicated by the arrows for the control case and the test.

layers across pure $n$-tetradecane and across a 7.5% by weight of 1-octanol in tetradecane, as determined using the surface forces apparatus (SFA), are shown together in Fig. 1. Both curves are plots of the scaled force $F/R$ where $R$ ($\approx 2$ cm) is the mean radius of curvature of the surfaces, as a function of surface separation $D$, i.e., the thickness of the liquid film confined between the surfactant monolayers. It should be noted that all distances were measured relative to contact of the two surfactant-coated surfaces in dry nitrogen. A positive force corresponds to repulsion between the surfaces, while a negative force corresponds to attraction.

For the pure tetradecane system at distances beyond approximately 30 Å, there is no detectable force. At separations smaller than this the force becomes attractive and the surfaces come into adhesive "contact" located at a distance of $D = 17$ Å, where the attraction between the surfaces is a maximum given by $F/R = -1$ mN m$^{-1}$.

It was possible to partially squeeze out the tetradecane molecules remaining between the two surfaces by mechanically forcing the surfaces closer together. Clearly, from the change in $D$ in this repulsive $F/R$ regime, the repulsion between the surfactant surfaces that opposes thinning of the tetradecane is soft and does not become a hard-wall repulsion until $D = 4$ Å. This type of behavior is indicative of the compressibility or fluidity of the surfactant surfaces which confine the liquid film and is not observed for monolayers such as CTAB (cetyltrimethyl ammonium bromide) or DMPE (L-$\alpha$-dimyristoylphosphatidylethanolamine) on mica which cannot be compressed more than 1–2 Å, even under high compressional loads.[13] Molecularly smooth, rigid surfaces such as bare mica would favor the layering of the symmetric tetradecane molecules within the gap

thereby leading to forces that oscillate between attraction and repulsion. Indeed, in such experiments,[9] it was impossible to surmount the hard-wall repulsion at 8 Å separation, whereas in the present experiments, the surfaces could be brought as close as 4 Å, as already mentioned. It should, perhaps, be stated here that when the intervening liquid was 2-methyloctadecane[8] rather than $n$-tetradecane the hard-wall repulsion was located at about 2.5 Å.

When the system was saturated with water vapor for 24 h the position of the force minimum moved in to $D = 10$ Å and the adhesion of the surfaces was greatly increased to $F/R = -100$ mN m$^{-1}$. Another effect of the presence of water was the increased compressibility of the monolayer which now could be squeezed completely out from the area of contact to $D = -29$ Å. It appears that penetration of water into the head group region of the monolayer enables the surfactant molecules to move more freely on the mica substrate. Further discussion of this phenomenon follows below.

The solid curve in Fig. 1 is the experimentally determined force for two CaS surfaces interacting across the tetradecane/octanol mixture. The differences in behavior between this and the pure tetradecane system are obvious. The presence of the alcohol in the system results in stronger attraction between the CaS monolayers, i.e., $F/R = -1.7$ mN m$^{-1}$. Furthermore, this minimum in potential is located closer in at $D = 11.5$ Å.

However the most striking effect of octanol on the force characteristics of the system occurs in the repulsive region at surface separations below 10 Å. Only a small applied force was required to push the liquid completely out from between the surfaces to $D = 0$ Å; in fact, negative distances were measured down to $-9$ Å at which point the forces became steeply repulsive. The negative surface separations reflect the compressibility of the monolayers and the enhancement of this compressibility due to the presence of octanol. Since octanol is polar relative to tetradecane it is intuitive that it would prefer to reside in the vicinity of the polar surfactant head groups, as does water (see above). Hence the fluidity of the monolayers is increased and the monolayers are more easily compressed.

## Light scattering measurements

$U(r)$ influences various measurable properties of a colloidal suspension.[14] The focus here is on the second virial coefficient which is obtainable from static light scattering experiments and is related to $U(r)$ through the well-known equation[15]

$$A_2 = 2\pi \int_0^\infty (1 - e^{-U(r)/kT}) r^2 \, dr. \tag{2}$$

The intensity of light scattered from optically isotropic scatterers of molecular weight $M$ in dilute solution is given by[16]
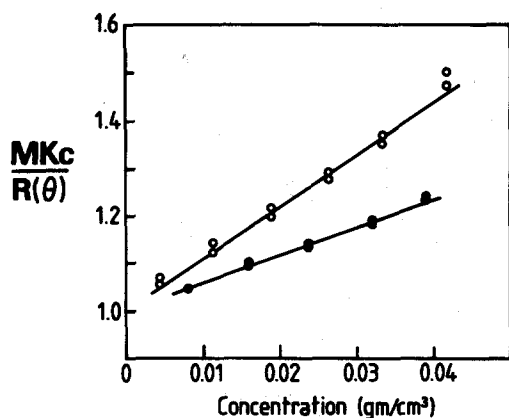
FIG. 2. Open circles: plot of $MKc/R(\theta)$ vs $c$ for the control case system of surfactant-coated calcium carbonate particles suspended in pure tetradecane. The results are for scattering angles of 90°, 60°, and 45°. The solid line is a linear fit to the data points of the 90° measurement. From this fit the value of $A_2/M = 5.45$ cm$^3$ g$^{-1}$ was obtained. Solid circles: same plot as above but for the test solvent, i.e., 7.5% by weight octanol in tetradecane. The fitted line yields $A_2/M = 2.9$ cm$^3$ g$^{-1}$.

$$\frac{Kc}{R(\theta)} = \frac{1}{M}\left(1 + \frac{2A_2}{M}c + c^2\right), \tag{3}$$

where $c$ is the concentration of the suspension (weight/volume), $K$ is an instrument-dependent constant, and $A_2$ is the desired second virial coefficient. Since $c$ is small the second order term can be ignored. The intensity ratio $R(\theta)$ is defined as $[I(\theta)/I_0] - 1$, where $I_0$ is the intensity of light scattered from the solvent alone ($c = 0$) and $I(\theta)$ is the intensity of light scattered from a dispersion of concentration $c$ at an angle $\theta$ from the transmitted beam. The scattering from the colloidal particles studied here is isotropic since the size of the colloidal particles (50 Å) is much smaller than the wavelength of light irradiating the sample (i.e., $\lambda = 6328$ Å). Therefore, $R(\theta)$ is independent of $\theta$.

Figure 2 presents light scattering data from the CaS stabilized calcium carbonate particles suspended in pure $n$-tetradecane and suspended in tetradecane with 7.5% by weight of 1-octanol. The data is plotted as $MKc/R(\theta)$ vs $c$ and is used to deduce $A_2/M$ via Eq. (3). The data from the control case, i.e., the pure tetradecane system, yielded $A_2/M = 5.5 \pm 0.3$ cm$^3$ g$^{-1}$. The quoted uncertainty is only due to the scatter in the experimental data. Further sources of error are discussed below. The test system gave $A_2/M = 2.9 \pm 0.3$ cm$^3$ g$^{-1}$; which is about 53% of the control case value.

## $U(r)$ from the direct force measurements

The potential of mean force, $U(r)$, between two colloidal particles stabilized by a monolayer of CaS in tetradecane may be inferred from the directly measured force profile. For a given separation $D$, the force, $F(D)$ between monolayers adsorbed on mica can be translated to the force between two colloidal particles via the familiar Derjaguin approximation.[17] That is to say, we consider the work of compression per unit area $E(D)$ to be the same for a colloidal surface as for a mica/CaS surface. This amounts to

TABLE I. Optical properties used in Eq. (5) for determining the Hamaker constants of two media (1) interacting across medium (2).

| System | Dielectric constant $\epsilon$ | Refractive index $n$ | Hamaker constant, $A$ (Joules) |
|---|---|---|---|
| Mica (1) across | $\epsilon_1 = 7.0$ | $n_1 = 1.60$ | $9 \times 10^{-21}$ |
| Hydrocarbon (2) | $\epsilon_2 = 2.0$ | $n_2 = 1.42$ | |
| CaCO$_3$ (1) across | $\epsilon_1 = 8.2$ | $n_1 = 1.51$–$1.60$ | $(3$–$9) \times 10^{-21}$ |
| Hydrocarbon (2) | $\epsilon_2 = 2.0$ | $n_2 = 1.42$ | |

assuming that the surfaces in the two systems basically interact via the same type of force or potential and therefore have a similar composition. It also presumes that the solid substrate beneath the surfactant layer has a negligible effect on the interactions. This supposition seems justified since the surfactant-coated mica surfaces exhibited a force law that is no longer oscillatory with an interaction exceeding that expected from the van der Waals forces between two bare mica surfaces across a hydrocarbon liquid.[18]

It is important to ascertain quantitatively whether we expect the different substrates in the two studies to influence the forces across the hydrocarbon medium between them. In the force measurements the substrate onto which the monolayers were adsorbed was mica, while in the light scattering study the core material of the colloidal particles was CaCO$_3$. Assuming that the properties of the CaS monolayers and tetradecane were the same in both studies, there still remains the question of the different effects of the substrates on the van der Waals forces across the $\sim 45$ Å film of hydrocarbon between them. We can calculate this using the expression for the van der Waals force between the two cylindrically curved surfaces (crossed cylinder geometry) of radius $R$ separated by a total distance $D_T$

$$F = AR/6D_T^2, \tag{4}$$

where the Hamaker constant $A$ for the interaction of medium 1 (mica or CaCO$_3$) across medium 2 (hydrocarbon) is given by[14,19]

$$A = \frac{3}{4}kT\left(\frac{\epsilon_1 - \epsilon_2}{\epsilon_1 + \epsilon_2}\right)^2 + \frac{3h\nu}{16\sqrt{2}}\frac{(n_1^2 - n_2^2)^2}{(n_1^2 + n_2^2)^{3/2}}, \tag{5}$$

where $\epsilon_i$ and $n_i$ are the dielectric constants and refractive indices of the media, and $\nu$ is their characteristic absorption frequency for light in the UV. For mica, hydrocarbon, and CaCO$_3$ the values listed in Table I are applicable, from which, using $\nu = 3.0 \times 10^{-21}$s$^{-1}$, we obtain the Hamaker constants shown in the last column.

The above calculation shows that the Hamaker constants in the two systems differ by at most $\Delta A = 6 \times 10^{-21}$ J, which implies that at the equilibrium separations between the mineral surfaces of $D_T = 45$ Å (two monolayers plus the liquid film) the maximum difference in the force minima would be $F/R = \Delta AR/6D_T^2 = 0.05$ mN/m. This is less than 10% of the measured values (see Fig. 1), and less than the errors in measuring the force minima. Consequently, it can be stated with surity that the contribution of

the substrate is negligible in the present systems, though there may be other systems where this would not be the case.

In the Derjaguin approximation, the force between two colloidal particles separated by a distance $D$ is given by[17]

$$F_0(D) = F(D)\frac{R_0}{2R}, \tag{6}$$

where $R_0$ is the radius of curvature of the spherical colloidal particles and $R$ is the mean radius of curvature of the cylindrically curved mica sheets used in the direct force measurements. From this $F_0(D)$, the work, $U(r)$, required to bring two particles from infinity to a center-to-center distance $r$ ($r = 2R_0 + D_w$), where $D_w$ is the position of the hard wall as determined from the direct force measurements, against the force $F_0$, can be found by integrating $F_0(r)$, once the interaction radius is specified. The determination of $R_0$ will be addressed below.

## Comparison between SFA and light scattering measurements

As already stated, $F_0(r)$ and hence $U(r)$ can be deduced from direct force measurements by means of the Derjaguin approximation [Eq. (6)]. This $U(r)$ can then be substituted into Eq. (2) to calculate the second virial coefficient $A_2$ one would expect to measure in a bulk colloidal system, assuming $E(D)$ is the same in both systems. However, it is clear from Eq. (6) that in order to calculate $U(r)$ one must know the exact value of $R_0$, the radius of the colloids. All other quantities in Eq. (6) were accurately determined experimentally, whereas $R_0 = 50 \pm 5$ Å was known to no better than 10%. $R_0$ was therefore chosen so that the corresponding $U(r)$ reproduced the experimental value of $A_2/M$ precisely for the pure tetradecane system. The value of $R_0$ that meets this criterion is $R_0 = 52.65$ Å. This is in complete accord with the measured hydrodynamic radius of $50 \pm 5$ Å and the outer radius inferred by neutron scattering (see the Experimental section).

Figure 3 presents the predicted colloidal interactions expressed in several ways. Figure 3(a) is the force vs distance profile predicted using the data from Fig. 1 and taking a particle radius of 52.65 Å. Figures 3(b) and 3(c) show the inferred potential $U(r)$ and $\{1 - \exp[ - U(r)/kT]\}$, the integrand of Eq. (6). Evidently the added alcohol should induce an added attraction between the colloidal particles as well as increasing the fluidity of the surfactant layer, as observed in the direct force measurements (Fig. 1).

By selecting $R_0$ in the manner outlined above, one may make a very sensitive test of changes in $A_2$, which are not subject to the uncertainties in $R_0$. Now, the above choice of $R_0$ fixes $R_0$ for the tetradecane/octanol test case. The $- 13.1$ Å shift in the position of $D_W$ in Fig. 3(a) implies an equal shift in $2R_0$; i.e., $R_0 = 39.55$ Å for the tetradecane/octanol system. With this choice of $R_0$, a value of $A_2$ for the tetradecane/octanol system can be calculated explicitly from the data in Fig. 3 using Eq. (2). Hence, we obtain a predicted $A_2$ which is 54% of the value for the
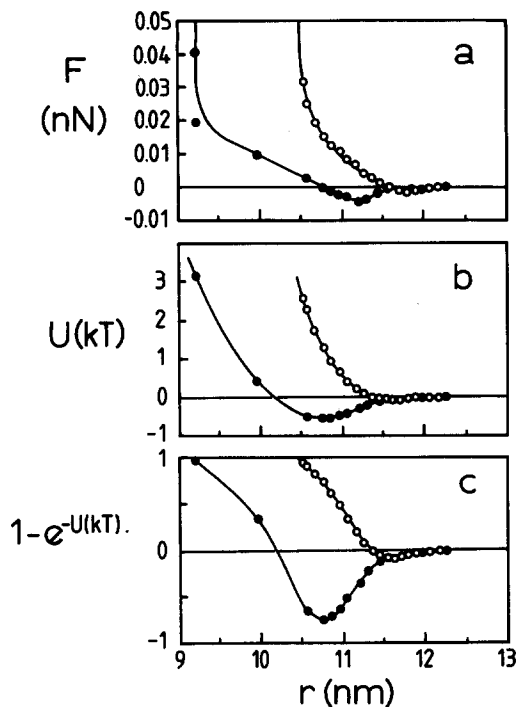


FIG. 3. (a) Predicted force $F_0$ vs distance $r$ profiles for the colloidal particles, as inferred from the SFA data of Fig. 1. Particle radius $R_0$ was taken to be 52.65 Å for the pure tetradecane system. (b) Predicted interaction potential $U(r)$ inferred from data in (a). (c) Statistical weights $\{1 - \exp[ - U(r)/kT]\}$.

pure tetradecane system. This is almost exactly the value measured experimentally by light scattering, i.e., 53%.

Clearly, for the systems investigated here, direct force measurements do indeed reflect the interactions of analogous bulk colloidal systems, both qualitatively and quantitatively. The existence of 7.5 wt % of octanol affects both systems in the same way. The attraction between the particles becomes stronger when alcohol is present by the same amount as measured between two isolated macroscopic surfaces, assuming the monolayers are equally compressible in both systems. This suggests that the penetration of octanol into the monolayers affects both systems to the same extent (see above for details of this phenomenon).

## Sources of error

Despite this remarkable agreement, certain effects which would worsen the accordance are now discussed. First, the method for selecting $R_0$ for the pure tetradecane "control case" is subject to uncertainties in the molecular weight $M$. A particular $M$ is required in order to calculate the value of $R_0$ which reproduces the observed $A_2/M$. A 15% increase in the molecular weight used would lead to a 5% larger $R_0$ value. This, in turn, would increase the predicted $A_2$ ratio by 0.009 thereby worsening the agreement slightly.

Another source of disagreement is a mixed solvent effect which influences the scattering in the test case. Scattering from a single particle in a mixed solvent is influenced

by two effects. First, the added alcohol changes the index of refraction of the solvent and thus alters the contrast. Second, the solvent composition is perturbed around the particle, so that there is additional scattering from the preferentially adsorbed octanol around the particle. When two such particles are brought together, these octanol-rich regions overlap and some of the octanol is displaced. This means that the scattering from the pair of particles is no longer exactly double that of two isolated particles.

Supplementary measurements were made to quantify the effect of a mixed solvent on the refractive index. The refractive index difference, $\Delta n_{to}$, between tetradecane and octanol is $\Delta n_{to} = 7 \times 10^{-4}$. The refractive index increment of a 2% by weight colloidal dispersion in tetradecane was found to be $\Delta n_{ct} = 1.4 \times 10^{-2}$, which is 20 times larger than $\Delta n_{to}$. The proposed octanol-rich region should have a maximum thickness comparable to the interaction zone in Fig. 1, i.e., 10 Å or less around each particle. The size of a particle, however, is approximately five times larger than the octanol-rich region. These two facts are assurance that the colloidal particles make the predominant contribution to the scattered light and so mixed-solvent effects insignificantly influence the present $A_2$ determinations.

Another problem involves the possible time dependence of the interaction potential $U(r)$. Commonly, in the direct force measurements, relaxation times from several seconds to minutes were required to attain equilibrium. In the tetradecane/octanol system, when the two CaS-coated mica surfaces were just brought into adhesive contact under a zero compressional force and allowed to remain there for times of the order of minutes, the surfaces relaxed to a separation approximately 5 Å closer than the position of the potential minimum. It seems that the fluidity of the monolayer enables the surfactant chains to interdigitate to a small extent. If the surfaces were then mechanically separated, the force of adhesion thus measured was about three times that measured if no relaxation were allowed. On the other hand, if after a relaxation time of several minutes the surfaces were separated mechanically at a very slow rate, the force of adhesion was indistinguishable from that measured in the instance of no relaxation since the surfactant chains were able to disentangle. It is this measurement procedure that allows for relaxations of the system both on bringing the surfaces into contact and on separation that gives the true equilibrium force law. This observation supports the notion of slow surfactant chain interdigitation and is further indication of the fluidity of the monolayer and the enhancement of fluidity due to the existence of octanol, since this phenomenon was not detected in the octanol-free system.

Similarly, slow relaxation processes may be expected in the colloidal system as well since the proximity of two particles causes redistribution of the highly constrained surfactant layers. This relaxation could easily exceed the microsecond time scale required for the particles to diffuse past each other, i.e., the colloidal interactions may be delayed significantly on the timescale of typical particle en-

counters. Nonetheless, although these relaxation effects are obviously significant in the SFA experiments, the fact that our comparison of $A_2$ is so good suggests that both the SFA and the scattering experiments are sensitive to the long-time or equilibrium value of $U(r)$.

Even supposing that both techniques used here are governed by the true static work of compression $E(D)$ of the surfaces, it is not clear that this $E(D)$ should be the same in the two systems studied, as we have postulated above. The two systems are indeed the same with regard to the solvents and surfactant but have quite different adsorbing substrates: viz., mica as opposed to calcium carbonate. We have noted that any effect owing to the direct van der Waals interaction between these substrates should be negligible. Thus the main effects of the substrate should arise through its influence on the alcohol and on the surfactant layer. Indeed, these effects are not mutually exclusive: The affinity of the alcohol for the surfactant head group, which is in close proximity to the substrate, is also of significance, particularly for systems of the type studied here.

The interplay between the substrate, the surfactant, and a polar "impurity" has been observed, in the past, for several colloidal oxide suspensions with adsorbed surfactant layers dispersed in nonaqueous media and containing trace amounts of water.[20] For example, the zeta potential of the rutile–Aerosol OT–xylene system increases with increasing water activity suggesting complex adsorption in the region close to the surface.[21] If in this system the surfactant concentration were held constant and only the water activity changed, the particles aggregated at high ($> 100$ ppm) water activities.[22] This behavior is the same as observed in the present investigation (i.e., an attractive force was determined and measured to increase with the addition of octanol), albeit less pronounced since octanol is far less polar than water. Similar effects on these colloidal systems have been seen when methanol, rather than water, was introduced[23] and appears to be a general phenomenon when both the adsorbing substrate and the impurity are polar.

The addition of some alcohol to certain water-in-oil microemulsions leads to a change in the elasticity and spontaneous curvature of the interface.[24] Microemulsion systems are, however, extremely complicated and it is difficult to compare such systems with those investigated here, other than the observation that alcohol does change the properties of both systems by penetration into the surfactant region.

The qualitative and quantitative agreement obtained between the mica system and the calcium carbonate system implies that both these substrates influence their particular systems to the same degree. The choice of these systems for our comparison appears to be fortuitious. Nonetheless, we have demonstrated that for these similar systems, direct force measurements do enable one to infer the interactions inherent to analogous colloidal systems.

## CONCLUSIONS

It has been shown that direct force measurements can quantitatively predict particle–particle interactions in colloidal dispersions, at least in the systems studied here. The success of this test raises the hope that data acquired from surface forces measurements can be used to predict colloidal interactions more broadly. The remarkable agreement, based on measurements taken at length and time scales differing by $10^{-7}$–$10^{-8}$ strongly supports the central assumption of equal force per unit area, together with assumptions of thermodynamic equilibrium used to make the prediction. It must, however, be borne in mind that the present test was quite limited and its significance should not be overgeneralized. We have little independent knowledge that the macroscopic surfaces are the same as the surfaces of the colloids, only that they are somewhat similar. Our success could be fortuitous but nonetheless, is extremely promising.

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