Effect of altered surface substrate chemistry on critical adsorption from a binary liquid mixture

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We have demonstrated the importance of the surface chemical character of the substrate in the phenomenon of critical adsorption—the long-range perturbation of chemical concentration in a critical binary liquid mixture by a boundary. By measuring the reflectivity of the solid/liquid interface between borosilicate glass and a mixture of carbon disulfide and nitromethane near its critical demixing point, we find that the substitution of methyl for hydroxyl groups on the glass surface inverts the sign of the long-range order-parameter perturbation.

Without the ability to control the strength of an applied magnetic field, the experimental study of magnetism would be considerably less interesting. Similarly, a full understanding of the effect of solid boundaries on liquid phase transitions requires that the solid/liquid interaction be tunable. In reflected-light studies of the critical mixing transition in a binary liquid mixture of polar (nitromethane) and nonpolar (carbon disulfide) molecules near a glass substrate, we have found that the chemical alteration of the surface of the substrate provides the desired control.

In 1978 the prediction was made that a binary liquid mixture just above its critical mixing point in temperature while having an average order parameter equal to zero in the bulk, would acquire a nonzero value within a bulk correlation length of a selectively adsorbing wall.[1] This phenomenon, which is called critical adsorption, has been observed experimentally with ellipsometry,[2] reflectivity,[3] and evanescent-wave-excited fluorescence at boundaries of critical binary liquids.[4] Recently, an analogous order has been found in x-ray-reflection and -scattering studies of a liquid crystal.[5]

In this report we discuss critical adsorption observations made with light reflected from the interface between a critical binary liquid mixture and a borosilicate glass substrate whose selective adsorption is chemically altered. We also consider room-temperature capillary-rise measurements of appropriate liquid/solid surface tensions.

For reflectivity observations we prepared 2-ml mixtures of high-purity (99 + %) (Ref. 6) nitromethane and carbon disulfide at the critical volume fraction of carbon disulfide (ϕ_c). Our volume-measurement uncertainty gives a value within 1% of the published value for ϕ_c, 0.601.[7] The sample cells followed an earlier design[3] with the following important changes. In place of Teflon glass/glass and glass/metal sealing gaskets, indium was used. The fill-hole seal used a commercial flange with a silver-coated stainless-steel gasket for the hydroxylated sample and a Teflon gasket for the methylated sample.[8] These improvements resulted in a lowering of the bulk-critical-temperature drift to + 2 mK/d for the hydroxylated sample at the time of the reflectivity measurement. The methylated system exhibited a drift rate of + 8 mK/d at the time of its measurement. The bulk critical temperature was measured by scanning slowly ($\approx$1 mK/3 min) in temperature and visually noting the presence of swirling of phase-separated eddies and/or a liquid/liquid meniscus. At the time of the reflectivity observations, the bulk transition temperatures were 63.401 ± 0.001 °C for the hydroxylated sample and 63.2315 ± 0.0015 °C for the methylated sample. Since the thermometers were different for the two samples and not absolutely calibrated, the significance of the difference between these values for T_c(bulk) is not clear. Generally, our measured T_c(bulk) is higher than the published value, 61.98 °C.[7] This might be due to impurities in our samples. Again, the lack of an absolute calibration reduces the significance of this comparison.

The glass surfaces were hydroxylated or methylated in the manner discussed below. Since substitution of methyl for hydroxyl groups lowers the polarity of the surface, the methylated substrate is expected to show a greater relative adsorption of carbon disulfide over nitromethane when compared with the hydroxylated substrate. The rule that a polar substrate attracts polar molecules has been well established from bulk adsorption studies.[9]

Hydroxylated substrates were prepared using the usual glass-etching solution based on chromic acid.[10] This leaves the hydroxylated surface shown in Fig. 1(a).[11] It is also expected that water is physisorbed on the surface.[11] The production of the methylated substrate was accomplished using a standard procedure for the silanization of adsorbents in liquid chromatography.[12] A hydroxylated substrate was first prepared as described above. Then, in order to eliminate physisorbed water, it was vacuum-baked at 200 °C for 5 h.[11] Next, the substrate sat for 5 min in dimethyldichlorosilane at room temperature. Finally, it was washed in methanol for 10 min. In order to avoid polymerizing the silane through exposure to water,[13] the last two steps were carried out in a dry bag. In a former attempt, without baking, a greasy macroscopic coating of silane polymer was produced.

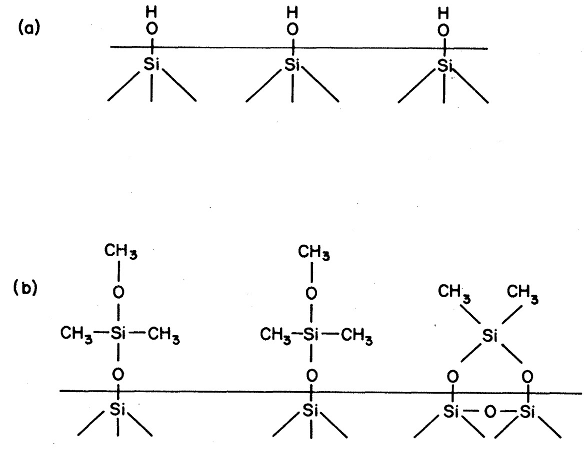

FIG. 1. (a) Hydroxylated glass surface; (b) methylated glass surface.

In order to check the selective adsorption properties of the glass substrates, subcritical capillary-rise measurements of the liquid/liquid meniscus of the carbon disulfide and nitromethane system were performed, as shown in Fig. 2, using reagent-grade chemicals. At the temperature at which the measurements were made (between 21 °C and 23 °C), the upper phase is 95 vol % nitromethane, while the lower phase is 95 vol % carbon disulfide.[7] Therefore it is expected that the difference between meniscus height in the capillary and in the bulk liquid (Δh) should increase as the polarity of the substrate decreases. A measure of the degree of selective adsorption is the contact angle θ that the meniscus makes with the glass substrate (measured on the carbon-disulfide-rich side). For strongly nonpolar or strongly polar substrates the extremes $\theta=0$ or π are attained, respectively. These limits correspond to perfect wetting of the substrate by the nonpolar or polar phases, respectively. The relationship between capillary rise (Δh) and contact angle (θ) is as follows: $\Delta h=[2\gamma/(\Delta\rho g R)]\cos\theta$,[14] provided that $R \ll \Delta h$. $\Delta\rho$ is the mass-density difference between the lower and upper phases. R is the inner radius of the capillary tube and g is the local acceleration due to gravity; γ is the surface tension between the two liquid phases. As in the reflectivity experiments, we used borosilicate glass substrates. The inner capillary radius was $R=0.068$ or 0.013 cm. For the hydroxylated substrate, we find that $R\,\Delta h$ is between -0.034 and -0.058 cm^2, while $R\,\Delta h$ is between $+0.0068$ and $+0.016$ cm^2 for the methylated substrate. Variability between different samples accounts for the range of values. The retraction method of capillary-rise observation was used at the suggestion of Widom;[15] before Δh is measured, the substrate is pulled through the liquid/liquid interface so as to leave behind the phase that preferentially wets the substrate. These measurements show that hydroxylated glass attracts the polar component of the mixture in preference to the nonpolar component, and that the reverse situation occurs for the methylated surface, as expected. Furthermore, since the absolute magnitude of $R\,\Delta h$ is smaller for the methylated system than for the hydroxylated system, we conclude that the carbon-disulfide-rich phase does not perfectly wet the substrate ($\theta\neq 0$) in the methylated case.

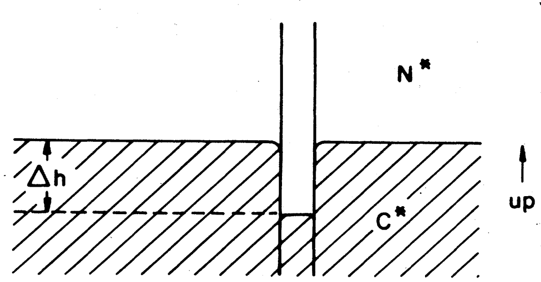

FIG. 2. Capillary-rise experiment. Δh is the capillary rise. The case $\Delta h<0$ is shown. N^* indicates the nitromethane-rich phase. C^* indicates the carbon-disulfide-rich phase.

The reflectivity of p-polarized light (R) as a function of temperature for the two substrates in contact with critical solutions of nitromethane plus carbon disulfide is shown in Fig. 3. The angle of incidence from normal, 77.6°, at the glass/liquid interface was just below that of bulk total internal reflection. These observations were made in the mixed state just above the bulk critical temperature ($\approx$63 °C). The apparatus was similar to that used in Ref. 3 with the following exceptions. The light-intensity measurements were collected with a computer, and a resistance-inductance bridge was used to measure temperature for the methylated sample. In the region shown in Fig. 3, the temperature was stepped at a rate of about 1 m°C/5 min. For the hydroxylated system the liquid was continuously mixed with a magnetic float. Both heating and cooling measurements were performed for this sample. The scatter in the data close to T_c(bulk) is due to the discrepancy between heating and cooling curves. For the methylated sample mixing was found to affect the reflectivity signal. Since for this sample the mixer was close to the substrate, it might have been able to mechanically disturb the region of critical adsorption. Because of this the system was first mixed at a temperature 0.06 °C above the bulk critical temperature and measurements were then made by cooling with the mixer off. The reflectivity measurements were normalized to the total internal reflection seen at high temperatures, as discussed in Ref. 3.

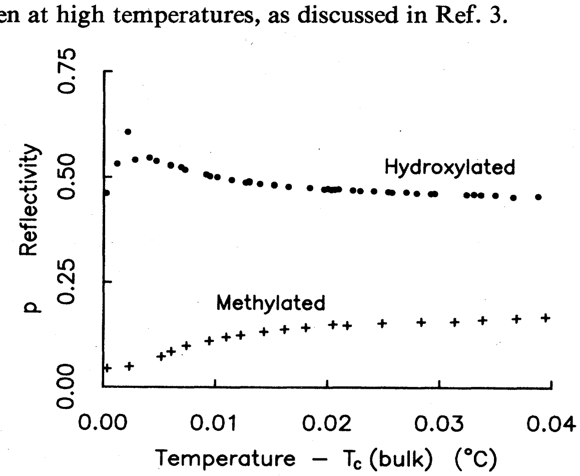

FIG. 3. Reflectivity above the bulk critical point.

In order to interpret these reflectivity measurements for critical adsorption effects it is first necessary to understand the bulk contribution. As discussed in Ref. 3, over a wide range of temperature above T_c the bulk contribution is predominately due to thermal expansion. For our hydroxylated sample, this is accurately expressed by the linearly varying bulk refractive index,

$$\epsilon_2^{1/2}=n_0+at \ , \tag{1}$$

where ϵ_2 is the bulk optical dielectric constant, $n_0=1.484$, $a=-0.26$, and t is the reduced temperature, given by $t=\Delta T/T_c(\text{bulk})$, where $\Delta T=T-T_c(\text{bulk})$. T and $T_c(\text{bulk})$ are in K. Using (1) to predict the bulk reflectivity over the temperature range shown in Fig. 3, we find insignificant variation. Furthermore, as was discussed in Ref. 3, critical anomalies in the bulk reflectivity are apparently slight.

For the methylated system the background reflectivity does not agree with the bulk behavior characterized by Eq. (1): the reflectivity is smaller than expected. This discrepancy cannot be ascribed to our uncertainty in the absolute angle of incidence (±0.25°). Sample contamination is a possibility since the drift rate for T_c(bulk) in the methylated specimen, while being comparable to that of earlier specimens (see Ref. 3), was a factor of 4 higher than for the hydroxylated sample discussed here. However, for another methylated sample, the bulk reflectivity was consistent with that of the hydroxylated specimen in spite of the fact that the drift rate for T_c(bulk) was a factor of 2 larger than that of the methylated system presented here. Our conclusion is that although the low bulk reflectivity in the methylated sample used to produce Fig. 3 is unexplained, the deviations from a constant reflectivity represent effects of critical adsorption. In the following discussion we take the value of the reflectivity at $\Delta T=0.035\,^\circ\text{C}$ to be the bulk reflectivity R_b in the critical region for either the methylated or hydroxylated sample, respectively.

We now establish a relationship between the deviation ΔR $(=R-R_b)$ from constant bulk reflectivity, and the order parameter $m(z)$, which is a function of the perpendicular distance (z) from the substrate. First, we relate the deviation ($\delta\epsilon$) in the local optical dielectric constant from its value at $z=\infty$ to $m(z)$; $\delta\epsilon(z)=\epsilon(z)-\epsilon(z=\infty)\approx cm(z)$. This expression and the value $c=0.77$ are derived in Appendix A.

The next step is to relate $\delta\epsilon$ and ΔR. This was done to lowest order in $\delta\epsilon$ in Ref. 16. The result is quoted in Appendix B. The reflectivity was found to be a function of the half-space Fourier transform of $\delta\epsilon(z)$,

$$\widetilde{\delta\epsilon}(k)=\int_0^\infty e^{ikz}\delta\epsilon(z)dz \ .$$

The transform argument k is twice the z component of the wave vector in the liquid far from the boundary. In our experiments, since θ is close to the bulk total internal reflection angle, k is small. This can be expressed in terms of the bulk correlation length ξ as follows: $k\xi\le 0.4$ for $T-T_c(\text{bulk})\ge 0.005\,^\circ\text{C}$. In other words, we are studying critical adsorption at large distances from the wall. Since k is small, we can expand $\delta\epsilon(k)$ in moments of $m(z)$ as suggested by Charmet and de Gennes.[17] This gives, to first order in k,[18]

$$\Delta R\approx dM_0^2-eM_1 \ , \tag{2}$$

where

$$M_0=\int_0^\infty m(z)dz \ ,$$
$$M_1=\int_0^\infty zm(z)dz \ ,$$

and d and e are zero and first order in k, respectively. They are both positive and independent of surface structure. Using the results of Appendix B, d and e are derived from ϵ_2, the bulk liquid optical dielectric constant, in the neighborhood of the critical temperature. Since, as discussed above, ϵ_2 and R_b are taken to be constant over the range $\Delta T=0$ to 40 m°C, d and e are also constant over this range. For the hydroxylated specimen, we used the ϵ_2 value given by Eq. (1) at $\Delta T=0$. For the methylated sample, because of the aforementioned disagreement with the bulk reflectivity of the hydroxylated sample, a different approach was taken. We found the value of ϵ_2 which corresponds to the reflectivity measured at $\Delta T=35$ m°C, $R=0.16$, which we took to be due to bulk alone. The values of ϵ_2 are 2.202 and 2.217 for the hydroxylated and methylated specimens, respectively. The resultant values for d and e are given in Table I. The methylated values are estimates because of the uncertainty in establishing ϵ_2. Note that the d and e values are comparable for the two specimens, and since, as discussed below, the M_1 term of Eq. (1) dominates, the fact that the corresponding coefficient, e, is essentially the same for both specimens is an important measure of consistency.

From Fig. 3 we notice that the methylated system showed a decrease in R from the bulk value. This can only be due to the M_1 term in Eq. (2) since the contribution of the M_0^2 term is always positive. We will discover later that the M_1 term provides the largest contribution to ΔR when ΔT is small.

We can find the value of M_1 as follows: Since only a single quantity ΔR is known for each temperature and there are two unknowns, M_1 and M_0, we first estimate M_0 in terms of M_1. Since we are interested in the small-k (large-z) behavior of $m(z)$, we consider the long-distance solution to theories which presume a contact in-

TABLE I. Moment estimates of critical adsorption.

Sample	d (nm^{-2})	e (nm^{-2})	ΔR ($\Delta T=5$ m°C)	M_1 ($\Delta T=5$ m°C) (nm^2)
Hydroxylated	1.2×10^{-3}	5.6×10^{-5}	+0.075	-1.1×10^{3}
Methylated	5.6×10^{-4}	5.0×10^{-5}	−0.10	2.8×10^{3}

teraction between the liquid and the wall:[18]

$$m(z) \approx m(z=0)\exp(-z/\xi) .$$

This gives an estimate for M_0 in terms of M_1:

$$M_0 \approx M_1/\xi . \quad (3)$$

ξ itself can be found from the relation $\xi = 0.3t^{-0.63}$, where the amplitude (in nm) and exponent are taken from observations of similar binary liquid mixtures.[19] Equations (2) and (3) give a quadratic equation for M_1 in terms of ΔR. ΔR values from Fig. 3 are given in Table I for $\Delta T = 5$ m°C. The consequent M_1 values are also listed. The contribution of the M_0^2 term in Eq. (2) is at least a factor of 3 smaller than that of the M_1 term for both samples at $\Delta T = 5$ m°C.

From Table I we see that while the size of M_1 and hence the strength of critical adsorption is of the same order of magnitude for the two substrates, the sign of M_1 switches from positive for the methylated surface to negative for the hydroxylated surface. This result is consistent with the sign of $m(z)$ suggested by the capillary-rise observations. A similar situation was observed by Beaglehole.[20] He found that the presence of a wetting layer at the liquid/vapor interface of a critical mixture of cyclohexane and methanol depended on the addition of water.

To summarize, observations of capillary rise and reflectivity show that the sign of the first moment of the order-parameter profile changes with the modification of surface polarity realized by replacing surface hydroxyl groups with methyl groups. Our observations agree with the rule that an increase in the polarity of the substrate causes an increase in the adsorption of the more polar component of the mixture. An interpretation of our results based on a microscopic theory for the wall-liquid interaction would be extremely valuable. One can speculate that our measurements of the effects of alteration of the first molecular layer of the substrate while leaving the bulk untouched might relate to the question of the relative importance of two types of liquid-substrate interactions: the long-range van der Waals dispersion force due to the bulk glass and the possibly short-range force due to the first molecular layer. Peliti and Leibler studied the question theoretically and concluded that long-range forces are irrelevant to critical adsorption.[21]

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APPENDIX A: LORENTZ-LORENZ RELATION

In order to relate m and $\delta\epsilon$, the molecular polarizability of the two components is averaged as in Ref. 22. We have

$$f(\epsilon) = f(\epsilon_N) + \phi[f(\epsilon_C) - f(\epsilon_N)] , \quad (A1)$$

where ϵ_N, ϵ_C, and ϵ are the optical dielectric constants of pure nitromethane, pure carbon disulfide, and the mixture, respectively. ϕ is the local volume fraction of carbon disulfide.

The function $f(x)$ is given by

$$f(x) = (x-1)/(x+2) .$$

From Ref. 23, we estimate that

$$f(\epsilon_C) = 0.3561 \quad \text{and} \quad f(\epsilon_N) = 0.2317 .$$

As discussed in the text, we are interested in deviations ($\delta\epsilon$) of the dielectric constant from the bulk value, as a function of the order parameter (m, see our comment in Ref. 1). To lowest order in m, Eq. (A1) gives the desired relation

$$\delta\epsilon = cm ,$$

where

$$c = \frac{(\epsilon+2)^2}{3}[f(\epsilon_C) - f(\epsilon_N)] .$$

APPENDIX B: OPTICAL THEORY

In Ref. 16 the reflectivity of an inhomogeneous dielectric with spatial variation in only the z direction is found. The system is uniform with $\epsilon = \epsilon_1$ for $z < 0$. For $z > 0$, the optical dielectric constant is a function of z, namely $\epsilon = \delta\epsilon(z) + \epsilon_2$, where $\epsilon \to \epsilon_2$, a constant, as $z \to \infty$. With light incident from $z = -\infty$, the reflected field is found to first order in $\delta\epsilon$. The Green's-function approach we used is similar to that of Charmet and de Gennes.[17] The amplitudes of the incident and reflected plane waves are related by the complex proportionality constant $\tilde{\rho}$:

$$\vec{E}_{\text{ref}} = \tilde{\rho}\vec{E}_{\text{inc}} .$$

The reflectivity is given by

$$R = |\tilde{\rho}|^2 .$$

As stated in the text, the quantity of interest is the half-space Fourier transform of $\delta\epsilon(z)$,

$$\widetilde{\delta\epsilon}(k) = \int_0^\infty e^{ikz}\delta\epsilon(z)dz .$$

The relationship between $\widetilde{\delta\epsilon}(k)$ and $\tilde{\rho}$ is

$$\tilde{\rho} = r + (2\pi/\lambda_0)^2 si\widetilde{\delta\epsilon}(k) .$$

The quantities r, s, λ_0, and k are independent of $\widetilde{\delta\epsilon}(k)$ and defined as follows for p polarization:

$$r = \frac{\epsilon_2 k_1 - \epsilon_1 k_2}{\epsilon_2 k_1 + \epsilon_1 k_2}$$

and

$$s = \frac{2\epsilon_1\epsilon_2 k_1[1-2\cos^2(\theta_2)]}{(\epsilon_2 k_1+\epsilon_1 k_2)^2} ,$$

where

$$\cos(\theta_2) = \left[1 - \frac{\epsilon_1}{\epsilon_2}\sin^2(\theta_1)\right]^{1/2} ,$$

$$k_1 = \epsilon_1^{1/2}(2\pi/\lambda_0)\cos(\theta_1), \quad k_2 = \epsilon_2^{1/2}(2\pi/\lambda_0)\cos(\theta_2) .$$

θ_1 is the angle of incidence measured from normal, λ_0 is the wavelength of the light in vacuum, and finally, $k = 2k_2$.

We can use these results to find d and e in the small-k expansion [Eq. (2)] for $\Delta R = R - R_b = R - r^2$. They are given as follows:

$$d = [(2\pi/\lambda_0)^2 sc]^2$$

and

$$e = 2(2\pi/\lambda_0)^2 rskc ,$$

where c is defined in Appendix A.

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