

Capillary Condensation from Vapors of *n*-Hexane/Perfluoro-*n*-hexane Mixtures

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We have used a modified surface force apparatus to study capillary condensation of near-saturated vapors of *n*-hexane/perfluoro-*n*-hexane mixtures in a model pore formed by the gap between two mica surfaces. The measured compositions and mean meniscus radii of curvature of the capillary condensates are in broad agreement with the predictions of the binary Kelvin equations. Our results also show that *n*-hexane is preferentially adsorbed at the mica/liquid interface of the condensed mixtures, with the extent of adsorption depending on the position in the liquid–liquid phase diagram of the mixture. In addition, liquid–liquid-phase separation was observed in condensates formed from vapors of bulk perfluoro-*n*-hexane-rich mixtures at, or very close to phase-coexistence. This results in the formation of novel two-phase or “double” condensates, consisting of an inner condensate of a *n*-hexane-rich phase within an outer condensate of perfluoro-*n*-hexane-rich phase. Capillary condensation from vapors coexisting with phase-separated bulk mixtures gives rise to condensates of the *n*-hexane-rich phase. Finally, we have observed that the composition of a mixed condensate can show a significant time-dependence in the initial stages of condensation.

1. Introduction

Capillary condensation from single component vapors has received considerable attention.^{1–5} In contrast, there have been relatively few studies of systems involving mixed vapors,⁶ which is perhaps surprising given that many systems of interest in applications involve more than one component. The introduction of another variable, namely the composition of the adsorbed phase, increases the complexity of behavior of such systems. In particular, one might expect interfacial wetting and confinement-induced changes in the phase behavior of liquid mixtures to play an important role in capillary condensation from mixed vapors.

1.1. Capillary Condensation from Mixed Vapors. Consider the system depicted in Figure 1a. As in the case of single-component fluids the undersaturated vapors of a liquid mixture will condense in a sufficiently small pore because of the reduction in free energy associated with replacing the solid/vapor interface with solid/liquid interface. The most basic questions to be asked are: what are the size and composition of the capillary condensate as a function of the partial pressures of the vapor components? In principle the answers to these questions are provided by the binary Kelvin equations:⁷

$$\ln\left(\frac{p_i}{p_{i,0}(X_{\text{cond}})}\right) = \frac{\gamma(X_{\text{cond}})}{r} \cdot \frac{V_{m,i}(X_{\text{cond}})}{RT}, \quad i = 1, 2 \quad (1)$$

where r is the mean radius of curvature of the meniscus, X_{cond} is the composition of the condensate, p_i is the partial pressure of component i , $p_{i,0}(X_{\text{cond}})$ is the partial pressure of component i over a bulk solution (with planar interface) of composition X_{cond} , and where $V_{m,i}(X_{\text{cond}})$ and $\gamma(X_{\text{cond}})$ are, respectively, the composition-dependent partial molar volume of component i

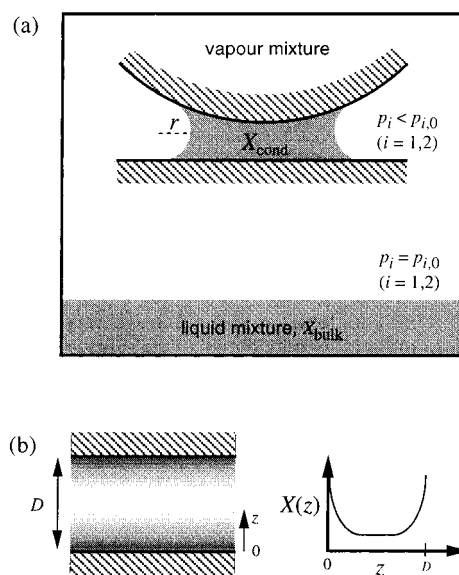


Figure 1. (a) Capillary condensation of the undersaturated vapors of a binary liquid mixture. The composition of the condensed phase, X_{cond} , and the mean radius of curvature of the liquid/vapor interface, r , are described by the binary Kelvin equations (eq 1 in text). (b) Preferential adsorption of one of the components at the liquid/pore interface gives rise to a nonuniform concentration profile, $X(z)$, within the condensed liquid.

and surface tension of the liquid mixture. In eq 1 it is assumed that the molar volumes and surface tension are given by the values for the bulk liquid mixture, and that the vapor may be treated as an ideal gas. Modified versions of the binary Kelvin equations have been proposed in connection with the modeling of hydrocarbon mixtures in oil-gas reservoirs⁸ and the separation of liquid mixtures by capillary distillation;^{9–12} however, the results have been the subject of debate.¹³

Equation 1 is based purely on a thermodynamic treatment of the effect of the liquid/vapor interfacial curvature on the chemical potentials of the components of a capillary-condensed

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mixture and hence does not explicitly address the presence of preferential adsorption at interfaces in liquid mixtures. Preferential adsorption of one component over the other at the liquid/solid interfaces means that the composition of a capillary condensate formed from mixed vapors will not be uniform throughout, but will display a dependence on distance from the liquid/solid interface (Figure 1b). The significance of such surface enrichment has been considered in detail in the study of homogeneous nucleation (e.g., refs 14 and 15), but has not received much attention in capillary condensation, where one might expect much bigger effects due to the large surface area-to-volume ratio of the condensed mixture. The capillary condensation of vapors of partially miscible liquids is expected to be particularly interesting in this respect, because interfacial adsorption in such systems displays a rich behavior as a function of position in the temperature/composition phase diagram. Confinement-induced changes in the phase behavior of such mixtures are also potentially of importance.

1.2. Binary Liquid Mixtures at Interfaces and in Confined Geometries. The study of adsorption at interfaces in binary liquid mixtures has a long history, and much of the early work is reviewed in the book by Kipling.¹⁶ An important advance was the recognition that in many cases, particularly for mixtures of partially miscible liquids at temperatures below (above) the upper (lower) critical solution temperature T_{crit} , the preferential adsorption is multimolecular, or multilayer in nature.^{16,17} In general, one of the two phases of a phase-separated binary mixture will preferentially wet the liquid/vapor or liquid/solid interface (as indicated by a contact angle, θ , of less than 90°). The adsorption of a multilayer film of the wetting phase from a solution of the nonwetting phase is then analogous to the adsorption of a liquid film onto a solid substrate from an undersaturated vapor of a wetting liquid.¹⁷

In many systems a transition from partial wetting ($0 < \theta < 90^\circ$) to complete wetting ($\theta = 0^\circ$) occurs at a temperature T_w , close to the critical temperature (for reviews on the subject of wetting transitions, see refs 18–20). (We note that not all systems display such a wetting transition, as shown by the work of Ross and Kornbrekke²¹ for example.) In terms of the multilayer adsorption discussed in the preceding paragraph, the wetting transition is reflected in a marked increase in the adsorbed layer thickness upon passing from the partial to the complete wetting state. For a path along two-phase coexistence, the thickness of the adsorbed layer increases from a finite to an essentially infinite value upon passing from the partial to the complete wetting state. For systems displaying a first-order wetting transition a finite increase in film thickness occurs for paths slightly off coexistence (the so-called prewetting transition).

A strong, temperature-dependent preferential adsorption, referred to as critical adsorption, has also been observed in the one-phase region near the critical point of a binary liquid mixture (e.g., refs 22–24). In simplistic terms, the correlation length of random concentration fluctuations in a binary liquid mixture diverges as the critical point is approached, which results in a divergence of the spatial extent of the diffuse layer of the preferentially adsorbed component at an interface.

In addition to studies of wetting and adsorption, there has also been considerable interest in the effects of confinement on the phase behavior of liquid mixtures. To date, most of this research has involved studies of binary liquid mixtures imbibed in porous solids. Interesting phenomena arise when the correlation length of concentration fluctuations in the liquid mixture becomes comparable to the dimensions of the confining pores

(a good introduction to the study of critical fluids in porous media has been presented by Frisken et al.²⁵). In terms of the phase behavior of confined liquid mixtures, recent studies have suggested that confinement leads to a decrease in the critical temperature in systems with an upper critical solution temperature;⁵ see, however, refs 26 and 27.

In the context of this paper the important concept is that of capillary condensation, or “capillary phase separation”, of the preferentially wetting phase of a binary mixture prior to two-phase coexistence in bulk. This pore-induced formation of a phase which is not stable in bulk is closely analogous to the formation of a stable liquid phase from undersaturated vapors and can be explained in similar terms (e.g., refs 28 and 29). Although we are primarily interested in condensation from mixed vapors it should be noted that there are very close similarities between the two phenomena.

Capillary condensation in mixtures of partially miscible liquids was apparently first recognized by Patrick and co-workers in 1925,^{26,30} on the basis of the interpretation of measurements of adsorption by silica gel from binary mixtures. Direct evidence of capillary condensation in binary liquid mixtures was later obtained using the surface force apparatus.³¹ These studies, however, were concerned with mixtures very far from the critical temperature and no attempt was made to study interfacial adsorption within the condensed phases. It is also worth noting that there appears to be no direct verification of the generalized Kelvin equation which describes condensation from binary liquid mixtures.

More recent studies have considered capillary condensation in systems close to the bulk critical point (much of this work has been reviewed by Gelb et al.⁵). The basic conclusion to emerge from these studies is that the phase coexistence curve of binary mixtures is narrowed and shifted (in concentration) toward the preferentially adsorbed component. This shift in concentration can be qualitatively explained in terms of preferential adsorption at the pore/liquid interface.^{5,32,33} The average concentration of a binary liquid mixture in a pore can be significantly influenced by enrichment of a given component at the pore interface, particularly for small pores. A major limitation of many of these studies is that the extent of preferential adsorption at the pore interfaces cannot be determined directly. In addition, the interpretation of many such studies is limited by polydispersity in pore sizes.

1.3. Previous Studies. In contrast to the case of capillary condensation in binary liquid mixtures imbibed in mesoporous solids, there have been very few studies of capillary condensation of mixed vapors. In very early work, Tryhorn and Wyatt studied the adsorption of saturated vapors of alcohol–benzene and acetone–benzene mixtures by charcoal produced from coconut shells.^{34,35} The final stage of the adsorption process was ascribed to capillary condensation of mixed vapors in the intergranular spaces of the charcoal. The composition of the adsorbed liquid during this stage was observed to change as a function of time, asymptotically approaching the composition of the bulk mixture. The change of composition with time was attributed to differences in the degree of vapor-pressure lowering of the two components arising from the negative curvature of the interface between the condensed liquid and the vapor phase. However, an interpretation of the results in terms of the binary Kelvin equations (eq 1) was not attempted. (Although we have not attempted to trace the first presentation of the binary Kelvin equations for condensation from vapor mixtures, an approximate form of the analogous equation for condensation from binary liquid mixtures was certainly known before the work of Tryhorn

and Wyatt.^{26,30} Also, the dimensions and morphology of the pores in the charcoal used in this study were not characterized.

The equilibrium between vapor and liquid for several binary mixtures confined in sintered metal and fritted glass plates was investigated by Shin and Simandl.¹² The compositions of the vapors coexisting with the confined mixtures of known composition were measured and compared to the predictions of a modified form of the binary Kelvin equations. However, the theory used by these authors has been criticized.¹³ Also, the pore sizes used in this investigation (50 and 120 μm) were so large that the effects of confinement would be expected to be relatively insignificant.

More recently, Alam et al. investigated the capillary condensation and desorption of (fully miscible) binary mixtures of nitrogen and argon in the cylindrical pores (diameter ≈ 4 nm) of Vycor glass.³⁶ No preferential adsorption or desorption was observed when the porous sample interacted only with the mixed vapors. By contrast, an unexpected enrichment of argon in the pores was observed when the Vycor was in contact with bulk liquid prior to desorption.

1.4. Outline of Paper. The study of capillary condensation from mixed vapors is still at an early stage, particularly from the experimental point of view. In this paper we describe an exploratory study of capillary condensation from near-saturated vapors of mixtures of the partially miscible liquids *n*-hexane and perfluoro-*n*-hexane. Our system corresponds closely to that depicted in Figure 1a. The measurements were performed using a modified surface force apparatus (SFA). Capillary condensation occurs in the narrow gap between two muscovite mica surfaces, and measurements of the mean refractive index of the condensed liquid as a function of surface separation yields information about the mean composition of the liquid as well as the extent of preferential adsorption at the mica/liquid interface. Near-saturated vapor mixtures were obtained by evaporation from bulk liquid and measurements were performed at various positions in the phase diagram of the bulk liquid mixture. (We have also measured the thicknesses of liquid films adsorbed from pure and mixed vapors onto the mica surfaces, the results of which are described elsewhere.³⁷)

The *n*-hexane/perfluoro-*n*-hexane system, which has an upper critical solution temperature, T_{crit} , of 22.65 $^{\circ}\text{C}$ at a critical mole fraction of perfluoro-*n*-hexane, $X_{\text{f,crit}}$, of 0.36,³⁸ was chosen for several reasons. The physicochemical parameters of the system are well characterized^{38–41} and the critical solution temperature is convenient for performing experiments at around room temperature. Also, the refractive indices of the two components are sufficiently different ($n_{\text{n-hexane}} = 1.375$, $n_{\text{perfluoro-n-hexane}} = 1.252$) as to allow the investigation of composition and adsorption by refractive index measurements. The interfacial wetting characteristics of such mixtures have also been the subject of several experimental studies to which our results can be compared.^{42–46} Finally, the vapor pressures of both components are relatively high, which means that equilibrium of the vapors above mixtures of the liquids is reached quickly.

2. Materials and Methods

The measurements were performed using a modified version^{47,48} of the Mark IV SFA.⁴⁹ The use of this apparatus in the study of capillary condensation has been described in detail in two recent reviews.^{48,50} Briefly, the apparatus consists of two back-silvered mica surfaces mounted in a crossed-cylinders geometry in a sealed chamber. The geometry of the gap between the surfaces is locally equivalent to that of a sphere (of radius ≈ 2 cm) on a flat surface. The vapor of a given liquid is obtained

by evaporation from excess liquid injected onto the bottom of the chamber. An analysis of the interference fringes (fringes of equal chromatic order; FEEO) produced by passing white light perpendicularly through the surfaces yields the separation between the surfaces, D , and the mean refractive index of the material between the surfaces, n . The presence of a liquid condensate between the surfaces gives rise to a discontinuity in the interference fringes at the position of the meniscus (see Figure 10), from which the surface separation at the meniscus can be measured. For liquids with a small contact angle on mica, the meniscus radius of curvature of the liquid/vapor interface of the condensed liquid is, to a good approximation, given by half the measured separation at the meniscus minus a small correction for the presence of an adsorbed liquid film on the mica surfaces.

In the case where the material between the surfaces is of uniform composition the measured refractive index n is constant (equal to the refractive index of the material in the gap) as a function of the surface separation D . The presence of a nonuniform composition, arising from adsorption at the mica surfaces (cf. Figure 1b), is reflected in a variation of n with D . If a slab model of adsorption is adopted then the thickness t of the adsorbed layers, assumed to be of equal thickness, is given by^{3,51}

$$t = \frac{D(n^2 - n_g^2)}{2(n_f^2 - n_g^2)} \quad (2)$$

where n_f is the refractive index of the adsorbed layer and n_g is the refractive index of the material in the gap between the adsorbed films.

The SFA is housed in a temperature-controlled cabinet, which is itself situated in a temperature-controlled room. With this setup the temperature of the apparatus can be controlled to ± 0.05 $^{\circ}\text{C}$. The light passing through the surfaces causes them to be slightly warmer than the chamber, which results in a slight undersaturation of the vapor at the surfaces. For a pure liquid, the actual value of the relative vapor pressure is calculated from the measured size of the capillary condensate using the Kelvin equation.^{47,48,52} (This is the inverse of the procedure used in previous SFA studies which demonstrated the validity of the Kelvin equation.^{3,53}) When the light is passed through three IR filters before being directed through the surfaces the relative vapor pressure at the surfaces is typically in the range 0.992–0.998 (see below), corresponding to a temperature differential of approximately 0.05–0.15 $^{\circ}\text{C}$. Smaller relative vapor pressures can be obtained by removing the heat filters, or by measuring before the vapor has reached equilibrium with the liquid in the chamber.

The *n*-hexane used in all experiments was from Ajax Chemicals (SPECTROSOL, for UV spectroscopy, purity > 99.5%). Perfluoro-*n*-hexane was obtained from PCR Inc. (99% isomeric purity) and from Lancaster Synthesis (98.2% isomeric purity). The liquids were distilled twice from either calcium hydride or molecular sieve type 4A. Note that the liquids were not degassed prior to use.

The phase separation temperatures of a range of *n*-hexane/perfluoro-*n*-hexane mixtures with mole fractions of perfluoro-*n*-hexane, X_f , between approximately 0.2 and 0.6 were determined visually. The solutions were prepared by weighing in glass ampules and then immediately frozen by partially submerging the ampule in liquid nitrogen. The samples were then sealed by melting the open neck of the ampule in a flame. The temperature of the mixtures was controlled and monitored to

within 0.1 °C by submerging the ampules into a large water bath housed in a temperature-controlled cabinet. The ampules were periodically shaken as the temperature of the bath was changed, and the phase state of the mixtures was determined by visual inspection.

To probe the composition of the capillary condensates formed from the vapor mixtures, information about the dependence of the refractive index of the mixtures on the composition is required. The refractive indices of several solutions with X_f in the range 0–0.4 were measured at 23.0 ± 0.1 °C (in the one-phase region of the phase diagram) using an Abbe refractometer. The range of concentrations for which measurements could be made was limited by the fact that only refractive indices larger than 1.3 could be measured.

Solutions (of volume ≈ 3 –10 mL) were prepared by weighing and immediately injected into the SFA chamber after measuring contact in nitrogen. The system was allowed to equilibrate for at least 3 h before commencing measurements, and all measurements with mixtures were performed with three heat filters in place. Phosphorus pentoxide or molecular sieve type 4A was used as a drying agent. In a given experiment measurements were typically performed on one or both of the pure liquids as well as on several mixtures. Between measurements on different solutions the chamber was flushed with dry nitrogen for approximately 90 min. Before injecting the next solution measurements of the adhesion and refractive index profile in nitrogen were performed in order to provide a check against gross contamination of the surfaces.

We have calculated the expected change in composition of the liquid mixtures due to evaporation into the SFA chamber of volume ≈ 90 mL and estimate that the error in the mole fractions of the prepared solutions due to this effect should be less than ± 0.02 . A more serious problem is the potential change in composition due to leakage from the chamber. On a few occasions where measurements with a given solution ran for a week, a significant drop in the level of the liquid on the bottom of the chamber was noted. In general, measurements with a given solution were performed within 1–3 days after injecting. It is difficult to estimate the potential change in composition due to leakage. Fortunately, the two components have similar vapor pressures and exhibit a very broad flat region in the vapor pressure versus composition curve,³⁹ both features which reduce the impact of evaporative losses on the composition.

3. Results and Discussion

We present the results and discussion in two sections. Observations on the bulk liquid mixtures are described first, followed by the results of measurements of capillary condensation from the vapors of mixtures at various positions in the liquid–liquid phase diagram.

3.1. Bulk Mixtures. Phase Diagram. Initially, the phase separation temperatures of a number of mixtures with a range of compositions (expressed in terms of the mole fraction of perfluoro-*n*-hexane, X_f) were determined, as described above, to compare to the previously measured phase diagram of the system. The results were in reasonable agreement with the phase diagram determined by Bedford and Dunlap,³⁸ as shown in Figure 2. At the end of the series of experiments described in this paper, the phase separation temperature of a mixture with $X_f = 0.36$ was checked and agreement with the results of Bedford and Dunlap was again observed.

Refractive Index Measurements. The refractive indices of several solutions with X_f in the range 0–0.4 were measured at 23.0 °C; the refractive index of pure perfluoro-*n*-hexane was

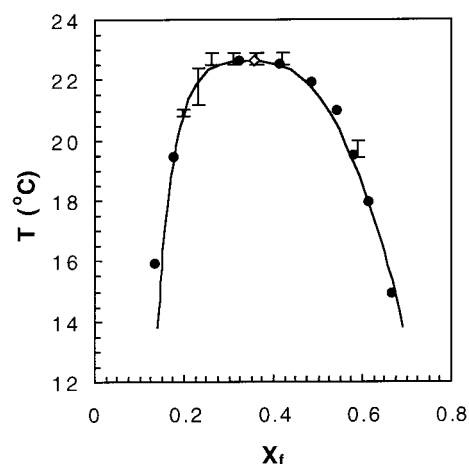


Figure 2. Liquid–liquid phase diagram of the *n*-hexane/perfluoro-*n*-hexane system. The filled circles represent the measurements of Bedford and Dunlap;³⁸ the critical point of the system ($T_{\text{crit}} = 22.65$ °C, $X_{f,\text{crit}} = 0.36$) is indicated by the open diamond. The solid line is a fit to the data of Bedford and Dunlap, using a functional form suggested by McLure et al.⁷¹ The error bars represent the visually determined phase-separation temperatures of mixtures of the *n*-hexane and perfluoro-*n*-hexane used in this work.

taken to be equal to 1.252, the measured value at 22 °C.⁵⁴ A least-squares quadratic fit to the data gave $n = 0.0875X_f^2 - 0.2102X_f + 1.3747$. This best-fit relationship between n and X_f was used to obtain the composition of the mixed capillary condensates from the measured refractive index for the entire range of temperatures studied (17–27 °C). We have thus neglected the variation in refractive index of the mixtures with temperature; in comparison to the error in the measured refractive index this approximation is insignificant.

Wetting Behavior. Previous studies have shown that perfluoro-*n*-hexane is preferentially adsorbed at the liquid/vapor interface in mixtures with *n*-hexane over a large range of concentrations.^{43,44} For temperatures above T_{crit} , a monolayer of perfluoro-*n*-hexane was observed at the liquid/vapor interface for X_f in the approximate range 0.2–0.7. Near the critical composition this monolayer capped a subphase which was enriched with perfluoro-*n*-hexane with respect to the bulk phase. The degree of this enrichment was observed to increase as T_{crit} was approached from above, consistent with critical adsorption of perfluoro-*n*-hexane at the liquid/vapor interface. In the two-phase region, just below T_{crit} , a macroscopically thick layer of the perfluoro-*n*-hexane-rich phase was observed at the liquid/vapor interface, i.e., the perfluoro-*n*-hexane-rich phase wets the interface between the less dense *n*-hexane-rich phase and the vapor phase. Enrichment of perfluoro-*n*-hexane at the liquid/vapor interface in mixtures with *n*-hexane has also been reported by Prange et al.⁴⁶ It has also been shown that the *n*-hexane-rich phase wets the interface between the perfluoro-*n*-hexane-rich phase and glass,⁴² quartz,⁴² and alkane-coated silica surfaces.⁴⁵

We have performed qualitative experiments in order to determine the wetting behavior of phase-separated mixtures of *n*-hexane and perfluoro-*n*-hexane in contact with the mica surface. Observations of the interface between the two liquid phases meeting a mica strip showed that the *n*-hexane-rich phase preferentially wets mica. Although accurate measurements were not attempted, the contact angle measured in the *n*-hexane-rich phase was equal to zero within the resolution of the observations, at least down to a temperature of approximately 15 °C. In another experiment, fine mica flakes were dispersed in a one-phase mixture of the two liquids. The density of mica is higher than that of either of the components of the mixture and so the

small flakes sink to the bottom of the mixture. Upon cooling, the mixture separates into two phases, with the more dense perfluoro-*n*-hexane-rich phase collecting in the bottom of the container. The mica flakes were observed to float up through the perfluoro-*n*-hexane-rich phase into the *n*-hexane-rich phase, suggesting the presence of a very thick adsorbed layer of the less dense *n*-hexane-rich phase on the surfaces of the flakes. At equilibrium, the interface between the two liquid phases was free of particles, consistent with a near-zero contact angle of the *n*-hexane-rich phase on mica.

These observations on the wetting and adsorption behavior in mixtures of *n*-hexane and perfluoro-*n*-hexane are consistent with simplistic predictions based on calculations of various Hamaker constants. Using the approach described by Hough and White⁵⁵ and dielectric properties obtained from refs 55–57 we have calculated the nonretarded Hamaker constants A , at 20 °C, for the configurations mica/*n*-hexane/perfluoro-*n*-hexane (m/h/p), mica/perfluoro-*n*-hexane/*n*-hexane (m/p/h), *n*-hexane/perfluoro-*n*-hexane/vacuum (h/p/v), and perfluoro-*n*-hexane/*n*-hexane/vacuum (p/h/v). The Hamaker constants calculated in this manner were $A_{m/h/p} = -4.2 \times 10^{-21}$ J, $A_{m/p/h} = 6.2 \times 10^{-21}$ J, $A_{h/p/v} = -5.9 \times 10^{-21}$ J, and $A_{p/h/v} = 7.8 \times 10^{-21}$ J. Note that in these calculations it was assumed that the liquids were pure, i.e., no attempt was made to calculate Hamaker constants for mixtures of the liquids. Recalling that a negative Hamaker constant implies the formation of a stable thin film,⁵⁵ the values listed above suggest that in *n*-hexane/perfluoro-*n*-hexane mixtures perfluoro-*n*-hexane will be preferentially adsorbed at the liquid/vapor interface and that *n*-hexane will be preferentially adsorbed at the mica/liquid interface, consistent with the observations described above.

3.2. Capillary Condensed Mixtures. As described earlier, near-saturated vapors of *n*-hexane/perfluoro-*n*-hexane mixtures were obtained by injecting solutions of known concentration onto the bottom of the SFA chamber. After allowing at least several hours for equilibration of the vapors above the liquid mixtures, measurements of the mean refractive index between the film-coated surfaces were made in order to determine the adsorbed film thickness (the results of which are described elsewhere³⁷). The mica surfaces were then brought into contact, resulting in capillary condensation of the mixed vapors in the gap between the surfaces. The condensates were observed to reach their equilibrium sizes within approximately 15 min, consistent with the transfer of material to the condensate occurring primarily through vapor-phase diffusion.⁵⁸ After measuring the equilibrium size of the condensate the surfaces were separated (without breaking the capillary-condensed liquid bridge between the surfaces) and measurements of the mean refractive index, n , of the condensed liquid as a function of the separation between the surfaces, D , were made. In a few experiments the mean refractive index of the condensed liquid was also monitored as a function of time after the initiation of condensation. Note that in the following all temperature values refer to the temperature of the SFA chamber; as described in Section 2 the temperature at the surfaces can be ≈ 0.1 °C higher.

Equilibrium Sizes of Condensates. Figure 3 shows the equilibrium values of the mean meniscus radii of curvature of capillary condensates formed from pure and mixed vapors of *n*-hexane and perfluoro-*n*-hexane. The data are from numerous experiments at temperatures in the range 19–27 °C, always with the bulk liquid mixture in the one-phase region of the phase diagram, and always with three heat filters in place. We did not observe any systematic change in the measured condensate sizes as a function of temperature and have thus presented all

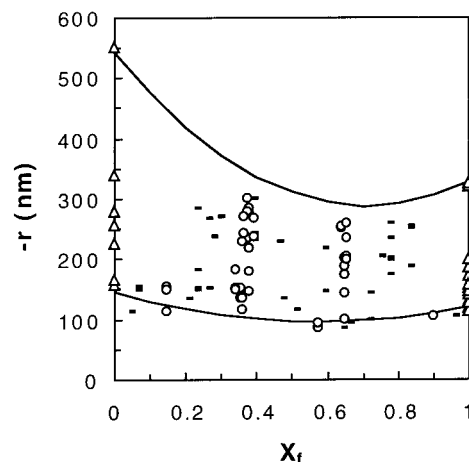


Figure 3. Meniscus radii of curvature $-r$ of capillary condensates formed from pure and mixed vapors of *n*-hexane and perfluoro-*n*-hexane as a function of the composition X_f of the (one-phase) bulk liquid mixture from which the near-saturated vapors were produced. The data for the mixtures are from a number of separate experiments performed at temperatures in the range 19–27 °C; the open circles are plotted using the nominal compositions of the bulk mixture in the chamber, the short dashes are plotted using the measured compositions, $X_{f,cond}$, of the condensates (see discussion in text). The data for the pure liquids (open triangles) were obtained in a number of separate experiments at temperatures in the range 17–25 °C. The solid lines represent the upper and lower limits on $-r$ calculated from the binary Kelvin equations (eq 1 in text) assuming that the relative vapor pressures of the components of the vapor mixtures lie between the limits of relative vapor pressure observed for vapors of the pure components.

the data in one figure. The open circles are plotted using the nominal composition of the liquid mixture from which the mixed vapors were produced. The short dashes represent compositions calculated from refractive index measurements in the condensed mixtures (see below). The radii of curvature were calculated by subtracting 1.5 times the measured film thickness from half the measured surface separation at the meniscus. This method of correcting for the presence of adsorbed films is strictly only valid for systems in which the disjoining pressure of the adsorbed film is described by van der Waals theory;⁵⁹ for mixed condensates it can only be considered as a first-order correction.

Values of the relative vapor pressure in experiments with pure liquids were calculated from the measured equilibrium sizes of the capillary condensates, using the Kelvin equation.^{47,48,52} On the basis of the results shown in Figure 3 the relative vapor pressures in experiments with pure *n*-hexane and pure perfluoro-*n*-hexane were in the ranges 0.994–0.998 and 0.992–0.997, respectively. The solid lines in Figure 3 represent the limits in $-r$ calculated from the binary Kelvin equations assuming that the relative vapor pressures of the components in the mixed vapors ($p_i/p_{i,0}$, $i = 1,2$) fall in the same range as observed for vapors of the pure liquids. Note that these curves were calculated using the properties (i.e., $p_{i,0}$, $V_{m,i}$, and γ) of *n*-hexane/perfluoro-*n*-hexane mixtures at 25.0 °C;^{38–40} we have thus assumed that (for one-phase mixtures) properties such as partial molar volumes and surface tensions do not vary significantly with temperature over the range studied. Figure 3 shows that the measured meniscus radii of curvature of the mixed condensates are in broad agreement with the predictions of the binary Kelvin equations.

Under the conditions used in this pilot study the relative vapor pressures are high, giving rise to relatively large (though still microscopic) condensates. With reference to Figure 1a, the typical “height” ($\approx -2r$) of the condensed liquid bridges was ≈ 400 nm, while the lateral radius, or half the “width”, of the

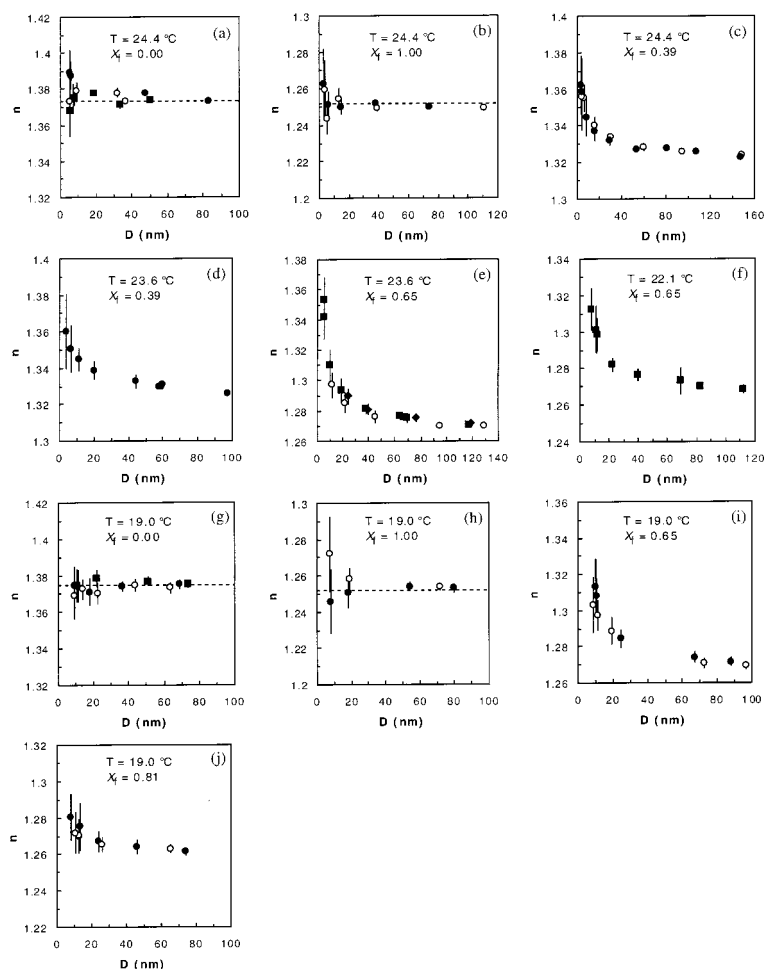


Figure 4. Typical refractive index profiles $n(D)$ in capillary condensates formed from vapors of *n*-hexane/perfluoro-*n*-hexane mixtures. (a) to (f) are from one experiment, and (g) to (j) from a separate experiment. The temperature T and the nominal composition of the bulk liquid mixture from which the vapors were produced X_f are indicated in each figure. The dashed lines in (a) and (g) represent the refractive index of pure bulk *n*-hexane; the dashed lines in (b) and (h) represent the refractive index of pure bulk perfluoro-*n*-hexane. Different symbols within a given figure represent measurements in different condensates under the given conditions.

bridge was of the order of 100 μm . In our geometry these dimensions correspond to a typical volume of the condensed liquid of the order of 10^{-14} m^3 . Although for some purposes it would be desirable to study smaller condensates, one advantage of having large condensates is that the mean refractive index in the mixture can be measured over a relatively large range of surface separations (up to $D \approx -2r$) without disturbing the equilibrium between the condensate and the vapor. Such measurements yield information directly relevant to the study of binary liquid mixtures at interfaces. In this sense the formation of large condensates of binary liquid mixtures from near-saturated vapors can be considered as a convenient way to obtain microscopic samples of confined binary mixtures, analogous to the study of capillary melting of solids formed by capillary condensation.^{48,60} A potentially important advantage of this approach is that problems associated with the slow diffusion of material in imbibed liquids might be avoided. Previous studies have shown that diffusion-limited transport of material in binary liquid mixtures can result in extremely slow equilibration of wetting layers (e.g., refs 61–63) and may give rise to metastability of binary liquids in porous media.^{5,64}

Refractive Index Measurements in Condensates. Figure 4 shows typical results of measurements of the mean refractive index as a function of surface separation for capillary condensates of pure and mixed liquids. The refractive indices measured in condensates formed from pure *n*-hexane and perfluoro-*n*-

hexane are, within error, equal to the refractive index of the pure (bulk) liquids, independent of the separation. In contrast, the refractive index in mixed condensates shows a definite increase as the separation is reduced, approaching the value for pure *n*-hexane. We are confident that the observed increase in refractive index at small separations in mixed condensates is experimentally significant, and that it is not due to the adsorption of contaminants. No such increase is observed in condensates of the pure liquids. Also, in a given experiment the same behavior is observed independent of the order in which pure and mixed vapors are studied.

The behavior of the refractive index profiles in mixed condensates can be attributed to preferential adsorption of *n*-hexane at the mica/liquid interface. If one adopts a slab model of the adsorption at the mica/liquid interface then eq 2 can be used to calculate the adsorbed layer thickness from the measured refractive index profiles. The condensed liquid is assumed to consist of a “bulk” reservoir of liquid of a given composition, which we refer to as the “composition of the condensate”, $X_{f,\text{cond}}$, in equilibrium with adsorbed layers with a composition enriched in *n*-hexane. If this slab model is reasonable then, from eq 2, a plot of n^2 versus $1/D$ should be linear, with the intercept corresponding to the square of the refractive index of the “bulk” liquid (the term n_g^2 in eq 2). Figures 5a and 5b show such plots for the data shown in Figures 4d and 4e, respectively. For the

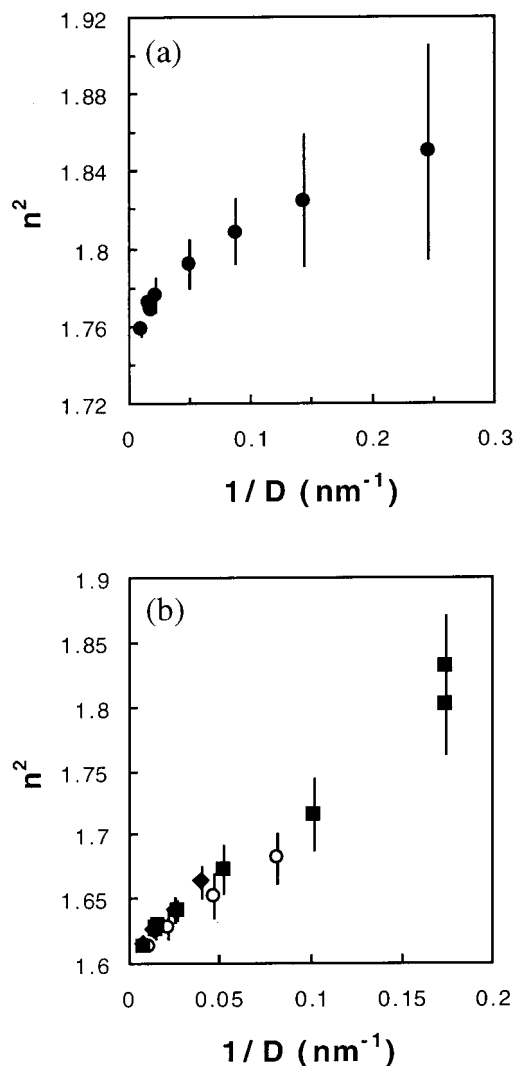


Figure 5. (a) and (b), the same data, respectively, as shown in Figures 4d and 4e, plotted as n^2 versus $1/D$.

condensate formed from the vapors of the bulk mixture with $X_f = 0.65$ the plot of n^2 versus $1/D$ is close to linear over the entire range of $1/D$ (Figure 5b). The intercept gives $n_g^2 \approx 1.60$, corresponding to $X_{f,cond} \approx 0.75$ (calculated using the measured relationship between refractive index and composition given earlier). The slight turnover in the plot of n^2 versus $1/D$ for the condensate formed from vapors of the bulk mixture with $X_f = 0.39$ (Figure 5a) can be attributed to the presence of relatively diffuse adsorbed films, as discussed below. In this case the limiting value of n^2 as $1/D$ approaches zero is approximately 1.74, corresponding to $X_{f,cond} \approx 0.30$.

In principle, the value of n_g could also be obtained from the measured refractive index profile as the limiting value of n at large D . However, for thick adsorbed films the limiting value of n is only approached at large separations, in many cases beyond the practical limits of measurement. In any case, for the measurements described here the values of n_g obtained from the two different methods generally agree to within ≈ 0.01 , corresponding to agreement to within ≈ 0.1 in the calculated value of $X_{f,cond}$.

Compositions of Condensates. For the relatively large condensates observed in these experiments the binary Kelvin equations predict that the composition of the condensates should be equal to the composition of the bulk liquid mixtures from which the vapors were produced, at least within the error in

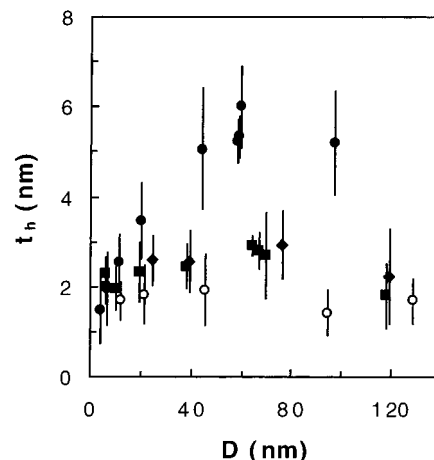


Figure 6. Equivalent adsorbed film thickness t_h of *n*-hexane in capillary condensates formed from mixed vapors of *n*-hexane and perfluoro-*n*-hexane, calculated from the refractive index profiles in Figures 4d and 4e, with the symbols unchanged. As described in the text, the filled circles are for a condensate with $X_{f,cond} \approx 0.30$; the other symbols are for condensates with $X_{f,cond} \approx 0.75$.

our determination of $X_{f,cond}$. In general, this is what we observed. In some cases, however, we observed differences of up to 0.2 in the values of $X_{f,cond}$, determined in the manner described above, and $X_{f,bulk}$, the nominal composition of the bulk liquid mixtures from which the vapors were produced. We believe that such small differences between the nominal compositions of the bulk liquid and the measured compositions of the condensates can be attributed to changes in composition of the bulk mixture due to evaporative losses. There is also the possibility that selective adsorption of one component by the drying agent in the chamber could alter the composition of the mixture. For the results presented here this complication is not important because the composition of a condensate is determined directly from the measured refractive index profile.

Adsorbed Film Thicknesses in Condensates. To calculate an adsorbed film thickness from the measured refractive index profiles a value of the refractive index of the adsorbed film (n_f in eq 2) is required. In the following we assume that the adsorbed layer consists of pure *n*-hexane (with refractive index $n \approx 1.372$), and report the calculated values as an “equivalent adsorbed film thickness” of *n*-hexane, t_h . To the extent that the slab model of adsorption is correct the value of film thickness calculated under this assumption can readily be converted to an adsorption excess of *n*-hexane.

Figure 6 shows the values of film thickness calculated in this way from the refractive index profiles shown in Figures 4d and 4e. For the condensates with $X_{f,cond} \approx 0.75$ the calculated film thickness is, within error, constant as a function of D . In contrast, for the condensate with a near-critical composition ($X_{f,cond} \approx 0.30$) the calculated values of film thickness show an increase with separation, approaching a constant value only at separations greater than approximately 50 nm. In both cases the calculated values of t_h suggest a preferential adsorption of *n*-hexane in excess of a complete monolayer (the length of a fully extended *n*-hexane molecule is ≈ 1 nm⁶⁵).

Figure 7 shows further examples of t_h versus D profiles for condensates formed from one-phase mixtures close to the critical point. As already mentioned, we attribute the initial increase in t_h with D to the presence of relatively thick adsorbed films at the mica–solution interface. The calculation of adsorbed film thickness on the basis of the slab model will obviously break down at separations where the adsorbed layers begin to overlap.

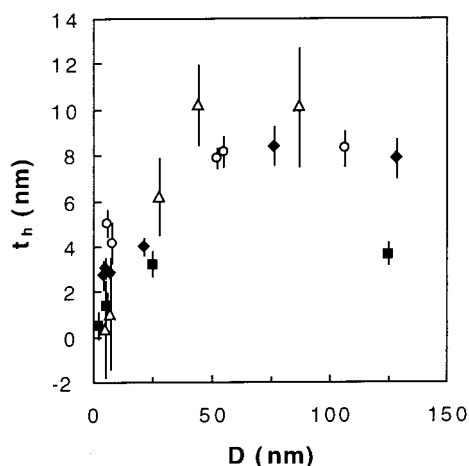


Figure 7. Equivalent adsorbed film thickness t_h of n -hexane in capillary condensates formed from mixed vapors of n -hexane and perfluoro- n -hexane. The data are for condensates with $0.35 < X_{f,cond} < 0.45$ at 23.0°C . Different symbols are from different experiments.

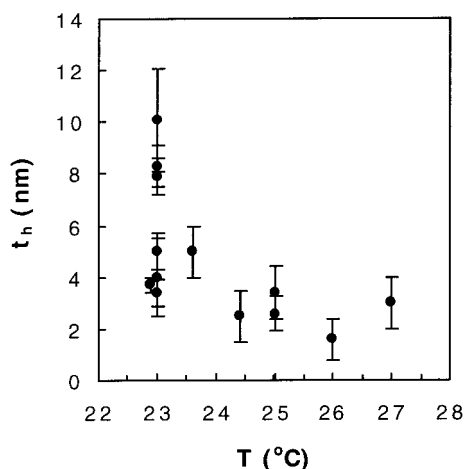


Figure 8. Equivalent adsorbed film thickness t_h of n -hexane as a function of temperature T for capillary condensates of n -hexane/perfluoro- n -hexane mixtures with $0.25 < X_{f,cond} < 0.45$.

If one assumes that the decrease in the values of t_h occurs at a value of the surface separation where the adsorbed films begin to overlap, then the data in Figure 7 suggests that the films are ≈ 5 – 20 nm thick. The fact that these values are larger than the calculated values of $t_h \approx 3$ – 10 nm merely reflects the fact that the adsorbed films are probably not pure n -hexane. Figure 8 shows values of t_h (obtained from measurements at large D) as a function of temperature for mixtures with compositions close to the critical composition. There is a trend toward increased film thickness as the critical temperature ($T_{crit} \approx 22.65^\circ\text{C}$) is approached from above.

These observations can be explained in terms of critical adsorption of n -hexane at the liquid/mica interface. As mentioned earlier, the extent of preferential adsorption in mixtures of critical composition scales with the correlation length of concentration fluctuations in the mixture. On the basis of published data,⁶⁶ the correlation length in n -hexane/perfluoro- n -hexane mixtures (with $T_{crit} = 22.65^\circ\text{C}$) at 23.0°C should be in the range 3 – 8 nm. The data in Figure 7 are then consistent with the presence of critically adsorbed films extending several correlation lengths into the solution. As the temperature is reduced toward T_{crit} the correlation length diverges, which would explain the trend observed in Figure 8. Finally, we note that the relatively large variation in the values of t_h (at large D) observed for near-critical mixtures can be attributed to slight

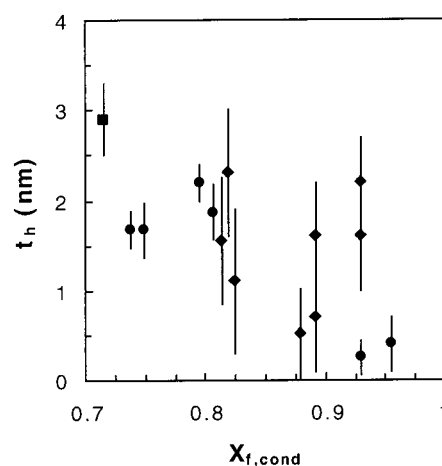


Figure 9. Equivalent adsorbed film thickness t_h of n -hexane as a function of composition $X_{f,cond}$ in capillary condensates formed from mixed vapors of n -hexane and perfluoro- n -hexane at 19.0°C . Different symbols are from different experiments.

differences in composition and temperature; critical adsorption effects are very sensitive to the distance from the critical point.⁴³

The data for condensates formed from near-critical mixtures could also be explained in terms of an increase in the critical temperature of the condensed mixtures. It has previously been observed that the critical temperature of binary liquid mixtures can be extremely sensitive to trace amounts of contaminants.⁶⁷ If the critical temperature of the condensed mixtures were increased due to small amounts of surface contaminants it is possible that thick adsorbed layers of an n -hexane rich wetting phase could form. (It is worth noting that in their study of wetting in n -hexane/perfluoro- n -hexane mixtures, Bowers et al. observed suprisingly thick films of an n -hexane-rich phase at a modified silica surface in mixtures several degrees above T_{crit} .⁴⁵) The “bulk” of the condensate would then consist of a coexisting perfluoro- n -hexane-rich phase. However, we have observed the presence of thick adsorbed films in condensates with $X_{f,cond} \approx 0.36$. Given that the liquid–liquid-phase coexistence curve for the n -hexane/perfluoro- n -hexane displays a broad maximum, it is unlikely that a coexisting perfluoro- n -hexane-rich phase would have such a composition. Further work is required to distinguish between the two possibilities. In any case, it is clear that the average composition of condensates formed from near-critical mixtures can be strongly influenced by preferential adsorption at the liquid/solid interface.

For bulk one-phase mixtures not too close to the phase coexistence curve the calculated values of t_h in the condensed mixtures are relatively small, showing no significant variation with D (see Figure 6). For condensates with $X_{f,cond} \approx 0.80$ at temperatures above T_{crit} the calculated values of t_h were in the range 1.5 – 2.0 nm, and showed no significant variation with temperature (at least in the studied range of 22.9 – 25.0°C). Figure 9 shows values of t_h as a function of composition of the condensed liquid at 19.0°C . Although the scatter in the data is relatively large, there is a trend toward thicker films at lower values of $X_{f,cond}$. (As described below, much thicker adsorbed films, of thickness of the order of 10 nm, were observed in perfluoro- n -hexane-rich condensates very close to the phase coexistence curve.) This trend is consistent with the expected increase in the thickness of an n -hexane-rich wetting phase as two-phase coexistence is approached (at 19.0°C two-phase coexistence of n -hexane/perfluoro- n -hexane mixtures occurs at $X_f \approx 0.65$ (see Figure 2)).

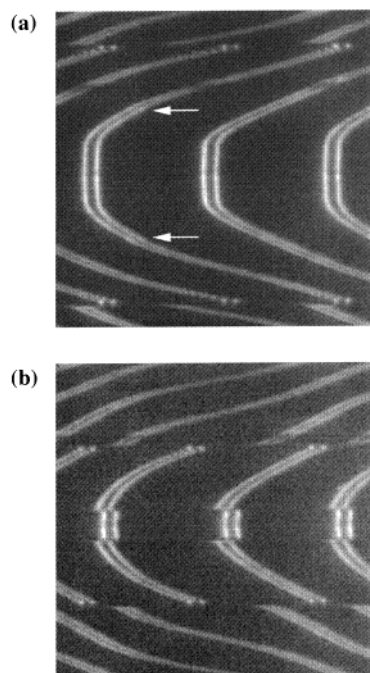


Figure 10. Images of FECO showing the existence of a two-phase or “double” capillary condensate formed from the vapors of a perfluoro-*n*-hexane-rich bulk mixture close to phase separation at 19.0 °C. The structure of the condensate is illustrated schematically in Figure 11. The liquid/vapor interface of the condensate gives rise to clear discontinuities in the FECO, visible in both (a) and (b). In (a) the mica surfaces are in contact and the interface between the two liquid phases in the condensate appears as bright spots on the even order fringe, as indicated by the arrows. (b) When the surfaces are separated the presence of the liquid/liquid interface is more clearly seen from the presence of a second clear discontinuity in the FECO.

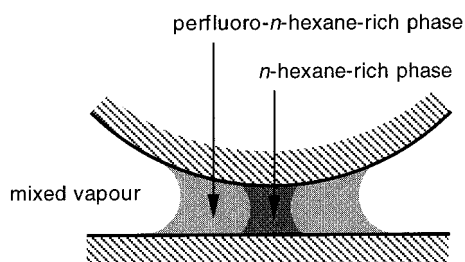


Figure 11. Schematic representation of the two-phase, or “double” capillary condensate observed in the FECO images in Figure 10.

Two-Phase Condensates. Interesting behavior was observed in experiments where the bulk liquid consisted of a perfluoro-*n*-hexane-rich phase at, or very close to, two-phase coexistence. In these experiments a two-phase mixture of the liquids was equilibrated at the same temperature as the SFA by placing the mixture in the SFA cabinet for several hours. The perfluoro-*n*-hexane-rich phase was then injected into the SFA chamber and allowed to equilibrate. Upon bringing the surfaces into contact a two-phase or “double” capillary condensate would sometimes form, as shown in the FECO images in Figure 10, and illustrated schematically in Figure 11. The stability of such double condensates was variable. Sometimes the double condensate was stable over the time scale of the observation (≈ 1 h). On other occasions a double condensate was not observed, while sometimes a double condensate would form initially, after which the inner condensate would continue to grow, ultimately “consuming” the outer condensate.

In experiments with sufficiently stable double condensates it was possible to induce the dissolution and reformation of the

inner condensate by bringing the surfaces out of and back into contact in the presence of the outer condensate. In this manner the refractive index could be measured within both the inner and outer condensates. It was on the basis of such measurements that the inner and outer condensates were identified as corresponding to *n*-hexane-rich and perfluoro-*n*-hexane-rich phases, respectively (as shown in Figure 11). At a given temperature the refractive indices of the two phases in the double condensates were equal, within error, to the values calculated from the compositions of the coexisting phases in the bulk mixture.

Importantly, in the experiments where the inner condensate could be dissolved by separating the surfaces, the presence of thick adsorbed films of *n*-hexane-rich phase on the surfaces was detected. As mentioned above, this is consistent with preferential wetting of the mica/liquid interface by the *n*-hexane-rich phase. On the basis of refractive index measurements in the absence of the inner condensate the thickness of the films was estimated to be of the order of 10 nm. (We have not yet attempted to study the temperature dependence of the thickness of such films, and hence cannot comment on the possibility of a wetting transition in this system.) In the presence of such films the formation of the inner condensate occurred when the surface separation was reduced to approximately 30–40 nm. This suggests that the inner condensate is formed by long-range coalescence of the wetting films of the *n*-hexane-rich phase, analogous to the formation of pure liquid condensates in vapor phase experiments.^{52,68}

The formation of double condensates can be described in terms of capillary phase-separation of the preferentially wetting *n*-hexane-rich phase within a condensate of perfluoro-*n*-hexane-rich phase. The size of the inner condensate will be determined by how close the condensed perfluoro-*n*-hexane-rich phase is to the phase separation point. Importantly, the volume of the perfluoro-*n*-hexane-rich phase is also limited by undersaturation of the vapors. The equilibrium structure of the condensate is thus very sensitive to the precise values of the relative vapor pressures of the components. The variability in the behavior of the double condensates is thus probably due to slight changes in the composition of the bulk liquid due to evaporative losses, or slight differences in the temperature differential between the bulk liquid and the surfaces.

In experiments with phase-separated mixtures in the SFA chamber only one-phase condensates were observed. Refractive index measurements in such condensates show that they consist of the *n*-hexane-rich phase. No significant variation of the refractive index as a function of surface separation was observed in such condensates, and the calculated compositions of the condensates agreed within error with the compositions of the *n*-hexane-rich phase in the bulk mixtures.

Time-Dependence of Composition. Thus far we have discussed primarily the equilibrium properties of the capillary condensates formed from mixed vapors. We conclude this section by describing some measurements of the composition of the condensates in the initial stages of formation. In these measurements the surfaces were separated to approximately 140 nm within 5 s after the formation of an initial condensate. Subsequent measurements of the refractive index in the growing condensate sometimes reveal a change in composition with time, as was observed in the experiments by Tryhorn and Wyatt.^{34,35} For example, Figure 12 shows the results of such measurements for the condensates whose equilibrium refractive index profiles are shown in Figures 4c and 4e. The condensates with $X_{f,cond} \approx 0.30$ show an increase in *n*-hexane concentration (as shown by an increase in refractive index) over the first few minutes of

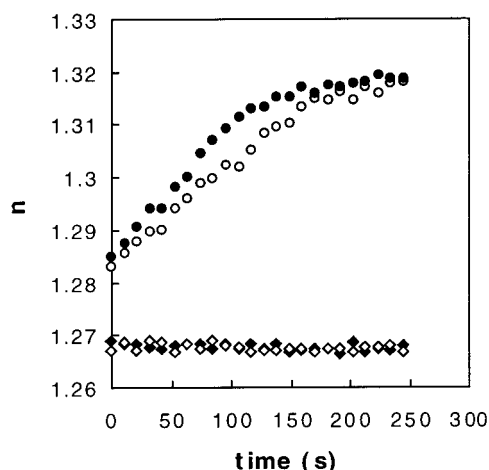


Figure 12. Refractive index n (measured at $D \approx 140$ nm) as a function of time for capillary condensates of n -hexane/perfluoro- n -hexane mixtures. The circles (open and filled) represent two sets of measurements for condensates with $X_{f,cond} \approx 0.30$ at 24.4 °C (with equilibrium refractive index profile $n(D)$ as shown in Figure 4c). The diamonds (open and filled) are for condensates with $X_{f,cond} \approx 0.75$ at 23.6 °C (with equilibrium refractive index profile $n(D)$ as shown in Figure 4e).

growth, whereas the condensates with $X_{f,cond} \approx 0.75$ display little change in composition as a function of time.

The magnitude of the increase in refractive index of the condensate with $X_{f,cond} \approx 0.30$ is too large to be explained in terms of time-dependent adsorption of n -hexane at the mica/condensate interface. Instead, the observed change in concentration must arise from differences in the rates of material transfer of the vapor components to the condensate. We note that the time scale characterizing the change in composition is comparable to the time scale characterizing the rapid initial growth of the condensate toward its equilibrium size. The precise dependence of the composition on time will be determined by an interplay between the absolute vapor pressures and diffusivities of the vapor components, as well as the relative degree of vapor pressure lowering due to curvature of the liquid/vapor interface of the condensate. A full treatment would require an extension of the type of calculation described in ref 58.

The observed dependence on time of the composition of mixed condensates is not merely a curiosity but is potentially very important in a number of regards. For example, the influence of the rate of material transfer on the composition of liquid nuclei is important in the theory of homogeneous nucleation in mixed vapors.^{69,70} Of more direct relevance is the importance of kinetic effects in the study of binary mixtures in porous materials. The results in Figure 12, together with the transient effects observed in the experiments with double condensates, show the importance of kinetic effects in the behavior of binary liquid mixtures in pores. In many porous materials, characterized by high tortuosity, the rates of achieving compositional equilibrium would be expected to be much slower than in the experiments described here. It is not difficult to imagine that in many cases the establishment of true equilibrium on the time scale of the experiments would be difficult to achieve.

4. Summary and Conclusions

The compositions and mean meniscus radii of curvature of capillary condensates formed from near-saturated vapors of (one-phase) n -hexane/perfluoro- n -hexane mixtures are in broad agreement with the predictions of the binary Kelvin equations. Measurements of the refractive index as a function of surface

separation in the condensed mixtures show that n -hexane is preferentially adsorbed at the mica/liquid interface. This is consistent with both macroscopic observations on the wetting behavior of mixtures in contact with mica, and with simplistic arguments based on calculations of nonretarded Hamaker constants. The extent of adsorption depends on the position in the liquid–liquid phase diagram of the mixture. For condensates with near-critical compositions, at temperatures near the critical temperature, relatively thick films are observed, which may reflect critical adsorption of n -hexane at the mica/liquid interface. In perfluoro- n -hexane-rich condensates below the critical temperature, the extent of adsorption increases as the phase curve is approached, consistent with the formation of a wetting layer of the n -hexane rich phase.

We have also observed the formation of two-phase or “double” capillary condensates formed from vapors of bulk perfluoro- n -hexane-rich mixtures at, or very close to phase-coexistence. The formation of such double condensates can be attributed to the capillary phase separation of an n -hexane-rich phase within a condensate of perfluoro- n -hexane-rich phase. Capillary condensation from vapors coexisting with phase-separated bulk mixtures gives rise to condensates of the n -hexane-rich phase.

Measurements of the change in refractive index as a function of time show that the composition of mixed condensates can vary significantly in the initial stages of condensation. Together with the transient behavior sometimes observed with double condensates, these results illustrate the importance of kinetic effects in the behavior of confined mixtures.

The results described in this paper demonstrate the potential of the SFA for use in studies of capillary condensation from binary vapors. The influence of interfacial wetting and liquid–liquid-phase separation in determining the properties of capillary condensates formed from mixed vapors deserves further attention. For future work it would also be desirable to develop a method for the accurate control, over a wide range of values, of the relative vapor pressures of the mixtures. This would allow a more thorough investigation of the validity of the binary Kelvin equations. In broader terms, our results demonstrate that the SFA could be applied to good effect in studies of binary liquid mixtures in confined geometries. In this respect, the study of small volumes of mixtures may enable one to avoid the problems of slow dynamics and metastability commonly encountered in experimental studies of binary mixtures in porous media.

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