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Prewetting in a Binary Liquid Mixture

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We present evidence for the existence of a prewetting transition in the mixed region of the phase diagram of the binary liquid mixture methanol-cyclohexane. Our measurements reveal the existence of a first order thin to thick film transition as the temperature is decreased towards the separation temperature T_S at a temperature T_{pw} above T_S and distinct from it. This transition is strongly hysteretic. The determined prewetting line approaches the coexistence curve tangentially. Also, the prewetting critical point is found to display 2D Ising-like criticality.

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Following a study of the first order wetting transition and the hysteresis associated with it at the vapor-mixture interface of the binary liquid mixture methanol-cyclohexane [1] at two phase coexistence, we present evidence for the existence of a prewetting transition in the one phase region of the phase diagram. It is generally accepted that a first order wetting transition at coexistence implies the existence of a prewetting transition off coexistence. This is a generic feature of the wetting phase diagram predicted by Cahn [2] in 1977 but that has so far resisted observation for binary liquid mixtures. Along the prewetting line, two films of different thicknesses coexist at the same chemical potential. In the case of a binary liquid mixture, the prewetting line manifests itself with a jump in the thickness of the adsorbed layer off coexistence and before bulk phase separation as the prewetting line is crossed. This line terminates at a prewetting critical point T_{cpw} where the jump in thickness vanishes. The low temperature end of this line intersects the coexistence curve tangentially at the wetting temperature T_w [3].

At two phase coexistence, the wetting transition has been discovered in a number of different binary fluid systems [1,4-6]. The prewetting transition, however, has only been discovered recently in the study of the adsorption of helium on cesium substrates [7] as predicted theoretically by Cheng *et al.* [8] and in the case of hydrogen on rubidium substrates [9]. Possible evidence for prewetting was also reported in a surface melt experiment on Caprolactam [10]. For binary liquid mixtures, Schmidt and Moldover [11] studied the system isopropanol-perfluoromethylcyclohexane. Their study was not unambiguously successful in locating the prewetting line. In a later paper, Schmidt [12] argued that this might be due to the wetting properties of this specific system. In comparing this system to a number of other systems, he places it among "the least favorable" for detecting this transition. This has led to the general consensus that in classical systems the prewetting line lies exceedingly close to the coexistence curve rendering its experimental observation very difficult [8]. This Letter focuses on prewetting in the methanol-cyclohexane system.

In our previous study of the wetting transition for the critical sample of this mixture at coexistence using ellipsometry [1], it was shown that the wetting transition is a clear first order transition in this system. In the wetting regime, either a very thin or a thick film of the methanol-rich phase intrudes between the cyclohexane rich phase and the vapor. The observed hysteresis showed the wetting transition to be a first order phase transition. Tentatively, we took the lowest temperature for which two different values for the ellipticity could be found to be the wetting temperature $T_w = 22.3^\circ\text{C}$.

We use a phase modulated ellipsometer [13] to measure the ellipticity $\bar{\rho}$ of the light reflected on the mixture-vapor interface. In the case where an adsorbed layer of refractive index $n(z)$ (z is the altitude) is present at the interface between a phase of index n_1 and a substrate of index n_2 , the ellipticity varies linearly with the adsorption at the interface [6]. This approximation is valid when $[n(z)^2 - n_2^2] \ll [n(z)^2 - n_1^2]$. The ellipticity can be converted into an adsorbed layer thickness using Drude's formula [14]. If the index through the film is assumed constant the ellipticity $\bar{\rho}$ varies linearly with the layer thickness. Measurements are taken typically every 2 min. This allows us to follow the system and the behavior with time and record stable and unstable values for the ellipticity. The refracted beam was used to monitor the bulk properties of the mixture. Visual observation of the refracted beam allowed us to check the separation temperature *in situ*; the separation temperature was also determined separately by visual observation. The separation temperatures determined using the above mentioned procedures were found to be the same to within 0.1 K (accuracy of thermometer).

The samples were prepared in 2 cm diameter and 8 cm height glass cylinders. These cylinders were heated to anneal the birefringence of the glass, filled halfway with the solution, flame sealed, and inserted horizontally in a brass block filled with thermostated water. The block is held onto the vertically mounted ellipsometer in such a way that the laser beam, passing through appropriately fitted windows on the block (for incident, reflected, and transmitted beams), falls at the center of the surface of

the solution. The samples studied have compositions between 5% and 50% molar fraction of methanol. The critical composition sample has a critical temperature $T_c = 47.5^\circ\text{C}$ suggesting the presence of 0.08 wt.% water impurity. The ellipticity was recorded as a function of the temperature in the following way. We start at a temperature several degrees above the bulk separation temperature. The temperature is then decreased in small steps of 0.1–0.6 K. The samples were equilibrated at every temperature studied and the ellipticity was followed in time until it was stable.

The measured stable values for the ellipticity reveal the existence of three distinctly different regions in the phase diagram. In region I for molar fractions of methanol above 17%, the ellipticity increases continuously as the temperature is decreased towards the separation temperature denoted T_S . This is displayed in Fig. 1, sample a, for the 17.5% sample. In region III, for molar fractions of methanol less than 7%, the ellipticity varies only slightly with temperature all the way to T_S . In region II, for molar fractions of methanol between 17% and 7%, the ellipticity increases slightly as the temperature is lowered. Then at a temperature T_{jump} above T_S , and distinct from it, the ellipticity undergoes a jump. Below T_{jump} , the ellipticity increases continuously with decreasing temperature up to or very close to the separation temperature T_S . This behavior is found when the temperature is lowered in small steps; when the temperature is increased, the ellipticity decreases continuously and does not jump to the smaller values as the temperature increases above T_{jump} . This region II will be identified as the prewetting region as discussed below. In Fig. 1, sample b, the ellipticity is shown as a function of the temperature for the 14.5% sample. The open symbols are obtained while heating; the dots are obtained while cooling. The jump occurs at 34.6°C , while the separation temperature T_S is 34.1°C . The ellipticity increases slightly as T_{jump} is approached from above and this probably takes place in steps of about a methanol molecular diameter as was observed at coexistence [15]. We plan to investigate this layering in a forthcoming publication. At T_{jump} , the ellipticity undergoes a clear jump of about 11 Å. Below this jump temperature, the ellipticity increases continuously up to the

separation temperature T_S .

At T_S or very close to it in regions I and II, the ellipticity goes up to much higher values that are unstable and that correspond approximately to the values characteristic of the wetting film at coexistence. The onset of these large unstable ellipticity values occurs at a temperature that is similar to the separation temperature determined independently and provides another way of locating the separation temperature *in situ*. In region III, no such increase of the ellipticity is observed.

Schmidt and Moldover [11] may also have observed a hysteresis: A jump in thickness was observed if the sample was cooled continuously; however, if the sample was equilibrated and stirred at each temperature studied, a continuous increase of the thickness was obtained. They attributed this behavior to nonequilibrium effects related to very slow mass diffusion in such systems. In our experiments we show that hysteresis occurs only in one region of the phase diagram and as addressed below such hysteresis is characteristic of the prewetting transition [16]. Also, for each curve, the hysteresis is observed only between T_{jump} and T_{ML} (Fig. 1); the rest of the curve (between T_{jump} and T_S and above T_{ML}) is not hysteretic. In addition to this, the reproducibility of these two temperatures and of the values of the ellipticity measured on the two branches for separate runs gives us confidence that we are not studying a nonequilibrium phenomenon. In order to study the hysteresis loop, our measurements were all done in at least two separate runs. In the first run, the temperature is decreased all the way to T_S allowing us to determine the low branch of the ellipticity and to measure T_{jump} . In the second run, the temperature is decreased to a temperature slightly higher than T_S (again determining T_{jump}) and is then increased to determine the upper branch of the ellipticity and the temperature T_{ML} .

In these experiments, we found it crucial to decrease the temperature in very small steps (0.1–0.6 K). If the temperature is decreased using larger steps ($\Delta T > 0.6\text{ K}$) the ellipticity starts fluctuating. For smaller steps ($0.3 \leq \Delta T \leq 0.6\text{ K}$) as the temperature is decreased, the ellipticity first increased to higher values and then decreased slowly to smaller values. The equilibration times are found to be of the order of half an hour to an hour. For steps of 0.1–0.2 K, the ellipticity changes smoothly. This behavior is characteristic for the measurements in the prewetting region and before T_{jump} ; the sensitivity to temperature gradients becomes more pronounced as this temperature is approached from above. The extreme sensitivity of wetting layers to temperature gradients was already illustrated experimentally by Durian and Franck [17]. Also in our previous study of the first order wetting transition in the same system [1] small temperature steps did not affect the ellipticity measured; however, larger steps were found to destabilize the ellipticity which would start fluctuating after the temperature step.

The observed transition from thin film to thick film is first order and hysteretic. The thick film persists at the

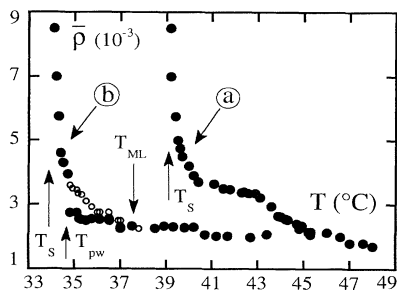


FIG. 1. Ellipticity versus temperature for the 17.5% sample (a), 14.5% sample: filled symbols for cooling and open symbols for heating (b).

surface when the temperature is increased above T_{jump} . In order to come back along the lower branch of the ellipticity, it was necessary to increase the temperature several degrees above the temperature of the jump. This branch is reversible as long as the temperature stays above T_{jump} . The upper branch is also reversible if the temperature is not increased above the temperature T_{ML} (Fig. 1, sample b) which denotes the metastability limit of the thick film where the two branches of the ellipticity become similar. This hysteresis poses the problem of the identification of the prewetting temperature T_{pw} . A similar hysteresis was observed in the study of the wetting properties of helium on cesium at coexistence below the wetting temperature [7]. Recent theoretical calculations show that along the prewetting line the line tension between thin and thick film domains diverges as the wetting temperature is approached [18]. This divergence of the line tension can account for the anomalously long lifetimes of metastable thick films when taken out of equilibrium [16]. Considering that we observe a thick film that persists at the surface when the temperature is increased above T_{jump} , the latter temperature could be identified as the prewetting temperature T_{pw} . Then, the thick film persists at the surface above the prewetting temperature because the nucleation of a dry patch of the equilibrium thin film in the metastable thick film is very difficult; the energy required to overcome the nucleation barrier is very large [16].

These measurements were performed for several molar fractions of methanol in the three regions mentioned. The low temperature end of the prewetting line is determined by simply locating the lowest molar fraction of methanol in region II for which a jump could still be observed and the highest molar fraction in region III for which the ellipticity does not vary much with the temperature. Also as noted above, the ellipticity increases very rapidly at T_S in regions II and I but not in region III. The crossover temperature between regions II and III corresponds to the wetting temperature and is found to be about 23°C in agreement with our previous determination ($T_w = 22.3^\circ\text{C}$) [1].

To characterize the high temperature end of the prewetting line, note that a rapid increase of the adsorption as a function of the temperature could persist in the adsorption curves even above the prewetting critical point. This was observed in the prewetting of helium on cesium [7] well above the prewetting critical point and in simulations of the prewetting transition [19,20]. This rapid increase above the prewetting critical point can be experimentally indistinguishable from the steps below this critical point. This indicates that in order to locate this critical prewetting point accurately it might not be sufficient to locate the point where hysteresis and a discontinuity in the adsorption curves cease to exist. In our case, however, the location of the prewetting critical point could still be roughly estimated to be between 16.5% and 17.5% since a continuous increase with no jump and no hysteresis is observed for the latter molar

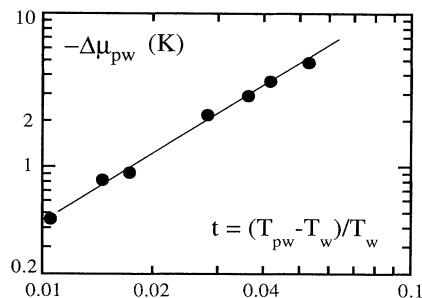


FIG. 2. Chemical potential difference between the prewetting line and the coexistence curve $\Delta\mu_{pw}$ (expressed in kelvin and is negative) as a function of the reduced temperature $t = (T - T_w)/T_w$ for $T_w = 22.3^\circ\text{C}$ (log-log scale). The slope of the line is 1.4.

fraction and for larger ones. Note that a very rounded residual steplike structure persists in the ellipticity curve for the 17.5% sample, but this occurs far from the separation temperature and the rapid increase is not pronounced. Moreover this residual structure becomes less pronounced for higher molar fractions. For the 16.5% sample, a clear jump and a hysteresis loop are observed. In this way we estimate the prewetting critical point to be $T_{\text{cpw}} = 39 \pm 1^\circ\text{C}$.

The determined prewetting line is found to be very close to the coexistence curve. The difference $T_{\text{pw}} - T_S$ is found to be 0.8°C for the 16.5% sample; this difference decreases with decreasing methanol molar fraction and is less than 0.2°C for molar fractions of 10% or less. From the determined prewetting line and the coexistence curve, we calculate the distance from coexistence (or chemical potential difference) along the prewetting line $\Delta\mu_{pw} \sim T \log_{10}(\phi_p/\phi_s)$ (defined in kelvin), where T is the temperature, ϕ_p the molar fraction at prewetting, and ϕ_s the molar fraction at coexistence both taken at the same temperature. Based on general thermodynamic arguments [3], Schick and Taborek [16] show that this chemical potential difference vanishes as the wetting temperature is approached as $\Delta\mu_{pw} \sim t^{3/2}$, where $t = (T - T_w)/T_w$, in the case where this transition is given by the competition between long range van der Waals forces that favor wetting and a chemical potential term that opposes it. In Fig. 2

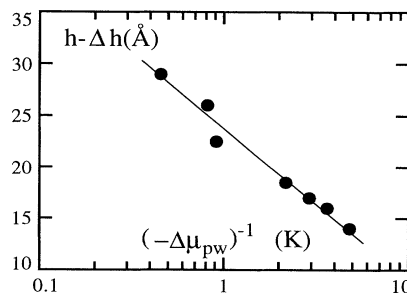


FIG. 3. Thickness of the thin film $h - \Delta h$ along the prewetting line versus the chemical potential difference $(-\Delta\mu_{pw})^{-1}$ (semilog scale).

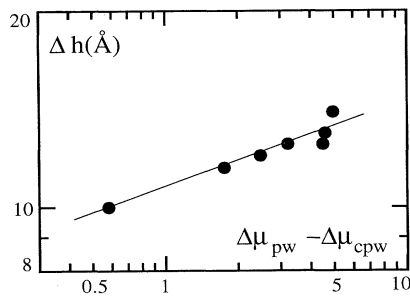


FIG. 4. Jump in thickness Δh versus the distance from the prewetting critical point ($\Delta\mu_{pw} - \Delta\mu_{cpw}$) along the prewetting line for $T_{cpw} = 39^\circ\text{C}$ (log-log scale). The slope of the line is 0.125. The dispersion on the points to the right is due to the difficulty of working near the wetting transition temperature where the difference between T_{jump} and T_S becomes very small.

we plot $\Delta\mu_{pw}$ as a function of t (with $T_w = 22.3^\circ\text{C}$) [1] on a log-log scale. The experimental points fall on a straight line the slope of which is found to be 1.4 in good agreement with the predicted value. This gives another confirmation that the wetting temperature used is indeed the correct one. The variation of $\Delta\mu_{pw}$ as a function of t also proves that the prewetting line and the coexistence curve approach each other tangentially as expected from a Clapeyron type relation. The thickness of the thick film is found to diverge as $h \sim \Delta\mu_{pw}^{-0.28}$ in agreement with the expected value of $-\frac{1}{3}$ for nonretarded van der Waals forces. The thickness of the thin film also increases as the wetting temperature is approached as has already been observed [7,21]. This increase is compatible with a logarithmic variation (Fig. 3) as expected for the case where short range forces favor wetting while the chemical potential term opposes it [3].

Having adopted the prewetting critical point temperature as $T_{cpw} = 39 \pm 1^\circ\text{C}$, we can examine how the jump in thickness Δh vanishes as this critical point is approached. This feature of the prewetting transition has already been discussed theoretically by Nakanishi and Fisher [22] who conjectured that this prewetting critical point should display 2D Ising-like criticality. In this case the difference in thickness is the order parameter which vanishes at this critical point. This conjecture was verified by Nicolaidis and Evans [20] in Monte Carlo simulations of this transition. Accordingly this jump in thickness varies as $\Delta h \sim (\Delta\mu_{pw} - \Delta\mu_{cpw})^{1/8}$. $\Delta\mu_{cpw}$ is the chemical potential difference at the prewetting critical point and $\Delta\mu_{pw}$ is the chemical potential difference on the prewetting line; the difference between the two measures the distance from the critical prewetting point along the prewetting line. In Fig. 4 a plot of Δh as a function of this distance from the prewetting critical point is shown in a log-log scale for $T_{cpw} = 39^\circ\text{C}$ ($\Delta\mu_{cpw} = -5.4\text{ K}$). The experimental points fall on a straight line. The resulting straight line has a slope of 0.125 ± 0.020 , in good agreement with the expected result. The error is mainly due to the fact that the prewetting critical point tempera-

ture was only roughly estimated. This remarkable finding establishes that this transition from thick film to thin film is indeed identical to a pure surface transition and displays 2D Ising-like criticality.

In summary we have characterized a prewetting transition in a binary fluid mixture. This transition is first order and strongly hysteretic. The determined prewetting line intersects the coexistence curve tangentially. The thickness of the thick film is shown to be governed by long range van der Waals forces. Also the observed transition is identical to a pure surface transition displaying 2D Ising-like criticality.

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