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Measurement of inter-particle forces from the osmotic pressure of partially frozen dispersions

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Abstract. When an oil-continuous dispersion is frozen two microdomains are formed: one, the pure oil solvent which is selectively solidified (I), the other, a concentrated 'liquid' dispersion of particles in oil (II). These two domains are intimately mixed within the frozen colloid and exist in a state of equilibrium determined by the system pressure and temperature. The position of equilibrium controls the proportion of the solvent which is solidified, and thereby the concentration of particles within the fluid microdomains (II). Combined with SANS measurements, to determine the inter-particle separation in these microdomains, an analysis based on osmotic pressure provides a measure of the inter-particle repulsion forces presented by the surfactant layers.

1. Introduction

The freezing points (T_f^*) of alkanes commonly used as the oil-continuous medium in dispersions are generally low (e.g. for hexane $T_f^* = -95$ °C). However, for cyclic alkanes, e.g. cyclohexane (C_6H_{12}), the freezing point is considerably higher which facilitates the study of solidified oil-continuous dispersions at near-ambient temperature as a function of pressure (figure 1). We have examined two different types of surfactant-stabilized dispersion in the frozen state in cyclohexane: (a) calcium carbonate ($CaCO_3$) particles stabilized by a calcium alkylbenzenesulphonate ($Ca(ABS)_2$) surfactant and (b) water-in-oil (w/o) microemulsion droplets stabilized by sodium bis(2-ethylhexyl) sulphosuccinate (aerosol-OT or AOT).

2. SANS measurements

The total SANS scattering from a system of monodisperse particles can be expressed as

$$I(Q) \propto P(Q)S(Q). \quad (1)$$

The measured scattering cross-section, $I(Q)$, contains a dimensionless intra-particle function, $P(Q)$, characterizing the size and shape of the individual particles, and an inter-particle structure factor, $S(Q)$, which includes spatial correlations arising from interactions between the particles.

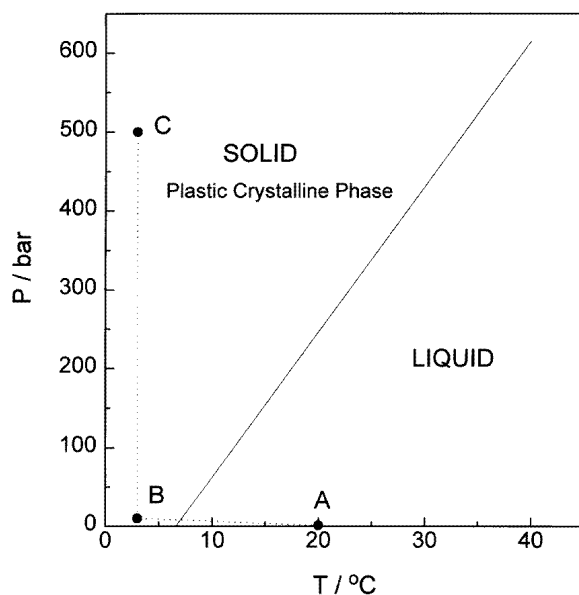


Figure 1. The pressure–temperature phase diagram for the l–s transition of cyclohexane. Points A, B and C refer to SANS measurements of figure 2 (see the text for details).

2.1. Particle (droplet) dimensions

For a dilute system of non-interacting particles at low volume fraction (typically $\phi < 0.03$) $S(Q) \sim 1.0$ and $I(Q)$ is then uniquely determined by the particle size and shape. In the case of monodisperse spherical particles, the radius is then easily obtained by fitting the observed $I(Q)$ to a form factor ($P(Q)$) for a single sphere. However, the microemulsion droplets and CaCO_3 particles are known to exhibit a small degree of polydispersity which can be accounted for using a modified Schultz distribution [1].

The particle and droplet systems that we have examined are both spherical and can be characterized by measurement of the core radius (r_c) and the thickness of the curved monolayer of surfactant (t_s). We have determined these dimensions using SANS measurements with contrast variation. For the CaCO_3 particles $r_c = 26 \text{ \AA}$ and the surfactant stabilizing the core particles is a mixture of calcium alkylbenzene sulphonates giving a layer thickness, t_s , of approximately 16 \AA [2, 3]. For AOT-stabilized w/o microemulsions $t_s = 9 \text{ \AA}$, and the droplet size is controlled by the water-to-surfactant ratio ω ($=[\text{H}_2\text{O}]/[\text{surfactant}]$). In this work we have used an ω -value of 10 for which r_c was determined as 19 \AA .

2.2. Particle (droplet) interactions

The predominant form of the $S(Q)$ -function for non-interacting hard spheres is a broad peak with a position of maximum intensity (Q_{max}) given by [4]

$$Q_{max} = \frac{c}{d} \quad (2)$$

where d = the mean inter-particle separation, and c = a constant dependent on the inter-particle configuration, $=2\pi$ for a random distribution of spherical particles.

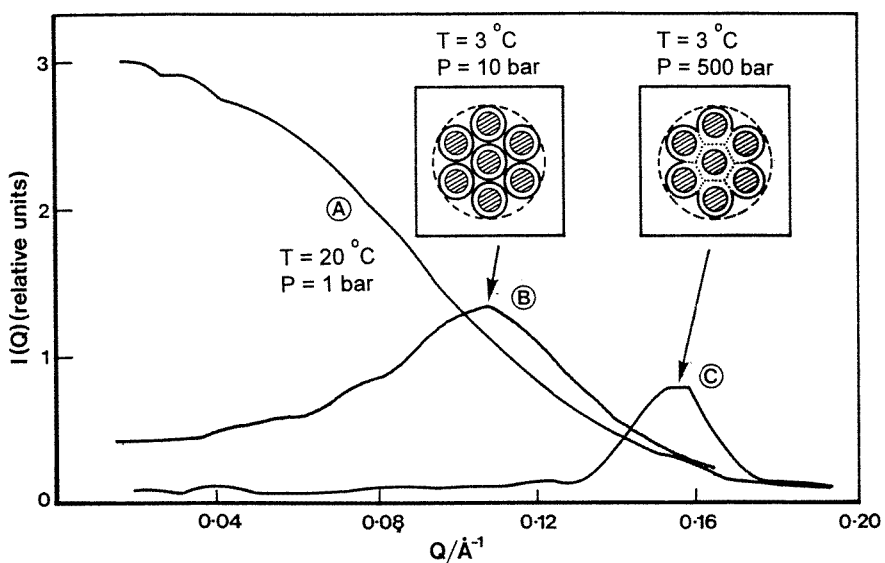


Figure 2. SANS $I(Q)$ -profiles for AOT-stabilized w/o microemulsion droplets ($\omega = 10$, $[AOT] = 0.10 \text{ mol dm}^{-3}$) in cyclohexane at the state points A, B and C shown in figure 1.

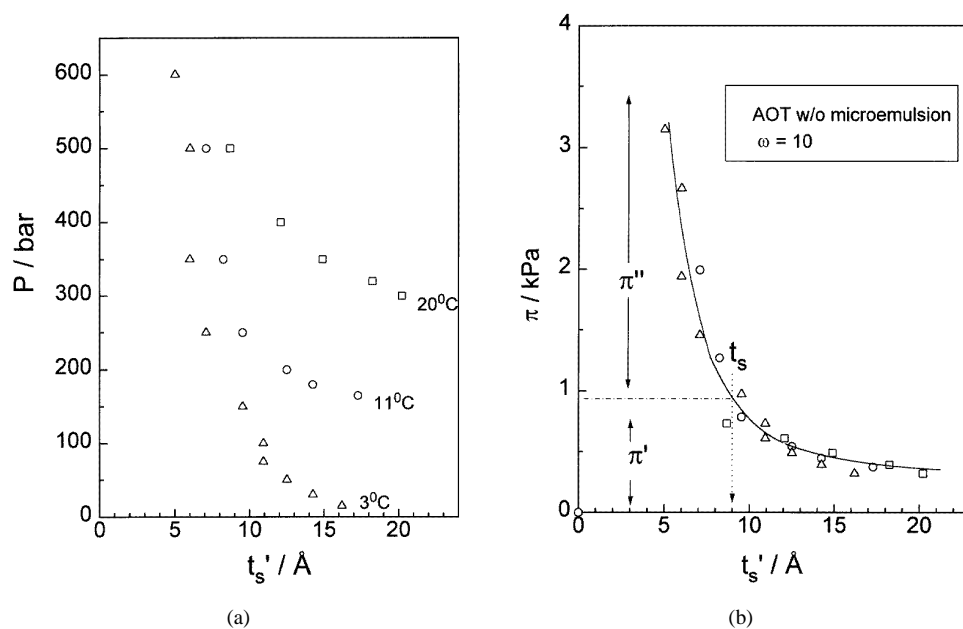


Figure 3. (a) The dependence of t'_s on hydrostatic pressure and temperature for the AOT $\omega = 10$ w/o microemulsion. (b) The correlation of the effective surfactant thickness (t'_s) with osmotic pressure (π) for the AOT $\omega = 10$ w/o microemulsion at 20 °C (\square), 11 °C (\circ) and 3 °C (Δ).

A typical set of $I(Q)$ -data is shown in figure 2 for $\omega = 10$ microemulsion droplets in cyclohexane. At 20 °C and 1 bar, cyclohexane is in the liquid state and the scattering closely

resembles that of a dilute system of spheres. On cooling to 3 °C a large proportion of the cyclohexane freezes to a pure solid-phase microdomain (I) which is in equilibrium with a fluid-phase microdomain (II) containing a high concentration of droplets. The scattering is then dominated by a strong $S(Q)$ -contribution arising from inter-particle correlations in the concentrated configuration of droplets within II. On gradually increasing the pressure to 500 bar the position of the $S(Q)$ -peak, Q_{max} , moves consistently to higher Q -values, indicating that the inter-particle separation is decreasing according to equation (2). This systematic response is both reversible and reproducible for all of the systems studied. The SANS behaviour of the corresponding CaCO_3 particle system shows a similar response to pressure and temperature on solidification of the dispersion. For both systems no phase separation is observed on melting a frozen dispersion, indicating that both colloids are stable in a solidified state.

In our experiment the response of the system to pressure and temperature variation is measured by the droplet separation in the ‘liquid’ microdomains within the frozen dispersion. A hexagonal close-packed arrangement of droplets (for which $c = \pi\sqrt{6}$) has been used in this calculation which is in accord with results of previous SANS studies on this system at high droplet volume fractions [5]. To represent the state of ‘compression’ of the surfactant monolayers between the points of contact of the droplets we define an ‘effective surfactant layer thickness’ (t'_s) representing the thickness of the compressed layer:

$$t'_s = \frac{d}{2} - r_c. \quad (3)$$

The dependence on pressure and temperature follows a consistent trend of behaviour with t'_s decreasing with increasing pressure, and/or decreasing temperature. This response is governed by a balance of opposing forces operating in the system between expansion and contraction of the fluid domains. This may be more clearly understood by considering the balance of energies (i) to concentrate the droplets against an osmotic pressure gradient and (ii) that released ($T \Delta S$ and $P \Delta V$) on ‘freezing out’ more of the pure solvent.

3. Treatment of the results

An analysis based on the osmotic pressure, π , of the droplets in the frozen dispersion was developed [3] which describes the simultaneous dependence of t'_s on both P and T :

$$\pi = \frac{\Delta S_f \Delta T - \Delta V_f \Delta P}{V_m^L} \quad (4)$$

where ΔS_f = the entropy of freezing of the pure solvent (cyclohexane); ΔV_f = the volume change on freezing of the pure solvent; $\Delta T = T - T^*$; $\Delta P = P - P^*$; and T^* , P^* = any freezing temperature and pressure of the pure solvent.

Isotherms showing the dependence of t'_s on pressure and temperature are presented in figure 3(a) for the $\omega = 10$ microemulsion in cyclohexane. The plots follow a consistent trend of behaviour with the droplet separation decreasing with increasing pressure, and/or decreasing temperature. The dependence of π on t'_s is shown in figure 3(b) which represents a unification of the three isotherms. It is clear that some energy needs to be expended before the droplets are brought into contact ($t'_s = t_s$) which arises from the increased osmotic pressure (π') of the system due to concentration effects.

The interdigitation of the surfactant layers on adjacent droplets is represented in figure 3 by the region in which $t'_s < t_s$ within which the curve appears to be approaching a limiting value of t'_s of ~ 5.0 Å. The general form of the curve, and absence of a minimum, is in

accord with the behaviour of sterically stabilized dispersions in better than ‘theta’ solvents for which attractive interactions are negligible compared to thermal energy.

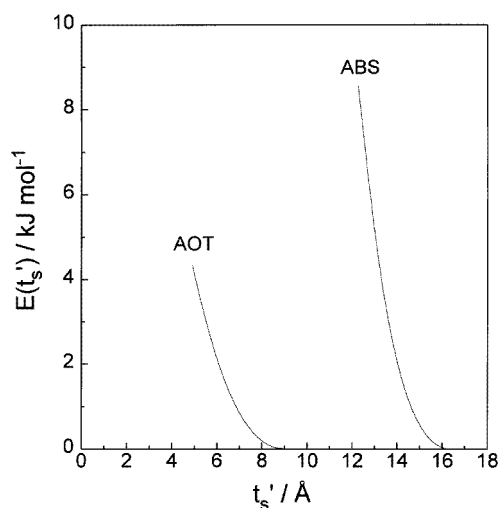


Figure 4. The inter-particle potential, $E(t'_s)$, for the $\omega = 10$ AOT w/o microemulsion and $\text{Ca}(\text{ABS})_2$ -stabilized CaCO_3 particles in cyclohexane.

A previous analysis of the osmotic pressure within the ‘overlap’ regime of concentration represented by π'' has been used to obtain the inter-particle pair potential, $E(t'_s)$, in the cluster of particles [6]:

$$E(t'_s) = \int_{t_s}^{t'_s} \left\{ \frac{\Delta S_f \Delta T - \Delta V_f \Delta P}{V_m^L} \right\} (r_c + t'_s)^2 dt'_s. \quad (5)$$

It is worth emphasizing that $E(t'_s)$ here represents a potential of mean force for particles in a *hexagonal close-packed configuration* which is not always the same as the pair potential between an isolated pair of particles. However, for systems where $t_s \ll r_c$ these quantities do become equivalent. Figure 4 shows $E(t'_s)$ for the AOT-stabilized w/o system as calculated from equation (5). The energies probed by the range of pressure and temperature employed are low and are considerably less than that required to fuse the droplets. Dynamic measurements show that for this system approximately 1 in 10^3 encounters result in fusion [7]. It is also clear that droplets moving with thermal energies of order kT will undergo ‘slightly soft’ collisions with some interpenetration (or compression) of the surfactant layers.

The inter-particle pair potential for the carbonate dispersion in cyclohexane at 3°C is also shown in figure 4. The form of the potential appears to be somewhat ‘harder’ than that of the AOT microemulsion; this may arise from the more irregular, branched structure of this surfactant.

We believe that this approach provides a promising method for probing interactions in colloidal dispersions with high sensitivity.

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