Interactions in mixtures of a microemulsion and a polymer

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We have studied the phase behavior of mixtures of a microemulsion and a nonadsorbing polymer. With a virial expansion we calculated the phase boundary curve of the mixture using an effective interaction potential, which includes both the polymer-induced depletion attraction and the square-well attraction between the bare microemulsion droplets. The calculated phase boundary curve fits the phase measurements well. The fitted values of the interaction parameters for the square-well attraction are found to be in good agreement with the previous neutron and light scattering results. The experiment demonstrates the effectiveness of using a polymer to probe the microscopic interactions in microemulsions and other non-hard-sphere colloidal suspensions. [S1063-651X(97)13405-5]

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In recent years there has been a growing interest in studying the phase behavior of various binary mixtures of colloidal particles [1], surfactant aggregates [2], and polymer molecules [3]. While the detailed microscopic interactions in these mixtures may be somewhat different, their phase behavior nevertheless can be explained generally by a simple binary hard sphere model [4]. For mixtures of a colloid and a nonadsorbing polymer, it has been assumed [5–7] that the colloidal particles are hard spheres and the polymer molecules behave as hard spheres toward the colloidal particles but can freely interpenetrate with each other. The hard-sphere-like interaction between the colloidal particles and the polymer molecules results in a spherical shell around each of the colloidal particles, within which the center of mass of the polymer molecules is excluded. The free energy of the mixture can then be reduced by grouping the colloidal particles together to share the depletion volumes. This gives rise to an effective attraction between the colloidal particles. The depletion attraction controls the phase stability of many colloid-polymer mixtures, which are of direct interest to industries [8].

The depletion interaction between the colloidal particles can be expressed in terms of an effective potential $U(r)$, which is the work required to bring the two colloidal particles from infinity to a distance r in a given polymer solution. It has been shown that $U(r)$ has the form [5,6]

$$U(r)=\begin{cases} U_0(r), & r\leqslant\sigma \\ -\Pi_p V(r), & \sigma<r\leqslant\sigma+2R_g \\ 0, & r>\sigma+2R_g, \end{cases} \tag{1}$$

where σ is the particle diameter, Π_p is the osmotic pressure of the polymer molecules, and R_g is their radius of gyration. In the above, the bare colloid interaction potential $U_0(r)=+\infty$ for hard spheres. The volume of the overlapping depletion zones between the two colloidal particles is given by [5,6]

$$V(r)=v_p\left(\frac{\lambda}{\lambda-1}\right)^3\left[1-\frac{3}{2}\left(\frac{r}{\sigma\lambda}\right)+\frac{1}{2}\left(\frac{r}{\sigma\lambda}\right)^3\right], \tag{2}$$

where v_p is the volume occupied by a polymer chain and $\lambda=1+2R_g/\sigma$. This potential has been used to calculate the phase diagram of the colloid-polymer mixtures [8,9], and recent phase measurements of several mixtures of colloid and nonadsorbing polymer have shown qualitative agreement with the calculations [3,10,11]. A more recent neutron scattering experiment by Ye *et al.* [12,13] directly measured the colloidal interaction in the mixtures and confirmed the functional form of $U(r)$ shown in Eq. (1).

While it is successful in explaining the phase behavior of many binary mixtures, the binary hard-sphere model is nevertheless a highly idealized theoretical model. In reality, there are many complicated, non-hard-sphere colloidal mixtures. Even in the study of the model colloid-polymer mixtures, the colloidal particles used in the experiments are not strictly hard spheres. These particles are stabilized either by surface charges or by a layer of surfactant molecules, and hence the interparticle potential has a weak repulsive tail. The interaction potentials for the surfactant aggregates and polymer molecules are probably much softer than those of the hard spheres. Clearly, a further study of non-hard-sphere colloidal mixtures is needed in order to extend the current theory to a more general form, so that different non-hard-sphere interactions can be included. In this way, one can critically examine the current theory for the depletion effect, and prepare model systems to mimic characteristic features of many industrial colloid-polymer mixtures.

In this paper we report a phase boundary study of a mixture of a microemulsion and a nonadsorbing polymer. The microemulsion used in the experiment contains surfactant-coated spherical water droplets, which are uniformly dispersed in an oil-continuous medium. These microemulsion droplets behave as ‘‘association colloidal particles,’’ and they interact with each other attractively [14]. Previous neutron and light scattering measurements have shown [14–16] that the bare interaction potential between the droplets can be

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described by a hard-core repulsion plus an attractive square well,

$$U_0(r)=\begin{cases} +\infty, & r\leqslant\sigma-w \\ -\epsilon k_BT, & \sigma-w<r\leqslant\sigma \\ 0, & r>\sigma, \end{cases} \tag{3}$$

where the square well width $w\simeq3$ Å and the well depth ϵ is proportional to the core size of the microemulsion droplets. Lemaire *et al.* [15,17] have proposed that the attractive interaction between the droplets arises from the mutual interpenetration of the surfactant tails. It should be mentioned that while it is successful in fitting the scattering data, the square well potential is nevertheless a simplified model potential. Attempts have been made to use other potentials to describe the attractive interaction between the microemulsion droplets [18]. In the experiment to be described below, we will use the square well potential so that we can compare our fitting results for the interaction parameters with those obtained from the previous scattering experiments. With Eqs. (1) and (3), we have the total droplet interaction potential $U(r)=U_0(r)-\Pi_pV(r)$. Note that $U(r)$ consists of three parts: a hard core repulsion, an attractive square well, and an additional depletion attraction. In the experiment to be described below, we will show that when the depletion attraction is known, one can use the polymer to probe the bare interaction between the microemulsion droplets.

The microemulsion chosen for the study consisted of sodium di-2-ethylhexylsulfosaccinate (AOT surfactant), n-decane (oil), and water. Both the AOT surfactant (Fluka Chemical) and n-decane (Aldrich) were used as received. Water used for the microemulsion samples was first distilled and then deionized. Because the microemulsion is a ternary system, one has two control parameters for the system: the volume fraction ϕ_d of the droplets (water + AOT surfactant) and the water to surfactant molar ratio n. The microemulsion samples used in the experiment had a fixed $\phi_d=30\%$, but their water-to-AOT molar ratio n was varied between 10 and 40. For these combinations of ϕ_d and n, we obtained a homogeneous and optically clear single-phase microemulsion at room temperature. The microemulsion has been well characterized previously using light and neutron scattering techniques [19–21], and the system, in many aspects, is analogous to a colloidal suspension. It has been shown [19–21] that at moderately low ϕ_d, the size of the water droplets is rather uniform and is linearly proportional to n.

The polymer used was monodispersed polyisoprene (PIP) with the molecular weight $M_w=100\,000$ and $M_w/M_n=1.05$. It was purchased from Polysciences. Decane has been known to be a good solvent for PIP [22]. Because it contains only hydrocarbons and no hydrophilic groups, the PIP chain will not adsorb onto the surfaces of the water droplets. To determine the radius of gyration R_g for the polymer chains in decane, we measured the scattered light intensity of a dilute polymer solution (with the concentration $C_p\leqslant5\times10^{-3}$ g/cm^3) as a function of the scattering wave number q. The value of R_g was then obtained from the Zimm analysis of the scattering data [23]. In Table I we list the measured values of R_g at different temperatures. The microemulsion-polymer mixture samples were prepared by two steps. First, the microemulsion samples were prepared by dissolving AOT in n-decane, and then adding an appropriate amount of water into the solution. To continuously add the PIP into the microemulsion, we first dissolved the PIP in decane with a concentration 0.06 g/cm^3. The PIP solution was then gradually added into the microemulsion while the sample was under thorough mixing. After each addition, the mixture sample was weighed and its polymer concentration was computed according to the added amount of the polymer in the titration solution and the total volume of the mixture sample. All the mixture samples were kept in a thermostat, which has a temperature stability better than ±0.05 °C.

TABLE I. Fitted values of the square well width w, the depth parameter α, and the radius of gyration R_g at different temperatures. Also listed is the measured R_g by static light scattering.

T (°C)	w (Å)	α (Å^{-1})	Fitted R_g (Å)	Measured R_g (Å)
15	2.99	0.041	87.4	89
20	2.98	0.040	93.1	97
25	2.98	0.043	98.5	93
30	2.98	0.042	108.2	108
35	2.99	0.044	114.9	110

The microemulsion-polymer mixture samples are found to become turbid (i.e., phase separation occurred) when their polymer concentration exceeds a critical value $\widetilde{C}_p$ (g/cm^3). To obtain the phase boundary of the mixture, we prepared a series of microemulsion samples in which the droplet volume fraction ϕ_d was fixed at 30%, but the water-to-AOT molar ratio n was varied from 10 to 40. For each of the microemulsion samples with a fixed n, the value of $\widetilde{C}_p$ was determined by carrying out the above described titration procedure until a cloud point was visually observed in the sample. The experimental uncertainties for the measured $\widetilde{C}_p$ were less than ±5%. Because the amount of the polymer solution added into the microemulsion was very small ($\leqslant5$ vol. %), the droplet volume fraction ϕ_d of the mixture samples is essentially the same as that of the corresponding microemulsion samples ($\phi_d\simeq30\%$). After the titration the mixture samples remained cloudy for many days and would not become clear even under rigorous shaking.

Figure 1 shows the measured $\widetilde{C}_p$ (circles) as a function of n at the temperature $T=20$°C. As mentioned above, the PIP chains are hydrophobic and they cannot adsorb onto the surfaces of the water droplets. Therefore, the phase separation in the mixture must be induced by the depletion attraction between the droplets. It is seen from Fig. 1 that the amount of the polymer needed to induce a phase separation in the mixture depends on the water-to-AOT molar ratio n, and the maximum value of $\widetilde{C}_p$ is located at $n\simeq30$. According to Eqs. (1) and (3), both the bare attraction between the microemulsion droplets and the polymer-induced depletion attraction contribute to the phase separation in the microemulsion-polymer mixture. Because the total amount of attraction needed for the phase separation is fixed, we conclude from Fig. 1 that the bare attraction between the droplets also depends upon n. It is interesting to note from Fig. 1 that when the depletion attraction is known, the polymer molecules can

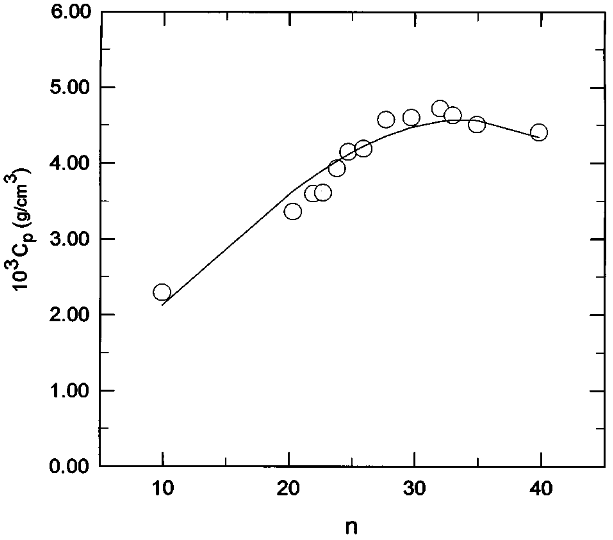

FIG. 1. Measured critical polymer concentration $\tilde{C}_p$ as a function of n at $T=20$ °C. The solid curve is a fit by Eq. (8) with $w=2.98$ Å and $\alpha=0.04$ Å^{-1}.

be used to probe the bare interaction between the microemulsion droplets.

To further characterize the interaction between the microemulsion droplets in the polymer solution, we calculate their second virial coefficient

$$(B_2)_d=2\pi\int_0^\infty[1-e^{-U(r)/k_BT}]r^2dr. \tag{4}$$

Substituting the potential $U(r)$ shown in Eqs. (1) and (3) into Eq. (4), we have

$$(B_2)_d\simeq(B_2)_{HS}\left\{1-3(e^{\epsilon}-1)\left[\left(\frac{\sigma}{\sigma-w}\right)^3-1\right]-\frac{(2R_g+\sigma-w)^6}{64R_g^3(\sigma-w)^3}f(s)\phi_p\right\}, \tag{5}$$

where $(B_2)_{HS}=(\pi/6)(\sigma-w)^3$ is the second virial coefficient for the hard core of the droplets of diameter $\sigma-w$, and $\phi_p=v_pn_p$ is the effective volume fraction occupied by the polymer chains with n_p being the polymer number density. The function $f(s)$ in Eq. (5) has the form

$$f(s)=\left[1-s^3\left(1-\frac{9}{16}s+\frac{1}{32}s^3\right)\right], \tag{6}$$

where $s=2(\sigma-w)/(\sigma-w+2R_g)$. In getting Eq. (5) we have assumed that the polymer osmotic pressure Π_p in Eq. (1) takes the form $\Pi_p=n_pk_BT$ (ideal gas), and the integration in Eq. (4) was carried out only up to the first order of n_p.

It is seen from Eq. (5) that $(B_2)_d$ consists of three terms. The first two terms represent, respectively, the contributions from the hard-core repulsion and the square well attraction of the droplets. The third term is the contribution from the polymer-induced depletion attraction. Because the depletion term increases linearly with ϕ_p, phase separation may occur in the microemulsion-polymer mixture when its polymer concentration becomes sufficiently large. With the calculated $(B_2)_d$, one can estimate the stability limit (spinodal condition) for the emulsion droplets in the polymer solution. At the limit of stability the system does not resist long-range fluctuations of the droplet concentration, and its reciprocal osmotic compressibility goes to zero. Using the virial expansion of the osmotic pressure for the droplets, one arrives at the spinodal condition [7],

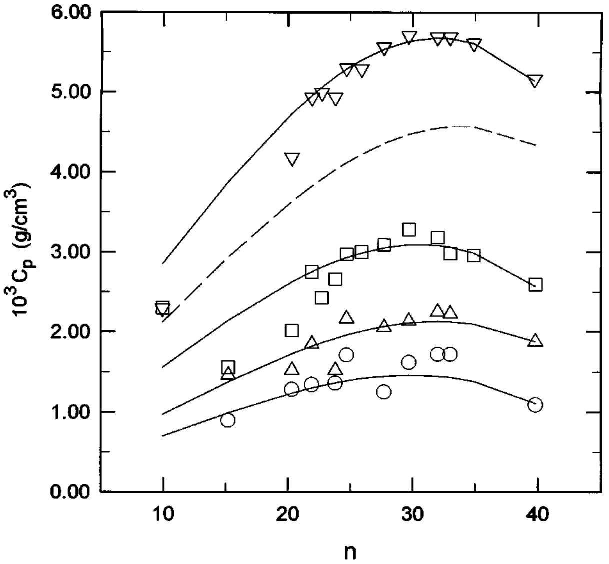

FIG. 2. Measured critical polymer concentration $\tilde{C}_p$ as a function of n at $T=15$ °C (inverted triangles), 25 °C (squares), 30 °C (triangles), and 35 °C (circles). The solid curves are the fits by Eq. (8), and the dashed curve indicates the fitted phase boundary curve at $T=20$ °C.

$$(B_2)_d=-\frac{(B_2)_{HS}}{8\phi_d}, \tag{7}$$

for small droplet volume fraction ϕ_d (up to the second order). Substituting Eq. (5) into Eq. (7), we obtain the critical polymer concentration $\tilde{C}_p$ for the onset of phase separation:

$$\frac{\tilde{C}_p}{C^*}=\frac{1+1/(8\phi_d)-(e^{\epsilon}-1)\left[\left(\frac{\sigma}{\sigma-w}\right)^3-1\right]}{F(\sigma-w)}, \tag{8}$$

where $C^*=M_w/[(4\pi/3)R_g^3]$ is the polymer overlap concentration and $F(\sigma-w)=f(s)(2R_g+\sigma-w)^6/[64R_g^3(\sigma-w)^3]$.

For our mixture samples, the droplet volume fraction was fixed at $\phi_d=30\%$ and the droplet size σ was varied by changing the water-to-AOT molar ratio n. Previous small-angle neutron scattering experiments [21] have shown that $\sigma=31.66+2.26n$ (Å). The square well depth ϵ has also been found to change with σ [14,16]. Using the light scattering technique, Dozier *et al.* [16] have found that $\epsilon=\alpha(\sigma/2)$. With these experimental results being substituted into Eq. (8), we were able to fit Eq. (8) to all the measured phase boundary curves using only two free parameters: the square well width w and the depth parameter α. The solid curve in Fig. 1 shows the fit with $w=2.98$ Å and $\alpha=0.04$ Å^{-1}. The fitted values of w and α compare well with the neutron scattering result $w \simeq 3$ Å [14] and the light scattering result $\alpha \simeq 0.05$ Å^{-1} [16]. It should be pointed out that in the above discussion, we have used the radius of gyration R_g as the effective droplet-polymer interaction range for the depletion potential in Eq. (1). Because the value of C^* is needed in Eq. (8), R_g was also involved in the calculation of the critical polymer volume fraction $\widetilde{\phi}_p = \widetilde{C}_p / C^*$. The recent neutron scattering experiments by Ye *et al.* [12,13] have indicated that a length scale somewhat smaller than R_g should be used for these purposes. To reduce fitting uncertainties, we treated R_g in Eq. (8) as a fitting parameter. Note that the main effect of R_g in the fitting is to change the overall height of the fitted phase boundary curve. The fitted values of R_g are listed in Table I.

We now discuss the measured phase boundary of the microemulsion-polymer mixture at other temperatures. Figure 2 shows the measured $\widetilde{C}_p$ as a function of n at $T = 15$ °C (inverted triangles), 25 °C (squares), 30 °C (triangles), and 35 °C (circles). The solid curves in Fig. 2 are the fits by Eq. (8) with w, α, and R_g being the fitting parameters. The fitted values of these parameters are listed in Table I. The dashed curve shows the fitted function $\widetilde{C}_p$ vs n for the mixture samples at $T = 20$ °C (see Fig. 1). It is seen from Table I that the fitted values of w and α remain fairly constant in the temperature range studied, and they compare well with the previous measurements [14,16]. Because the value of R_g in the fitting controls the overall height of the fitted phase boundary curve, we expect the fitted R_g to be subjected to experimental uncertainties similar to those for the measured $\widetilde{C}_p$. In the experiment, $\widetilde{C}_p$ was determined by a visual observation of the cloud point. Nevertheless, the fitted values of R_g shown in Table I are in good agreement with the measured R_g by static light scattering.

In summary, we have studied the phase behavior of a microemulsion-polymer mixture at different temperatures. With a virial expansion we calculated the phase boundary curve of the mixture using an effective interaction potential, which includes both the polymer-induced depletion attraction and the square-well attraction between the bare microemulsion droplets. The calculated phase boundary curve fits the phase measurements well. The fitted values of the interaction parameters for the square-well attraction are found to be in good agreement with the previous neutron and light scattering results. The experiment demonstrates the effectiveness of using a polymer to probe the droplet interaction in the microemulsion. We expect this simple polymer titration method to be useful in the future for measuring the microscopic interactions in other non-hard-sphere colloidal suspensions, which are of direct interest to industries.

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