Experimental study of phase separation in films of molecular dimensions

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Phase separation induced by the close proximity of two surfaces occurs in thin films of incompletely miscible liquids. This phenomenon is thermodynamically analogous to capillary condensation of liquid from vapor and leads to a discontinuity in the force between two surfaces across the liquid. We present measurements of the distance at which phase separation takes place in nonpolar liquids containing water at activities from 0.7 to 1 between two kinds of chemically different mica surfaces. The generality of the effect is established by similar results obtained with other sparingly soluble solutes. The importance of surface adsorption and kinetic effects is discussed and comparisons are made with a modified Kelvin equation. The results are relevant to recent theoretical and simulation studies of the phase behavior of liquids in narrow pores and thin films.

INTRODUCTION

The best known example of how phase behavior in a confined system differs from bulk is that of capillary condensation. Because of the presence of the solid surfaces the first-order transition from vapor to liquid occurs at a different chemical potential than in the bulk. If the liquid phase wets the solid surface the liquid-vapor interface has negative curvature, and the resulting pressure difference ΔP across this meniscus may be calculated from the Laplace equation

$$\Delta P = \gamma / r , \qquad (1)$$

where γ is the surface tension of the condensed liquid against vapor and r the total radius of curvature of the interface (negative in this case). For an ideal gas the equilibrium radius of curvature is related to the vapor pressure of the liquid by the Kelvin equation:

$$kT \ln(p/p_s) = \gamma / r(\rho_l - \rho_g) , \qquad (2)$$

where ρ_l, ρ_g are the number densities of the liquid and gas, and p, p_s the vapor pressure and the vapor pressure at saturation, respectively. This is the physical chemist's view of capillary condensation—the curved interface of a wetting liquid in a pore or slit means that it will coexist with an undersaturated vapor.

It is not, however, necessary to introduce a meniscus into the problem. Ultimately, capillary condensation is merely a consequence of the existence of a free energy associated with the solid surface, which is different in vapor and in liquid. The surface free energy becomes important in systems where the surface area is large compared to the volume and as a result the phase behavior of confined fluids is considerably more complex than that of a bulk fluid.

This complexity has been the subject of much theoretical work over the past few years. Computer simulation techniques,[1] lattice models[2] as well as density-functional theories[3-6] have been used to study the behavior of fluids between walls in close proximity. Since the Kelvin equation does not explicitly include interactions between the walls and between the walls and fluids it is expected to break down at small separations. This is especially so for situations where the liquid completely wets the solid phase, where thick wetting films exist even at an isolated surface.[7,8] Between two surfaces close together competition between capillary condensation and prewetting can lead to a rich variety of surface-induced phase transitions.[2,9]

We have over the last decade carried out experimental studies of capillary condensation, and the first verification of the Kelvin equation for small radii of curvature was published by one of us.[10] These experiments were performed by allowing cyclohexane to condense around two curved mica surfaces ($R \approx 1$ cm) in contact and then, after separation, determining the equilibrium separation of a stable neck of cyclohexane as a function of the vapor pressure. The results showed that the Kelvin equation was accurate down to radii of curvature of 4 nm, and especially that there are no significant curvature effects on the surface tension of a simple liquid. Our technique allows us to study the condensation in what is in effect a single slit and we thus avoid the complex topology of the mesoporous solids usually employed in experimental investigations of capillary condensation.[11]

The geometry of our system is such that the bridging neck of capillary condensed liquid has two radii of curvature of opposite sign but very different magnitudes. Typically, $r_1 \approx -10$ nm and $r_2 \approx +10$ μm (see, for example, Fig. 1 in Ref. 10), so that $1/r_2$ may be neglected and the radius of curvature of the meniscus is related to the surface separation D by

$$|r| = D / 2\cos\theta , \qquad (3)$$

where θ is the contact angle of the liquid on the mica.

We have lately turned our attention to capillary condensation of a sparingly soluble liquid solute from another liquid.[12,13] The analogy with the usual Kelvin equa-
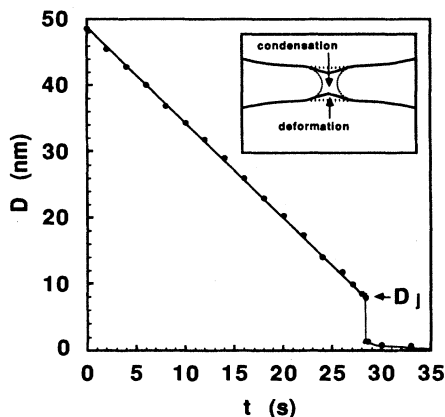
FIG. 1. Surface separation D as a function of time t for two mica surfaces driven together with a constant driving speed (≈ 1.2 nm/s). The liquid medium is octamethylcyclotetrasiloxane (OMCTS) containing water at an activity of ≈ 0.9. One of the surfaces is mounted on a double-cantilever spring of stiffness $\approx 10^5$ N m^{-1}. Note the very sudden increase in speed at a separation of 9 nm, where the two surfaces are pulled together by the spontaneous condensation of a water bridge between them. The inset shows the appearance of the surfaces (as deduced from the shapes of the interference fringes) as this water bridge forms just before the inward jump.

tion, first suggested by one of us,[13] has since been given theoretical foundation.[9] In effect, in Eq. (2) the surface tension is simply replaced by the interfacial tension γ_i and p/p_s by the activity a of the solute. In conjunction with these experiments we made an important observation: We were able to detect the first-order phase transition associated with the capillary condensation as a discontinuity in the force between the two surfaces, occurring at separations up to about 10 nm.[13] This connection between capillary condensation and surface-induced phase separation appears not to have been made in the earlier literature (see, for example, Ref. 2). The same process of "sponaneous" capillary condensation at finite surface separations also occurs in vapor,[14] but is more difficult to study quantitatively because of the larger van der Waals forces in such systems. Clearly, our experimental system is ideally suited for comparison with theoretical studies of the phase behavior of fluids in slits.

The practical importance of capillary condensation is immense. The adhesion of surfaces, powders, and particles under ambient conditions is usually completely dominated by capillary condensation. Our earlier observations demonstrated that it is equally important in dispersions, especially in nonpolar liquids, where trace amounts of dissolved water capillary condense between particles. In both vapor and liquid media this affects properties such as floc volumes,[15] flow of powders and lubrication[16] and the friction of surfaces.[17] The efficient recovery of crude oils trapped in the narrow pores of reservoir rocks may also involve capillary condensation effects.[18]

We here present a quantitative study of the capillary condensation problem in binary liquid mixtures—

specifically water dissolved in nonpolar liquids. In a previous publication the competition between solvation forces and surface-induced phase separation of water occurring at low water activities was studied.[19] We have now extended these measurements to higher water activities where no equilibrium solvation forces are measurable, and have also looked at another system of two incompletely miscible liquids—that of methanol in octane. The contact angle of water on mica immersed in these nonpolar liquids is of the order of 10°—small enough for us to set $\cos\theta \approx 1$ in Eq. (3), but far from the regime of perfect wetting.

Two surfaces of molecularly smooth mica are allowed to approach each other and the separation at which capillary condensation occurs is measured as a function of the activity of the dissolved species (water). This has been done for two chemically distinct mica surfaces that show very different short-range interactions across water. Potassium mica gives rise to a strongly repulsive hydration force, whereas hydrogen mica shows a purely attractive force at short range. The results provide information on the dependence of the first-order phase transition on surface properties and the activity of the solute—dissolved water. We also gain some understanding of the kinetic limitations of the condensation process—an effect which is rarely considered elsewhere.

EXPERIMENTAL

The technique uses the surface force apparatus, which has been extensively employed to study the interactions between surfaces at small separations, including van der Waals, electrical double-layer, steric, solvation, and hydrophobic forces.[20,21] Two mica sheets, silvered on the back sides, are mounted facing each other in a crossed-cylinder configuration. One of the surfaces is mounted on a spring of variable stiffness ($10^2 - 10^5$ N m^{-1}) and the separation between the surfaces is determined by multiple-beam interferometry.[22] This optical method also allows the refractive index of the intervening medium to be determined, and the shapes of the surfaces and any changes thereof can be monitored. The interferences fringes were recorded with a video camera positioned at the exit slit of a grating spectrometer and subsequently analyzed with a video micrometer. The distance resolution thus obtainable is about ± 0.3 nm and the time resolution 0.02 s. Forces are measured by calibrating the relative motion of the surfaces in the absence of a force and then deducing any interaction at shorter range from the deflection of the spring. In this study we use the fact that an attractive force will lead to an instability in the spring system as soon as the gradient of the attraction exceeds the spring constant. Forces that are increasingly attractive at small separations thus result in instabilities, manifested as spontaneous inward "jumps" of the two surfaces, often into molecular contact, although adsorption of molecules to the surfaces may cause changes in the "contact" position. Further detail on these experimental techniques can be found in Refs. 10, 13, and 21.

The muscovite mica used in these experiments has a lattice charge that is fully neutralized in vapor by potassi-

um ions on the surface. If the sheets are dipped into a dilute solution of hydrochloric acid ($pH3$) these potassium ions are completely replaced by hydrogen ions which remain on the surface if it is withdrawn and the solution blown off.[23,24] This procedure was used to obtain surfaces, both molecularly smooth, and with different short-range interactions.

The water activity in the nonpolar liquids was controlled by equilibration of a droplet of nonpolar liquid between the surfaces through vapor with lithium chloride solutions. The water activity is equal to the fraction of saturation in these nonpolar liquids, where water is nonassociated. The ambient temperature was 22 °C, controlled to within 0.1 °C, but small temperature gradients (<0.3 °C) in the measuring chamber due to the heating effect of the light beam lead to a maximum error in the activity of about 1%. In the case of methanol an activity of close to unity (not controlled) was used.

The nonpolar liquids (octamethylcyclotetrasiloxane, octane, decane, tetradecane, and *trans*-decalin) were analytical grade, purified by double distillation under nitrogen at reduced pressure. The analytical grade methanol was similarly purified but distilled at ambient pressure. The lithium chloride was analytical grade, used as received and the water was doubly distilled.

RESULTS

To gain a qualitative understanding of the phenomenon being studied, it is instructive to first examine the behavior of the two surfaces as they are brought together with a constant, slow driving speed. The surface separation as a function of time is plotted in Fig. 1 (the liquid is octamethylcyclotetrasiloxane), where it can be seen that at a separation of $D_j = 9$ nm there is a very dramatic increase in the speed of approach. The surfaces are in fact pulled into contact faster than the time resolution of the video (0.02 s) permits us to observe. Note that the driving speed used here is sufficiently slow that no hydrodynamic effects due to the viscosity of the liquid are noticeable, unlike the similar data presented in a series of experiments specifically designed to measure this viscosity.[25] The position at which the jump occurs is independent of the driving speed of the surfaces, at least for speeds in the range 0.3–5 nm/s.

As the surfaces are being pulled in a very significant surface deformation occurs (see inset to Fig. 1) viz. the surfaces become pointed and appear to be sucked together around the region of closest separation. This is readily deduced from the appearance of the interference fringes. Furthermore, the jump distance is *independent* of the spring constant. As an example, a series of measurements in tetradecane yielded the following values for three different spring stiffnesses K: $K = 2.4 \times 10^2$ N m^{-1}—$D_j = 8.5$ nm; $K = 1.9 \times 10^3$ N m^{-1}—$D_j = 8.7$ nm; $K \approx 10^5$ N m^{-1}—$D_j = 8.7$ nm. These observations show that the force causing the inward jump is very different from that of an ordinary equilibrium interaction where the force would be expected to vary with separation.
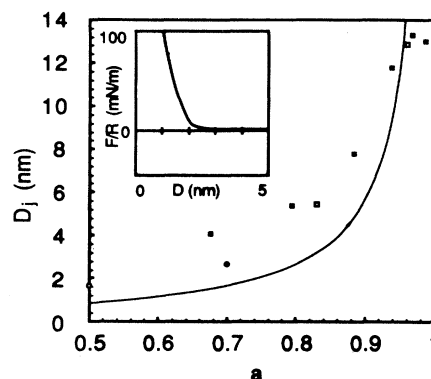
After the surfaces have come into contact an annular

FIG. 2. Surface separation D_j at which phase separation of water takes place as a function of the activity, a, of dissolved water. The surfaces are naturally occurring potassium mica in OMCTS. Solid squares are results obtained on increase of the activity, open squares on subsequent reduction, in the same experiment. Open circles are results from Ref. 19. The solid line shows the expected result if the phase separation occurred in agreement with the Kelvin equation (see Eq. 4). Note the larger than expected condensation distances at activities below about 0.94. Above 0.95 no further increase in separation is observed. The inset shows a schematic depiction of the short-range forces between two potassium mica surfaces immersed in aqueous solution at near-complete coverage of potassium ions (Ref. 27).

capillary condensate of water forms around the contact zone.[13] Clearly, it is the formation of this condensate at a finite surface separation ($D = D_j$) that pulls the surfaces into contact. The condensation (or phase transition) is accompanied by the formation of a curved water-nonpolar liquid interface and the resultant negative Laplace pressure in the condensate leads to the deformation of the surfaces and the very sudden inward jump. The force law consequently exhibits a step functionlike behavior. In summary, at large separations there is a van der Waals interaction, too weak to be measurable and closer in, at some critical separation, spontaneous condensation occurs, resulting in a very large attraction that pulls the surfaces together irrespective of the spring stiffness.

The surface separation at which the inward jump occurs between potassium mica surfaces is plotted as a function of the water activity in Fig. 2. The liquid is octamethylcyclotetrasiloxane, which has been extensively studied over the past few years.[19,20,25] For comparison, the results expected from the Kelvin equation are given as the solid line. In a near-wetting situation the Kelvin equation would predict the formation of an equilibrium annulus at a separation

$$D_j = 2\gamma \cos\theta / kT (\rho_l - \rho_g) \ln a_w , \qquad (4)$$

which is the quantity that has been plotted in Fig. 2 (with $\cos\theta \approx 1$). Note the positive deviations at activities below about 0.95, above which no further increase in the jump distance with activity occurs. At activities close to 1 the condensates are very large and take a long time to redissolve on separation of the surfaces. Similar results were obtained with water condensing from *n*-decane between
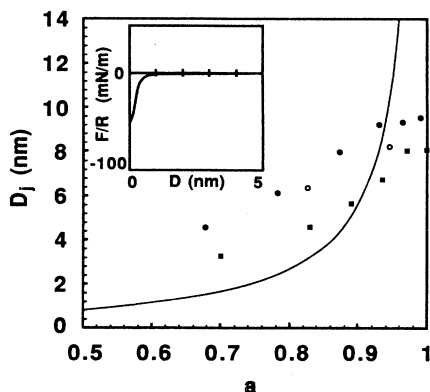
FIG. 3. Condensation separation vs water activity for hydrogen mica surfaces in OMCTS. The circles and squares are the results of two separate experiments performed by gradually increasing the water activity (solid circles) and then decreasing (open circles) or first decreasing (solid squares). Note the positive deviations from the Kelvin equation (solid line) at water activities below 0.9–0.94 and the negative deviations at higher activities. The approximately 1.5 nm discrepancy between the two series of measurements is typical of the variability from experiment to experiment and reflects an uncertainty in the position of contact ($D = 0$). The inset shows the force measured in water between mica surfaces covered with hydrogen ions (Ref. 28).

mica surfaces, and have also, qualitatively, been observed with *trans*-decalin, various isoparaffins and in the molten polymers polydimethylsiloxane and polybutadiene.

Another series of experiments was carried out with hydrogen mica (see the Experimental section). The results of two of these are shown in Fig. 3, together with the predictions of the Kelvin equation. A similar positive deviation is found at the lower activities, but the negative deviations close to saturation are more pronounced. The difference in absolute values between the two series of points is typical of the variability found both for hydrogen and potassium mica, largely due to an uncertainty in the position of molecular contact. The measured surface separations are relative to mica-mica contact in dry nitrogen, but because of the presence of a physisorbed layer on the mica,[21] this is probably an underestimate of the true mica-mica separation. The difference, however, may vary from experiment to experiment, by up to 1 nm.

Finally, some measurements were made in another system of incompletely miscible liquids, methanol dissolved in octane. Here identical jumps of 3.4 nm were observed for spring stiffnesses of both 10^3 N m^{-1} and 10^5 N m^{-1}. The concentration of methanol was slightly below saturation, but was not accurately controlled.

DISCUSSION

These and previously reported data by us are, to our knowledge, the most direct experimental observations of phase transitions in thin films. The discontinuity in the force that we observe is precisely what is expected to happen at a first-order phase transition. A quantitative

analysis of the results, however, requires an appreciation of exactly what is being measured. At separations $D > D_j$ we measure either no force (presumably there is an immeasurably small, attractive van der Waals force) or, at water activities below about 0.75 (see Ref. 19), an oscillatory solvation force that is modified by the presence of water. This change in the solvation force from that found in the pure nonpolar liquid must be due to surface adsorption of water. Other, less surface-active solutes show a much less dramatic effect on the solvation force at comparable mole ratios.[26] From refractive index measurements we know that the amount of adsorbed water is small, certainly less than a 1 nm thick layer per surface even at activities of 0.99.[13]

The force that suddenly "switches" on at $D = D_j$ is *not* the force in the phase-separated liquid (water), but rather the attraction due to the formation of a liquid-liquid interface with negative curvature. It is the negative Laplace pressure in a liquid bridge that pulls the surfaces together, and the magnitude of this pressure prevents us from being able to measure the force across the condensate. We do not know the lateral extension of the bridge as it forms, though presumably it is quite small (in this geometry the pressure in a condensed bridge is independent of its size and depends only on the interfacial tension and the macroscopic radius of curvature of the surfaces.[10,13] In order for the pressure inside the bridge to be negative and the bridge to be mechanically stable the lateral diameter must be much larger than the separation of the surfaces. The volume of such a bridge thus increases sharply with surface separation and it is clear that its formation must become increasingly improbable with increasing separation. The amount of available phase-separating solute only increases by about one third over the range of our measurements. We cannot be sure at what point kinetic and diffusion effects become dominant, but it seems likely that such is the case when the observed jump distance no longer increases with solute activity.

The Kelvin equation is only expected to be accurate in the limit of large separations. From Figs. 2 and 3 it is evident that the Kelvin equation is not really obeyed over any significant range in activities. Close to saturation kinetic effects may well preclude phase separation at larger distances and at smaller activities there are positive deviations. The most straightforward interpretation is that in this regime surface adsorption of water causes the phase separation to occur at larger distances.

The difference between the results with hydrogen mica and potassium mica reflects, we believe, the difference in the mica-water-mica interaction previously found in the two cases. A mica surface covered with potassium ions shows a steep, steplike repulsion at short-range and no adhesion between the surfaces is measurable.[27] This is due to some type of ion hydration at the surface and is illustrated qualitatively in the inset to Fig. 2. Between hydrogen mica surfaces in water, on the other hand, the short-range interaction is attractive and there is a small but finite adhesion[21,28] (see inset to Fig. 3). This difference has previously been shown to have a large influence on the adhesion behavior of mica surfaces in vapor[24] and this is another manifestation of the importance

of short-range interactions for surface properties. In a simpleminded way we may think of the affinity of water as being greater for the potassium-covered surface and consequently condensation will occur at larger separations. Possibly, water adsorption to the surface is greater in the case of potassium mica.

A notable feature of capillary condensation in porous solids is the common occurrence of hysteresis. Whether it is due to some collective effect in the pore networks or simply a consequence of metastability in individual pores[29,30] is not certain. Some information relevant to this question is provided by studying the disappearance of the bridges on separation of the surfaces. Bridges formed at lower water activities (<0.95) snap as the surfaces jump apart on separation because of insufficient rigidity of the spring system. At higher water activities (>0.95) the bridges remain after the jump apart has occurred and are stable at separations far in excess of the distance at which they form. In our experiments we therefore do see hysteresis of the phase-separation process, and this supports the view that hysteresis in capillary condensation is due, at least partly, to metastabilities in thin films, and is not just a result of a complex interplay of pore geometry and interconnectivity.[29]

In conclusion, we hope that these results will show that the surface force apparatus is a powerful tool for investigating both static and dynamic aspects of phase behavior in very thin films. The technique lends itself to the study of a host of related phenomena such as cavitation,[31] wetting films, solidification in thin films, etc.

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