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Measurement of the interfacial tension of demixed colloid–polymer suspensions

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Abstract The interfacial tension of a demixed colloid–polymer mixture is measured using the spinning drop technique. For a demixed system of colloidal silica (diameter 20 nm) and polydimethylsiloxane ($M_w = 97000$) in cyclohexane a value of 1.5×10^{-2} mN/m is obtained.

Key words Interfacial tension – demixed suspensions – colloid–polymer mixtures

Introduction

Mixtures of colloidal spheres and non-adsorbing polymer show rich phase behavior. In these mixtures the polymers induce an effective attraction between the colloidal particles through the mechanism of depletion interaction [1, 2]. The range and strength of this interaction can be adjusted by the size and concentration of the polymer. Above a limiting polymer concentration the attraction between the colloids becomes so strong that the mixture separates in a colloid-rich and a polymer-rich phase divided by an interface. The nature of the coexisting phases depends on the size ratio of the polymers and the colloids [3]. For size ratios larger than $R_g/r_c = 0.3$ (R_g is the radius of gyration of the polymer and r_c is the radius of the colloid) and moderate colloidal volume fractions one finds coexistence between a colloidal-gas and a colloidal-liquid phase as is predicted by the theory [3–5] and confirmed by experiments [3, 4, 6–8].

In contrast to demixed colloid polymer suspensions the interfacial properties in demixed polymer solutions [9, 10, 12, 13] and in complex coacervates and their equilibrium liquid [11] have been studied. In these systems one finds typical values for the interfacial tension in the range 0.01–0.001 mN/m. The interface in demixed colloid polymer mixtures is also an interesting object to study. The coexisting phases only differ in concentration of polymer and colloid and the interface has a thickness of at least one colloidal diameter which makes it thick compared to interfaces in molecular systems. A first estimate of the interfacial tension in this system is then provided by the scaling relation kT/σ^2 where σ denotes the diameter of the colloidal particle. For a particle diameter $\sigma = 20$ nm, one therefore expects a value of 0.01 mN/m.

In this article we will present results of first measurements of the interfacial tension of a demixed colloid–polymer mixture. The measurements have been done using the spinning drop technique [16–18, 9] on a mixture of sterically stabilized silica and the polymer polydimethylsiloxane in cyclohexane.

Experimental

System

The system we studied consisted of a mixture of colloidal silica spheres (stearyl-coated Ludox HS40, Dupont, $r_c = 10$ nm (TEM), polydispersity 10%) and polymer coils (PolyDiMethylSiloxane (PDMS, Janssen Chimica) of mol.wt. 97 000 g/mol, $R_g = 14$ nm [15]) dissolved in cyclohexane (Janssen). All components have a refractive index of 1.44 differing at most 0.005 making the solutions fully transparent.

Phase diagram

The phase diagram of this mixture is determined using the method of dilution lines. A series of mixtures was prepared with different compositions of colloid and polymer. These were then diluted or concentrated by adding or evaporating cyclohexane until the phase boundary was crossed. In Fig. 1 we present the phase diagram as determined by visual observation. The phase separation always resulted in two phases separated by a very sharp and flat interface on which surface waves could easily be excited by just tilting the tube. These are indications that the interfacial tension is low. The spinning drop experiments discussed below have been done in the mixture indicated by the black dot in Fig. 1.

To calculate the interfacial tension the density difference between the coexisting phases is needed. Because of a lack of material the density difference was not measured but estimated from the phase diagram. To make this estimate we have to make only one assumption, that is that all the colloid is in the dense phase and all the polymer is in the dilute phase. Knowing the overall composition, the density of silica (1.791 g/ml), the density of PDMS (0.774 g/ml), the density of cyclohexane (0.994 g/ml) and that the volume of the upperphase is 1/15 of the total volume, we calculate $\Delta\rho$ to be 300 mg/ml. The actual value might be somewhat smaller because some colloid will be in the upper phase and some of the polymer will be in the lower phase.

Spinning drop

To measure the interfacial tension we used a home-built spinning drop tensiometer [14]. The spinning drop tube

Fig. 1 Phase diagram of the colloid–polymer mixture of size ratio $R_g/r_c = 1.4$. The black dot corresponds to the composition at which the spinning drop experiments were done
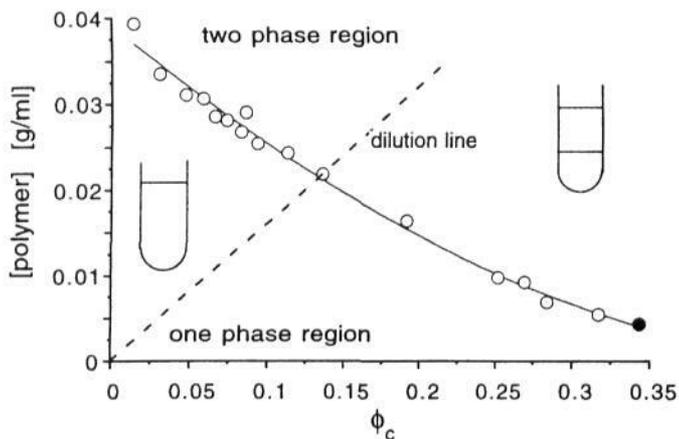
was made of Wilmad precission bore glass, internal diameter 3.96 mm, length 31.4 mm and was sealed with Teflon stops. The angular velocity was measured using an optical sensor. The droplet was observed through a microscope and its length and diameter were measured with a crosswire and a micrometer.

The samples were prepared by first filling the tube with the dense phase after which a small drop of the less-dense phase was added with a glass capillary. By rotating at high ω, an elongated thread of the dilute phase was formed and centered on the rotational axis. By decreasing ω this thread broke up into individual droplets. The angular velocities at which the measurements were done were in the range of $50 < \omega < 250$ [rad/s]. After allowing the system to equilibrate for 1–2 h the length and diameter were measured. All the measurements were carried out at 25 °C.

The volume of the dilute phase was found to be critical for the formation of droplets. When this volume was too big, all sorts of irregular axial symmetric droplet shapes developed. These shapes did not show any relaxation towards more symmetrical shapes. The evaporation of cyclohexane, limited the equilibration time to 1–2 h. The formation of air bubbles made further measurements then impossible. In spinning drop experiments this equilibration time is often 6–8 h.

Results and discussion

The theory derived by Princen et al. [16] was used to calculate the interfacial tension. In this theory the shape of a droplet is calculated by balancing the Laplace pressure over the interface and the centrifugal pressure over the interface. The parameters needed to do the calculations are the length and diameter of the droplet (measured), ω (measured) and the density difference between the coexisting phases (estimated, see experimental).

Two photographs of droplets formed in the spinning drop tube are shown in Fig. 2.

In Fig. 3 we present the values of $\gamma/\Delta\rho$ at different angular velocities. There seems to be a trend that $\gamma/\Delta\rho$ decreases as ω increases. This can be a consequence of the fact that not enough points have been measured at high ω to gain good statistics.

Averaging the values from Fig. 3 we find $\gamma/\Delta\rho = 5 \times 10^{-8}$ [m³/s²]. The value of γ we then calculate is $\gamma = 0.015$ mN/m. The experimental value of γ and the value from the simple scaling argument given in the Introduction are in good agreement.

Recently, Vrij [20] has adapted the statistical mechanical perturbation theory of Kalikmanov and Hofmans for planar liquid–vapor interfaces [19] to calculate the

Fig. 2 Two droplets formed in the spinning drop tube. **A** The length of this droplet was about 1.9 mm and the angular velocity was 152 rad/s; **B** The length of this droplet was 1.4 mm, the angular velocity was 248 rad/s. The contrast between in and outside of the droplet is low because of the matching of the refractive index
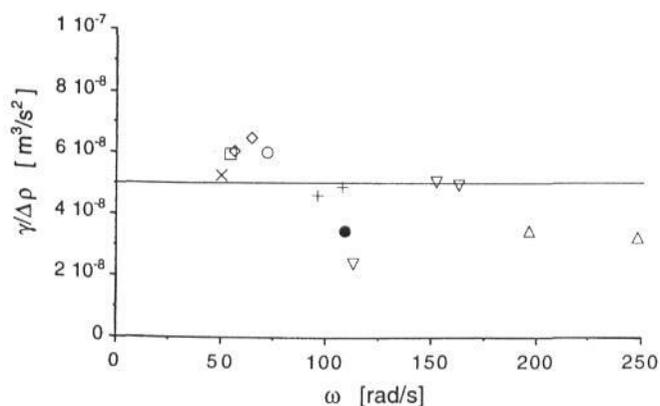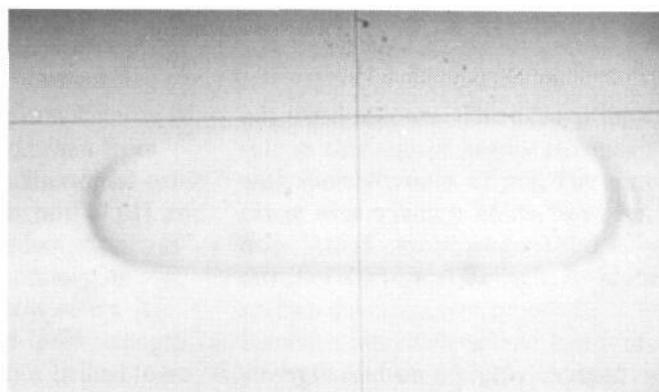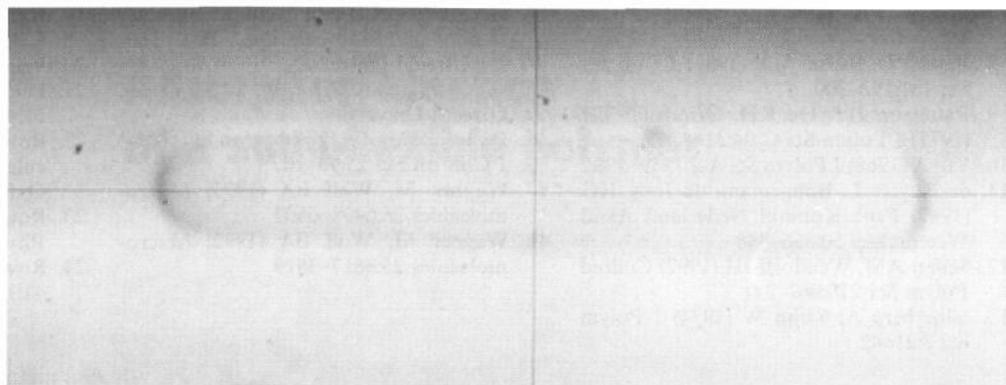
Fig. 3 $\gamma/\Delta\rho$ as a function of ω. Points having the same symbol correspond to droplets measured at different rotational speeds. The point indicated by the open triangle at $\omega = 250$ [rad/s] corresponds to the droplet from Fig. 2a, the one indicated by an open triangle at $\omega = 150$ [rad/s] corresponds to the droplet in Fig. 2b

interfacial tension in demixed colloid polymer suspensions. For the case that $R_g/r_c = 1$, $\phi_c = 0.325$ and a polymer volume fraction $(N/V)\frac{4}{3}\pi R_g^3 = 0.55$ Vrij [20] finds a value of 0.005 mN/m.

At this moment there is no theory for the interfacial free energy and the concentration profile for demixed colloid polymer mixtures. Like in the case of the phase diagram [5, 21] the non-additive hard sphere of Widom and Rowlinson [22–24] may provide a good starting point for such a theory.

Further investigations, both theoretical and experimental, are required to improve the understanding of the interfacial properties of demixed colloid polymer mixtures.

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