Cohesive force apparatus for interactions between particles in surfactant and polymer solutions

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Abstract

Measurement of forces between two individual particles in the millimeter and micrometer size range is difficult to accomplish and yet these are the particles that are normally encountered in many commercial systems. A cohesive force apparatus (CFA) first used by one of the authors [E.D. Shchukin, R.K. Yusupov, E.A. Amelina, P.A. Rebinder, Kolloidn. Zh. 31 (1969) 913] was modified here for studying cohesive force down to 1 nN between particles of various size, shape and chemical nature under different conditions. In this work, the interaction between fused glass surfaces in solutions containing surfactants, polymers and salts was investigated by measuring the detachment force using the cohesive force apparatus. The cohesive force between glass surfaces was found to gradually decrease with increase in pH due to a corresponding increase in their negative zeta potential. Addition of salt can increase the cohesive force significantly. Interestingly, the cohesive force was observed to increase significantly with the increase of DTAB concentration because of the hydrophobic interactions between monolayers of DTAB on glass. However, the force decreased with further increase in DTAB concentration due to electrostatic repulsion between surfaces and decrease of hydrophobic interactions when DTAB bi-layers are formed. In the case of the hydrophobically modified polymer, polyvinylcaprolactam (PVCAP), the cohesive force was shown to be directly proportional to the molecular weight of the polymer and the loading force. The cohesive interactions between PEO adsorbed glass also showed the force to increase as a function of the PEO concentration, reach a maximum, and then decrease gradually, the increase being due to the reduction in the zeta potential of the glass and the decrease due to steric effect between the fully covered layers. Interaction of anionic surfactant with the pre-adsorbed PEO layer can reduce the cohesive force between the surfaces.
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1. Introduction

Cohesion between particles in close proximity in liquids plays a critical role in many processes ranging from papermaking [2] and filtration [3] to colloidal contaminant transport [4] and fiber interactions in the textile and paper industries. Inter-particle cohesive force is also the principle physico-chemical factor controlling phenomena such as friction and lubrication, rheology of disperse systems, as well as adhesion of microorganisms [5]. Currently, there is a lack of adequate theoretical information on cohesive forces between particles in different environments, mainly due to difficulties in conducting measurements in situ. This is particularly the case with concentrated solid dispersions. It is to be noted that most practical systems are concentrated in nature at least sometimes during their processing. In this regard, of practical interest is the development of an understanding of modification of surface layers to optimize cohesive force between particles and this requires monitoring of forces under a broad range of conditions.

Atomic force microscopy can monitor forces between regular nano particles and flat surfaces. Measurement of forces between two individual particles in the millimeter

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and micrometer size range are not easily accomplished and these are the particles that are normally encountered in many commercial systems. We have recently successfully tested the new apparatus built for studying cohesive interactions between particles under various conditions. The effect of surfactants and polymers on particle–particle cohesion was monitored in relation to flocculation and dispersion [6–8].

The cohesive force apparatus (CFA) is based on a new approach for direct force measurement using a sensitive and pliable magnetoelectric system. This technique allows measurement of cohesive force down to 1 nN, i.e. to the strength of individual forces between particles in practical systems. The technique is useful to monitor the effects of salt and surface active additives (surfactants and polymers) on cohesive forces.

2. Experimental

2.1. Materials

Two bare glass beads of 3.0 mm diameter (SiO_2 75%, CaO 12.5%, Na_2O 12.5%, Fisher Scientific Co.) were used as probe and substrate. Before each measurement, these glass surfaces were thoroughly cleaned using hydrochloric acid and rinsed with deionized water. For zeta potential measurements, glass beads of the same composition were ground using a pestle into micron size particles. Zeta potential was measured using a zeta meter.
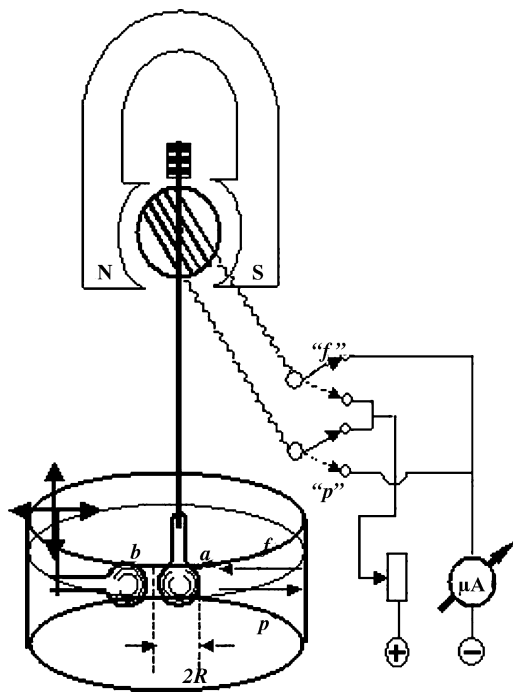
For the study of hydrophobic interactions between surfaces modified by cationic surfactants and polymers, dodecyltrimethylammonium bromide (DTAB, Aldrich Co.), sodium dodecylsulfate (SDS, Aldrich Co.), polyvinylcaprolactam (PVCAP, MW: 1.5, 85 and 320 K, provided by International Specialty Products) and polyethylene oxide (PEO, Polymer Laboratories, Inc.) were used.

2.2. Methods

Fig. 1 shows the schematic diagram of the cohesive force apparatus (CFA) first proposed and used by Shchukin [1,6–10], a highly sensitive and reliable equipment for measuring the cohesive force between individual particles or fibers of any kind in any medium [11–17]. The principle part of this equipment is a magnetoelectric dynamometer. One particle (a) is attached to a rotating hand and another (b) to a manipulator. Applied electrical current compresses particles in contact with a force f; the current versus force relationship obtained by direct calibration is linear over a wide range. For experiments in liquid media, one of the particles is attached to a special L-shaped holder. The vertical part of the holder extends the rotation axis of the magnetoelectric system; the menisus does not create any additional moment of rotation and thus does not influence the measurements.

3. Results and discussion

3.1. Effects of ionic strength and pH on the cohesion force between bare glass surfaces

Fig. 2 shows the results of electrophoretic measurement of glass particles in 0.01 M NaCl solution. The isoelectric point is around pH 1.9. From pH 2 to 6, the zeta potential decreased sharply, and in the higher pH range, it remained almost constant. The results obtained for cohesive force for these surfaces at different ionic strengths are shown in Fig. 3 as a function of pH. It is clear that as the pH is increased,

Fig. 1. Scheme of instrument for measuring cohesive force p between two macroscopic particles after they have been pressed together with force f.
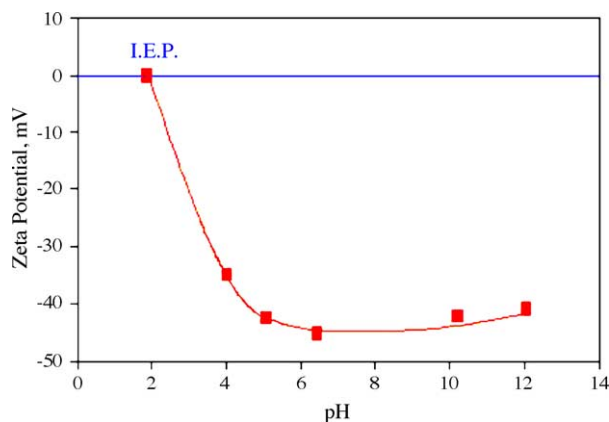

Fig. 2. Zeta potential of glass as a function of pH.
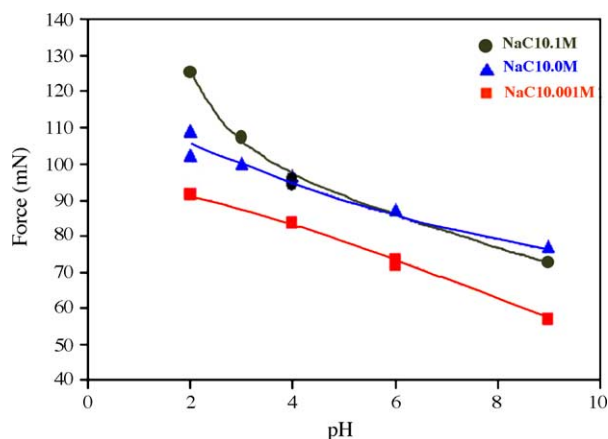
Fig. 3. Effects of ionic strength on the cohesion force between bare glass surfaces as a function of pH.

Fig. 4. Effects of dodecyltrimethylammonium bromide on cohesive force between glass surfaces as a function of pH at 0.01 M NaCl.

the cohesive force gradually decreases due to the increase of the absolute value in the negative zeta potential of the glass surfaces. The positive cohesive force under conditions close to the point of zero charge may come from van der Waals attraction that is stronger than the electrostatic repulsion. The effect of the ionic strength on the cohesive force is significant between 0.001 and 0.01 M NaCl. However, further increase in ionic strength above 0.01 M causes no measurable effect because the double layer compression itself becomes less significant at high ionic strengths.

3.2. Hydrophobic interactions between particles

Dodecyltrimethylammonium bromide ($CH_3(CH_2)_{11}$ $N(CH_3)_3^+Br^-$, DTAB) has been used as the surfactant to investigate the hydrophobic interaction between glass surfaces coated with surfactant. As mentioned earlier, the isoelectric point of glass is pH 1.9 and hence the cohesive force was measured at pH 2 and 6 to probe the hydrophobic interaction between DTAB adsorbed glass surfaces along with that between bare glass particles for comparison purposes. In pure water (pH 5.8–6), the glass surface is hydrophilic and highly negatively charged. It will attract the positively charged DTA+ surfactant with the hydrophobic chains orienting towards the bulk solution and thus inducing the hydrophobic force between the glass surfaces. The initial hydrophobization of glass surfaces by DTAB is attributed to electrostatic activation. However, the hydrophobic interaction comes into effect when DTAB aggregates (hemimicelles) formed on the surface. The effect of DTAB on the cohesive force at the same concentration can be seen in Figs. 4–7 as a function of pH. At the low DTAB concentration, the effect of DTAB on the force is negligible, but when the DTAB concentration is increased to 7×10^{-4} M as shown in Fig. 5, the cohesive force increased measurably due to the hydrophobic chain–chain interaction between adsorbed DTAB species on glass to form hemimicelles. When DTAB concentration is very high (3×10^{-3} M), it can
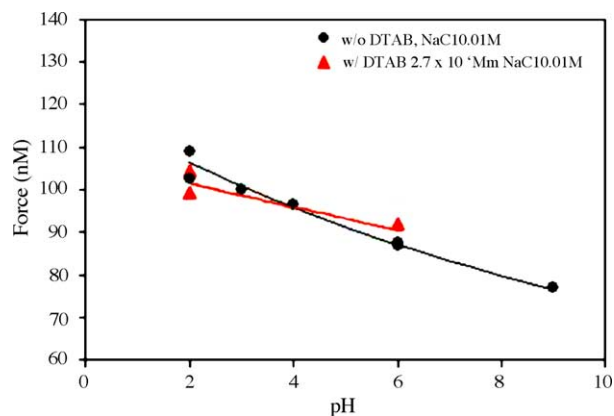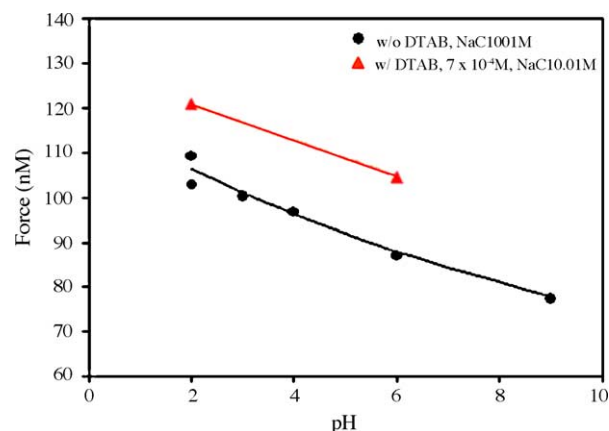

Fig. 5. Effects of dodecyltrimethylammonium bromide on cohesion force between bare glass surfaces as a function of pH.

be seen that the hydrophobic effect becomes less dominant and the measured force is even lower than that for the case of bare glass surfaces (Fig. 6) and this is attributed to the electrical repulsion between the surfactant bi-layers on the particles. Amine coated surfaces show higher cohesive
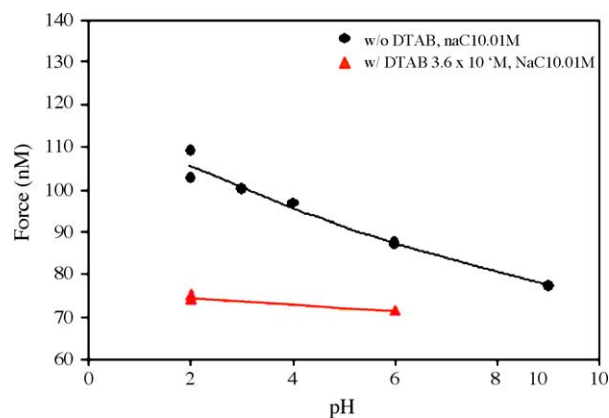

Fig. 6. Effects of dodecyltrimethylammonium bromide on cohesive force between bare glass surfaces as a function of pH.
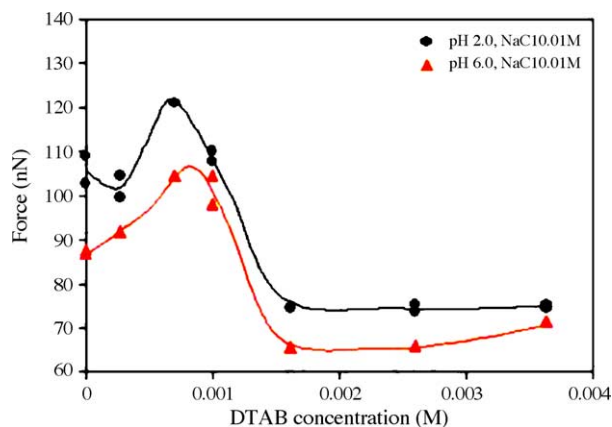
Fig. 7. Effect of dodecyltrimethylammonium bromide concentration on cohesion between glass surfaces in 0.01 M NaCl.

Fig. 8. Effect of ionic strength on cohesion between glass surfaces in 0.001 M dodecyltrimethylammonium bromide solution.

force than the bare glass at the same pH and ionic strength conditions. Even at pH 2, the higher cohesive force arises from the hydrophobic interactions between the positively charged amine head groups oriented towards the solution. At pH 2.0, very little adsorption of the positively charged surfactant is expected on glass because the negative charge density of the glass is very low. However, the small amount of DTAB adsorbed is able to induce sufficient hydrophobic force to produce cohesion between the glass particles. The cohesive force is illustrated in Fig. 7 as a function of DTAB concentration at 0.01 M NaCl. As the DTAB concentration in solution is increased, the cohesive force also gradually increases. In the low DTAB concentration range (<0.001 M of DTAB), DTA^+ head groups continues to adsorb on the negatively charged glass till a monolayer that shows maximum hydrophobicity due to the interaction between hydrophobic tails is reached. However, further increase in DTAB concentration causes a decrease in the cohesive force since additional DTA+ can adsorb on pre-adsorbed DTAB with cationic head groups oriented towards the solution. This will result in the buildup of electrostatic double layer repulsion and cause decrease in hydrophobic interactions and in turn a decrease in cohesion. At still higher DTAB concentrations (>3.6×10^{-3} M of DTAB, CMC of DTAB is 10.8 mM [18]), the cohesive force remains constant as possibly the adsorption density is also constant above the critical micelle concentration of the surfactant.

The effect of ionic strength on the cohesive force at constant DTAB concentration is shown in Fig. 8 as a function of pH. The data shows the increased cohesive force due to reduced double layer repulsion at the higher ionic strength. The force measured at pH 2.0 is higher than that at pH 6.0 at both low and high ionic strength conditions.

Thus the small electrical potential around the isoelectric point play a role in cohesion even when the cationic surfactant cover the glass surface. Furthermore, the ability of the cohesive force apparatus to detect even such small changes is very clear from these tests.
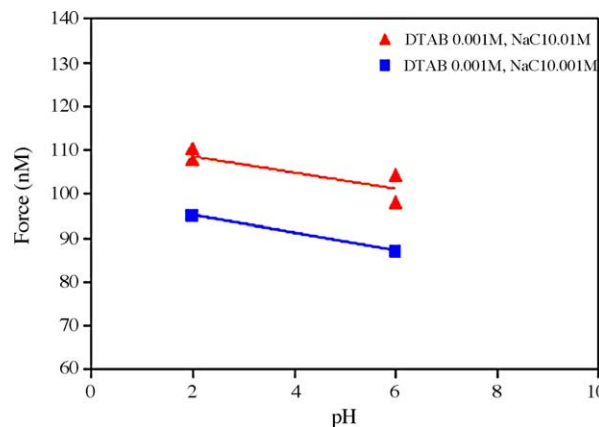
3.3. Effect of polyethylene oxide and sodium dodecylsulfate

Interactions between polymers and surfactants on the solid surface were investigated by determining cohesion between glass surfaces as a function of polyethylenoxide (PEO) concentration at three concentration levels of sodium dodecylsulfate (SDS). In this case, SDS was added subsequent to the adsorption of PEO. Cohesive force between PEO adsorbed layers increased first due to masking of the charged sites by the adsorbed PEO. At higher adsorption, PEO layers exhibit steric repulsive interaction and hence a decrease in the cohesive force.

Addition of SDS decreases the cohesive force due to the electrostatic repulsion between anionic head groups of SDS that binds on pre-adsorbed PEO on the glass. This experiment clearly showed the proposed interactions between polymer and SDS [19] and its effect on the cohesive force (Fig. 9).

3.4. Effect of molecular weight [20] and loading force

The effect of molecular weight of the polymer was tested by conducting tests in the presence of 1.5, 85 and 320 K
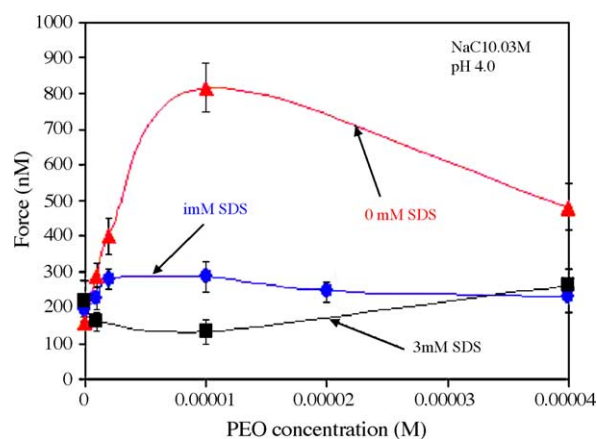

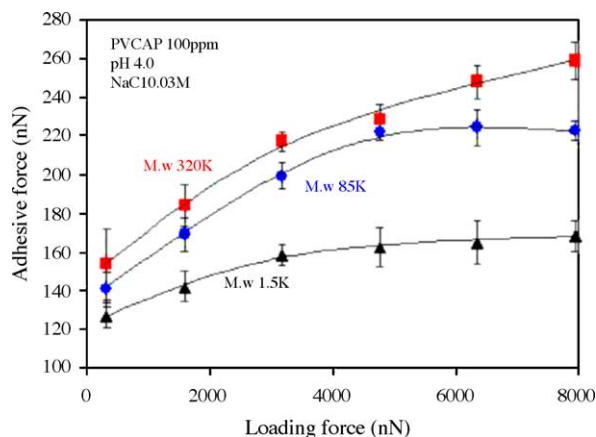Fig. 9. Effect of PEO and SDS on cohesive force between glass surfaces.

Fig. 10. Effect of loading force on cohesive force between glass surfaces in the solution containing 100 ppm of PVCAP.

polyvinylcaprolactam (PVCAP) in 0.03 M NaCl solution at pH 4. The glass was equilibrated with the solution for more than 1 h and then the cohesive force was measured. As shown in Fig. 10, cohesive force increased as a function of the loading force and molecular weight of the polymer.

Polymer adsorption increases the cohesion between glass surfaces. Interestingly, polymer chains of high molecular weight provide higher cohesive force at higher loading force possibly due to the interpenetration of the adsorbed polymer layers on the two surfaces. Again, it is to be noted that the cohesive force apparatus offers a new way to monitor in situ quantitatively the interactions between various surface active species on solid surfaces.

4. Summary

4.1. Effect of media parameters (ionic strength and pH) on cohesive force

The isoelectric point of the glass particles is around pH 1.9. From pH 2 to 6, the zeta potential decrease rapidly, but stays constant at higher pH range. As the pH is increased, the cohesive force gradually decreases due to the increase in the negative zeta potential of the glass surface. Addition of salt can increase cohesive force between the surfaces at low ionic strength. But further increase in ionic strength causes no measurable effect.

4.2. Effect of surface modification by polymers and surfactants

4.2.1. Hydrophobic interaction between dodecyltrimethylammonium bromide (DTAB) adsorbed glass surfaces

DTAB has been used to investigate the hydrophobic interaction between surfactant modified glass surfaces. The cohesive force was found to increase significantly due to the

hydrophobic interaction between adsorbed surfactant layers on glass and due to the neutralization of the anionic site by the cationic ammonium ions. With further increase in DTAB concentration, the force decreases again since DTAB adsorbs with a reverse orientation (ionic heads facing outward) once the surface is fully neutralized, further adsorption of the ammonium ions will take place with a reverse orientation i.e., ionic heads facing towards the bulk solution.

4.2.2. Non-ionic polymer (PEO) and anionic surfactant (SDS)

The effect of polymer adsorption due to hydrogen bonding between oxygen of PEO and silanol of glass on the cohesion was clear from the higher force observed compared to that of bare glass surface. The addition of SDS showed decreased cohesion due to its interaction with pre-adsorbed PEO on the glass.

4.2.3. Hydrophobically modified polyvinylcaprolactam (PVCAP)

In the case of PVCAP adsorbed glass surfaces, the cohesive force increased with molecular weight and loading force. This suggests interpenetration of adsorbed polymer layers leading to increased cohesion.

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