Control of a wetting transition by substrate surface chemistry: The interplay of long- and short-range forces

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Using a capillary rise technique, we have explored the wetting of borosilicate glass surfaces by a polar + nonpolar liquid mixture of nitromethane + carbon disulfide for a series of surface preparations in which we replace polar hydroxyl groups with nonpolar methyl groups. Besides finding a Cahn transition of incomplete to complete wetting we have discovered circumstances under which this transition is *suppressed*, at least to within 1.0 K of the critical mixing point. We offer the following interpretation for this last result: a long-range substrate-liquid interaction which is unfavorable to wetting by the carbon disulfide–rich phase.

I. INTRODUCTION

In 1977, Cahn predicted the appearance of wetting transitions at the boundary of a two-phase system in coexistence.[1,2] While strictly speaking, the Cahn transition from incomplete to complete wetting is not necessarily a critical phenomenon, it was expected to occur as the bulk system approached its critical point. Cahn's prediction, which was derived from a mean-field theory based on short-range substrate liquid interactions, was confirmed by the discovery of such transitions with temperature as the control parameter in binary-liquid mixtures at a liquid-vapor interface[3] and a liquid-solid interface.[4] The reduced temperatures of these transitions were $t_w = (T_w - T_c)/T_c = -0.014$ and -0.049, respectively, where T_w is the wetting transition temperature and T_c is the critical temperature (in K).[5]

Recently, theoretical work on wetting has focused on the role of long-range substrate-liquid interactions.[6-10] Even in mean-field theory, the problem is analytically complicated, being analogous to the effect of a time-dependent force on the classical motion of a particle in a potential.[11] It has been shown that long-range forces (LRF's) can have drastic effects on wetting behavior, such as the alternation of the Cahn transition from second to first order.[7] Most importantly for the present discussion, de Gennes first argued that a LRF unfavorable to wetting shifts the wetting transition to the critical point.[6]

In this report, we present capillary rise wetting observations in which temperature and substrate surface composition are the control parameters. Our observations confirm the earlier discoveries of Cahn transitions and present evidence for the suppression of this transition by a long-range substrate-liquid force. Our knowledge of this force for the particular system under discussion is reviewed.

II. OBSERVATIONS

We use a capillary rise technique to measure the strength of the interfacial forces against gravity. The rise (d) of the liquid-liquid interface inside a capillary tube relative to the interface in the bulk gives an indirect mea-

surement of the macroscopic contact angle, θ, between the substrate and the interface. The dihedral angle θ is defined as measured through the lower phase.[12] Complete wetting by the lower (upper) phase is indicated by $\theta = 0(\pi)$. Intermediate values of θ correspond to incomplete wetting. When the magnitude of d is much larger than the inner capillary radius, the relationship between d and θ is particularly simple, given by[13]

$$d = 2\sigma \cos(\theta)/\Delta\rho g r , \qquad (1)$$

where $\Delta\rho$ is the mass density difference between the two coexisting phases, σ is the liquid-liquid surface tension, g is the gravitational acceleration, and r is the capillary radius. One observes that in the case of complete wetting by either phase the absolute magnitude of d is maximal.

The binary-liquid mixture studied was carbon disulfide (a nonpolar molecule) + nitromethane (a polar molecule) at its critical composition (0.60 volume fraction carbon disulfide[14]). Throughout the temperature range studied in this work, the nitromethane-rich phase was the lighter of the two phases, and hence was the top liquid phase. Borosilicate glass capillary tubes prepared with polar hydroxyl groups on their surfaces were used as reference systems. (See the Appendix for sample preparation details.) The three types of hydroxylated specimens (designated as H-1, H-2, and H-3 in the Appendix) gave essentially the same result for $d(T)$.[15]

In reflectivity studies[16] the binary liquid discussed here was observed to make the transition to complete wetting[17] by the nitromethane-rich phase against hydroxylated glass surfaces as the bulk liquid approached coexistence. Thus, we expect that $\cos(\theta) = -1$ for these reference systems. This assumption is consistent with the measurement of $d(T)$ for the hydroxylated surfaces, as will now be shown. For a completely wet system Eq. (1) predicts $|d| \sim t^{\mu - \beta}$ since $\sigma \sim t^\mu$ and $\Delta\rho \sim t^\beta$ where $\mu \approx 1.26$ (Ref. 18) and $\beta \approx 0.33$.[19] Thus we expect $|d| \sim t^{0.93}$. For the purpose of fitting the power law, a correction to d good to third order in r/d was applied.[20] It accounts for the departure of the meniscus from a spherical shape [required for Eq. (1)] when the capillary rise is comparable to the tube radius. We find an exponent of 0.95 ± 0.01 (statistical error

only) using a fit value for T_c equal to $63.47 \pm 0.04\,°C$ over the fitting region $50 \leq T \leq 62\,°C$. This is consistent with the expected exponent and the measured T_c (using a visual method[21]) for the particular sample employed, $63.50 \pm 0.02\,°C$. The fit curve is the lower curve shown in Fig. 1. The inverse of the same curve, which corresponds to complete wetting by the carbon disulfide–rich phase, is shown as the upper curve.

The chemically altered substrates in our experiment were prepared in the same manner as the hydroxylated controls, but with the additional step of chemical modification of the surface. The Appendix gives the details of these sample preparation procedures. In all cases, they involved a silylated reagent, either dimethyldichlorosilane (DMDCS) or trimethylchlorosilane (TMCS). These compounds adsorb to silica, replacing or covering native polar hydroxyl groups with nonpolar methyl groups.[22–24] The degree of methylation was not characterized independently in this work.

The capillary rise of silylated tubes was measured along with that of the control tubes in the sample cell shown in Fig. 2. This comparison method minimizes the ambiguity in the capillary rise determination due to the curvature of the bulk meniscus. We used as our operational definition of the bulk meniscus height the height of the central, horizontal region of the bulk meniscus. Similarly, the heights of the centers of the menisci inside the capillary tubes were used to define the heights of the capillary menisci. We measured heights visually using a cathetometer (a telescope mounted on a vertical translation stage). On
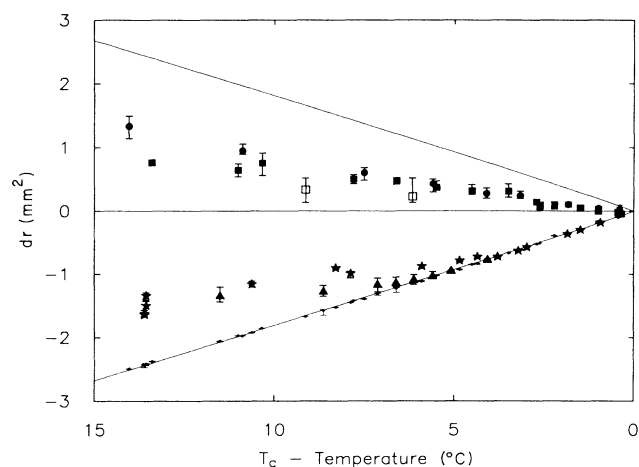

FIG. 1. The product of capillary rise and capillary radius (equal to dr) vs temperature for hydroxylated and silylated glass substrates. The temperature is relative to the critical temperature. Positive (negative) ordinate corresponds to wetting by the carbon disulfide–rich (nitromethane) phase. See Fig. 2 for the geometry of the experiment. Small circles indicate hydroxylated (control) substrates. They are preparations H-1, H-2, and H-3 as described in the Appendix. The almost-linear curve in the lower half of the plot is from a fit to hydroxylated data (see text for details). It indicates complete wetting of the substrate by the nitromethane-rich phase. The corresponding curve for complete wetting by the carbon disulfide-rich phase appears in the upper half of the plot. It is the inverse of the first curve. Large symbols indicate wetting on silylated substrates as follows. Triangles and stars (two different samples): preparation A-DMDCS (see Appendix for details of sample preparation); squares: preparation B-DMDCS (solid squares are data from the initial 18 days of the life of the sample with measurements taken at successively higher temperatures, open squares are measurements during the subsequent 5 days, indicating an aging effect); circles: preparation B-TMCS. "Error" bars indicate the maximum and minimum capillary rise measured for several different vertical heights of the bulk meniscus along each tube. The symbols are plotted at the average value for each tube. The tube radius was 134 μm in all measurements, except for the star measurements which used a 188-μm radius tube.
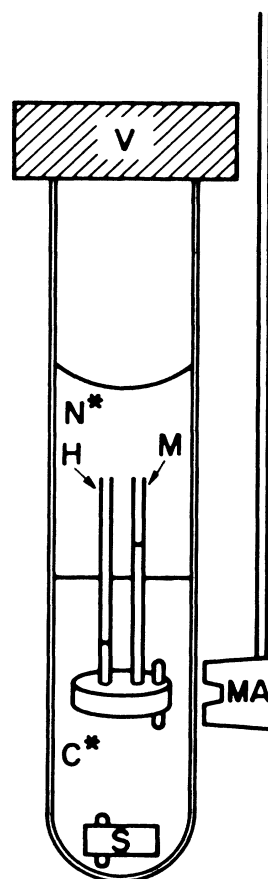

FIG. 2. Sample cell schematic (side view). Up is toward the top of the page. Overall height is approximately 22 cm. H and M are the hydroxylated and methylated (i.e., silylated) capillary tubes, respectively. N^* and C^* are the nitromethane-rich and carbon disulfide-rich phases, respectively. The space above N^* is filled by vapor. The glass sample cell is closed off with a Teflon vacuum valve (V) (Ace Glass 8193). The magnet MA holds the tubes in position through a Teflon support structure which includes an encapsulated magnet. On occassion, an auxiliary stirrer (S) was used.

most runs, a colorless, precipitate was observed near the bulk meniscus, but outside the capillary tubes. We are uncertain as to its origin. We suspect that it was polymerized silane although a control preparation in which silylated tubes were sealed in an all-glass ampule failed to produce the precipitate.

To ensure thermal equilibrium, the sample was mixed thoroughly after each temperature step, and the tempeature was held steady (to within 15 mK) in a water-bath thermostat for at least 2 h before any measurements were made. The capillaries were then raised and lowered magnetically several times to ensure that the composition inside them was the same as outside. Measurements of the capillary rise were made for at least six different vertical translations of the tubes. At all times a receding meniscus was produced in the tube under study before it was allowed to reach equilibrium. This approach is as recommended by Zisman.[25] The observed capillary rise as a function of temperature for silylated and hydroxylated tubes is shown in Fig. 1. The lower solid line discussed earlier indicates complete wetting by the nitromethane-rich (N^*) phase $[\cos(\theta) = -1]$. The upper solid line indicates complete wetting by carbon disulfide–rich (C^*) phase $[\cos(\theta) = +1]$. Any results between these extremes indicates incomplete wetting. Note that $d > (<)0$ indicates wetting by the $C^* (N^*)$ phase.

The silylated substrates show noticeable scatter when incompletely wet. This variation depended systematically on the position of meniscus in the capillary tube, suggesting an uneven degree of silylation. Completely wet specimens show negligible scatter. The average results are plotted in Fig. 1, with the "error" bars indicating the maximum and minimum readings.

The capillary rise of incompletely wet tubes was also found to change monotonically with time. For example, over a period of 3 days, the difference in d between a silylated and a hydroxlyated tube (expressed as a fraction of d for the hydroxylated tube) changed from 45 to 38 %. This aging phenomenon appeared to deaccelerate, since over another 56 days, the fractional difference was 33%. And, over another 12 days, the fractional difference changed by less than 1%. These observations were for a A-DMDCS sample (see the Appendix for preparation details) at $T_c - T = 14$ °C. Through such tests, we were able to establish that while sample aging was noticeable for incompletely wet specimens, it did not alter the essentials of the observations, which we will now summarize.

The silylation preparations detailed in the Appendix produced two classes of reproducible wetting behavior, as illustrated in Fig. 1. Type-A preparations exhibited a Cahn wetting transition in which incomplete wetting by N^* changed to complete wetting (as on the control) with increasing temperatuare. These observations confirm the earlier observations of a wetting transition in a binary-liquid mixture (2,6-lutidine + water) on a solid substrate (glass).[4] In our three type-A preparations, we found wetting transitions at reduced temperatures of $t_w = -0.017$, -0.010, and -0.074. The last result was for a sample which was at the lower end of the range of accessible capillary rises for the particular length capillary tube employed—at the lowest temperature studied (greatest

capillary depression) some positions of the capillary tube indicated incomplete wetting and others complete wetting. At higher temperatures, this particular system was completely wet for all positions of the tube. Based on our experience with the other two type-A specimens which we were able to observe as everywhere incompletely wet at sufficiently low temperatures, we can confidently assign a transition temperature to this last specimen.

The wetting contact angle for a silylated tube can be deduced by combining the silylated tube capillary rise (d_s) and the control (hydroxylated) tube capillary rise (d_h) as follows [using Eq. (1)]:

$$\cos(\theta) = d_s / d_h \qquad (2)$$

These results for type-A preparations are shown in Fig. 3. The Cahn transition between incomplete and complete wetting by N^* is clearly seen.

In the second class of wetting behavior, type-B preparations maintained incomplete wetting by C^*, as shown in the capillary rise and especially the contact angle plots, Figs. 1 and 3, respectively. This condition persisted at least as close as 1.0 K below T_c $(t < -0.003)$. This is in contrast with the range of t_w observed for our type-A surfaces and in the experimental work cited earlier: $t_w \leq -0.010$.

Recently, the phenomenon of sustained incomplete wetting has been discovered in similar systems: the liquid-vapor interface of cyclohexane + methanol + water (optional)[26] and the interface of borosilicate glass with ludtidine + water + KCl.[27] In these two systems the concentration of the third component played the same role as substrate silylation in our work: it was used to control the wetting transition.
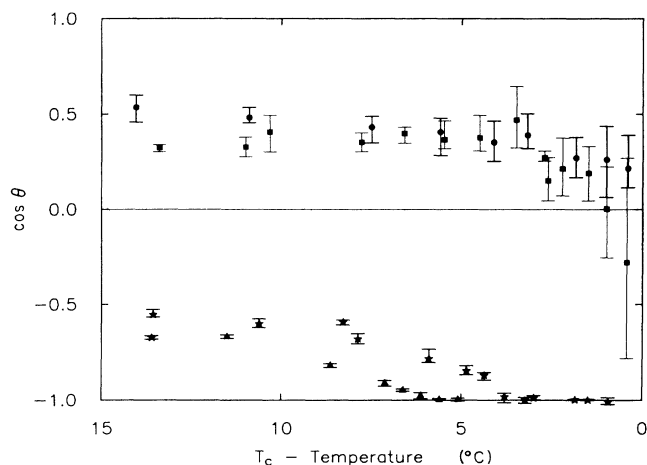

FIG. 3. Cosine of the contact angle (θ) vs temperature for silylated substrates. The temperature is relative to the critical temperature. Symbol definitions are the same as in Fig. 1. A preparations (triangles and stars) show wetting transitions while B preparations (circles and squares) remain incompletely wet to within 1 K of the critical point.

III. INTERPRETATION

Our results can be interpreted as an interplay between short-range forces responsible for selective chemisorption via hydrogen bonding and a long-range force of uncertain origin. We start this discussion by reviewing our knowledge of these forces and their consequences for wetting.

Short-range forces can be modeled in Landau theory[28] by a contact contribution to the free energy of the liquid-substrate system: $-h_1 m(z=0)$. Here h_1 is the strength of the short-range interaction; $m(z)$ is the order parameter of the system (the local volume fraction of carbon disulfide minus the critical value) averaged in the directions parallel to the flat substrate surface; and z is the perpendicular distance from the substrate. $z < 0$ corresponds to the liquid side. For the polar (nitromethane) + nonpolar (carbon disulfide) liquid mixture under study a plausible origin of this force is hydrogen bonding[29-31] between nitro groups on nitromethane and the silanol (hydroxyl) groups on the borosilicate glass substrate. This reversible chemisorption mechanism is considerably weaker between carbon disulfide and the substrate.[31] Therefore a hydroxlyated glass substrate preferentially adsorbs nitromethane over carbon disulfide. Adsorption measurements of analogous mixtures have established this phenomenon.[32] Direct evidence for preferential adsorption of nitromethane over carbon disulfide comes from critical adsorption studies.[21,33] In such experiments, selective adsorption is amplified by the approach of the liquid to its critical mixing point.

If we begin with a fully hydroxylated surface, and decrease the polarity of the surface through silylation, h_1 will increase (less attraction for nitromethane) as will the equilibrium value of m at $z=0$ [in the original hydroxylated system $m(0)$ is negative]. The final stage of this process was seen in a second critical adsorption measurement[34] in which a DMDCS reaction similar to the type-B preparation discussed here revealed preferential adsorption of carbon disulfide over nitromethane on silylated glass. In addition this same treatment was found to reverse the sign of capillary rise (at $\approx 25\,°C$) from capillary depression (wetting by N^*) on a hydroxylated surface to capillary rise (wetting by C^*) on a silylated surface. In keeping with these observations, we assert that h_1 is a monotonically increasing function of the ratio of methyl to hydroxyl groups on the glass substrate surface. Furthermore, since h_1 determines the value of the order parameter at the surface, we also assert that the phase that wets is selected in the same manner as the sign of critical adsorption. That is $h_1 > (<)0$ implies C^* (N^*) wetting and there is capillary rise (depression).

Besides short-range forces, long-range forces (LRF's) exist between the substrate and the liquid. These forces can be modeled in Landau theory[8,9] by a power-law contribution to the free-energy density: $-h_{LR}(z)m(z)$ where

$$h_{LR}(z) = A/z^\omega . \tag{3}$$

A is a constant to be determined. We assume that the system has two coexisting phases, labeled α and β, and a sharp interface between them. We always define α to be

the wetting phase. l is the thickness of the wetting phase. From Eq. (3), we expect that the contribution of the long-range substrate-liquid force to the interfacial free-energy potential of the system is (neglecting the short distance contribution which is l independent):

$$V_{LR}(l) = \int_0^\infty -h_{LR}(z)m(z)dz$$

$$\approx -A(m_\beta - m_\alpha)/[(\omega-1)l^{\omega-1}] . \tag{4}$$

While LRF's have been judged to be irrelevant to critical adsorption,[35] we shall see that they have profound consequences for wetting. In reflectivity studies of nitromethane + carbon disulfide on hydroxylated borosilicate substrates, the approach to complete wetting was observed as a single-phase liquid was brought to two-phase coexistence by varying temperature.[16] The bulk liquid was rich in carbon disulfide, the nonwetting material. It was found that $l = (2.7\pm0.3)[(T-T^*)/T^*]^{-0.258\pm0.020}$ nm for $29.0 < l < 63.0$ nm. Here, T^* is the temperature at which the fixed composition sample reached coexistence (for the particular experiment under discussion, $T_c - T^* = 1.2$ K). To use this result to gain information about the LRF in this system, we consider the free energy of the system to be given by V_{LR} plus the following term which expresses the cost in free energy of the system not being at coexistence: $(m_\beta - m_\alpha)Hl$. Note that in this situation $\alpha = N^*$ and $\beta = C^*$. H is a bulk field which is the thermodynamic distance from coexistence. For the system under study, we can use ideal mixture theory to find H [see Appendix A in Ref. 16]: $H = B(T - T^*)$. B is a constant which must be positive since the bulk liquid (β) is carbon disulfide-rich and an increase in l will increase this part of the free energy. Minimizing the free energy of the system yields the equilibrium wetting layer thickness as a function of temperature: $l = (-A/B)^{1/\omega}(T-T^*)^{-1/\omega}$. Comparing with the observed result, we have $\omega = 3.9\pm0.3$ for $29 < l < 63$ nm. We see that $A < 0$ in Eq. (3) in order to have wetting by nitromethane-rich material, as observed.

What is the origin of the LRF between the substrate and the liquid in this system which produces this wetting effect? By reviewing possible mechanisms we will show that an adequate answer to this question is lacking at this time.

The first type of LRF to be considered is an induced force between materials due to spontaneous electromagnetic fluctuations. It goes by the name of the dispersion or van der Waals force.[36] The dispersion force is a function of the absorptive part of the frequency-dependent dielectric permittivities of the three materials involved: the borosilicate glass substrate and the two liquid phases. We will first assume that the substrate is homogeneous up to the liquid-glass boundary. For this reason, we call the resultant dispersion force a "bulk" dispersion force.[37] If we define λ_c to be the characteristic wavelength for electromagnetic absorption then $\omega = 3$ for $z \ll \lambda_c$, the nonretarded case and $\omega = 4$ for $z \gg \lambda_c$, the retarded case. In the extreme retarded limit $z \to \infty$, h_{LR} is a simple function of the dc electric constants of the three media.[38] Assuming that phase-separated liquids correspond to pure nitromethane and carbon disulfide,[39] we find that the bulk

dispersion force in this system is unfavorable to wetting by nitromethane and therefore cannot explain the reflectivity observations,[40] a fact which was orginally pointed out by Kayser.[41] Recently, Kayser[42] has discovered that this result is true for a wide range of z and temperature and for the mixtures used in this work. Thus the actual LRF is not a bulk dispersion force. As pointed out by Lipowsky,[43] another type of dispersion force to be considered regards the substrate as inhomogeneous (possibly due to acid etching in preparation[44] and/or surface roughness). In this theory a reduced effective dielectric constant of the surface might give rise to an attractive dispersion force.

Kayser has considered a completely different explanation for the long-range force which promotes wetting of a hydroxylated glass surface by the N^* phase over the C^* phase. He proposed a LRF mechanism based on the formation of an unscreened cloud of cations which comes from the glass surface and is concentrated in the N^* phase.[41] In this ion theory the N^*-C^* interface is repelled from the glass substrate because of the electrostatic repulsion of cations dissolved in the N^* phase. Thus N^* wetting of glass is produced. Kayser concluded that this mechanism could explain the observed thickness of N^* wetting layers on borosilicate glass in gently stirred mixtures of nitromethane + carbon disulfide at coexistence.[16] However, in the limits of distance over which it obeys a power law, the unscreened ion force has the exponent $\omega \leq 2$, in contradiction with the measured value. Thus we find that the actual LRF is also not an unscreened ion force. An alternative approach would be to include the effects of dissolved anionic impurities. This might modify the ionic force through screening in such a way as to give agreement with the observed value of ω.

The LRF's discussed depend on surface chemistry to varying degrees. The bulk dispersion force arises from the electromagnetic properties of the substrate and the fluids forming the wetting layer, integrated over large distances compared to molecular sizes. Hence, bulk dispersion forces are independent of surface chemistry, and should provide the same long range force for the different surface preparations discussed here. On the other hand, the ion force mechanism requires an ionizable surface. The replacement of hydroxyl by methyl groups at the surface should tend to reduce the strength of an ion force. Surface dispersion forces may also depend on surface chemistry.

We can now summarize our knowledge of the substrate-liquid forces in the system under study. A plausible explanation for short-range forces is hydrogen bonding. It controls the order parameter at the surface and hence selects the wetting phase. In addition, it is apparent from the study of the equilibrium growth of wetting layers from a single-phase bulk as a function of temperature that there is also a long-range force between substrate and liquid which has a power-law exponent of $\omega = 3.9 \pm 0.3$ for layer thicknesses between 29 and 63 nm. We find that this long-range force is due to neither a bulk (homogeneous substrate) dispersion force nor an unscreened ion force. Candidate alternative explanations are a surface dispersion force and a screened ion force. Of

course, the first two types of forces must be considered in a complete description. At this point the dominant long range force mechanism(s) is not known.

In order to interpret the experiments presented here, where we have altered surface substrate chemistry, we speculate that since the short- and long-range forces arise from different mechanisms, they differ in a drastic way in their dependence on surface chemistry. Specifically, we assert that as we vary the surface methyl-hydroxyl ratio through silylation, while the short-range field (whose strength is denoted by h_1) changes sign (as demonstrated in the critical adsorption experiments) the LRF maintains the same sign. As argued earlier we might expect the long range force to depend on surface preparation. However, there is no reason to expect a priori that as h_1 passes through zero that the LRF should also change sign. Rather, we assert that the sign of h_{LR} remains the same [$A < 0$ in Eq. (3)] as was established for the fully hydroxylated substrate.

With this assumption we can understand the behavior of the LRF when the roles of the coexisting phases are reversed, i.e., the wetting phase becomes the phase excluded from the substrate (the spectator phase) and vice versa. Recall that since $A < 0$, when $\alpha = N^*$ and $\beta = C^*$, from Eq. (4) we have $V_{LR} > 0$. If we consider the reversed situation, i.e., $\alpha = C^*$ and $\beta = N^*$, then we see that the LRF must be unfavorable to wetting (i.e., $V_{LR} < 0$). Simply stated, with the assumption that the sign of the long-range force in Eq. (3) is not changed as the sign of the short-range force reverses due to silylation, we find that the LRF always favors N^* wetting, and opposes C^* wetting.

We can now consider the interplay of short- and long-range forces in the wetting observations presented here. By our earlier arguments, the short range force selects the wetting phase and should therefore be regarded as always promoting wetting. De Gennes[6] and Nightingale and Indekeu[9] argued that if the LRF also promotes wetting, i.e., $V_{LR} > 0$, then the Cahn transition occurs before the critical point is reached. This fits the observations for our type-A preparations. Since h_1 is sufficiently negative (i.e., there are enough surface hydroxyl groups) the system selects the N^* phase as the wetting phase, and there is capillary depression. V_{LR} is positive since the wetting phase ($=\alpha$) is N^* in Eq. (4). Recall that the fully hydroxylated substrates (type H) were completely wet by N^* over the observed temperature range. The chemical substitution in preparation A raises the value of h_1 closer to zero, shifting T_w toward T_c, until the Cahn transition falls in the temperature range of this experiment. As pointed out by de Gennes,[6] the addition of the long-range substrate field favorable to wetting ($V_{LR} > 0$) supports the wetting transition, possibly at a new temperature. As shown in Fig. 1 of Ref. 6, the minimum in the free energy of the system as a function of the distance of the liquid-liquid interface from the substrate is pushed toward infinite distance (complete wetting, thick wetting layer) by such a long-range force. Thus the Cahn transition is maintained in type-A systems.

Turning to B preparations, we have the C^* phase wetting ($h_1 > 0$, capillary rise). This is confirmed by our critical adsorption experiments which showed that for a

preparation similar to DMDCS preparation B $h_1 > 0$.[34] For these systems, the Cahn transition is suppressed: the system is incompletely wet over the observed temperature range. This can be understood as the effect of a long range force which does not favor the wetting phase (i.e., $V_{LR} < 0$). Repeating our earlier argument, since $A < 0$, Eq. (4) reveals why V_{LR} is negative: α has switched from $\alpha = N^*$ in the heavily hydroxylated cases (types H and A) to the present case (type B) where $\alpha = C^*$. As pointed out by de Gennes (see Fig. 2, Ref. 6) and Nightingale and Indekeu[9] an LRF unfavorable to wetting will maintain a minimum in the free energy at a finite wetting layer thickness for all temperatures below the critical region (the bulk-correlation length being much smaller than the wetting layer thickness). Thus incomplete wetting is sustained on type-B samples, at least as close as 1.0 K to the critical temperature.

Finally, Nightingale and Indekeu[9] realized that in order to sustain incomplete wetting up to the critical point in type-B samples, the long-range force must not overwhelm the short-range force and establish wetting by the N^* phase. They found that this condition could be expressed as follows $\omega > y_H (=d - \beta/v)$. Here d is the spatial dimensionality and v is the correlation-length exponent. For the three-dimensional Ising system under study,[19] this amounts to $\omega > 2.5$. Assuming that the exponent of the LRF is unchanged by silylation we see that this requirement is satisfied by the ω value deduced from our reflectivity studies for the approach to complete wetting,[16] $\omega = 3.9 \pm 0.3$.

IV. CONCLUSION

In summary, we have controlled wetting transitions through altered surface chemistry. The Cahn transition has been promoted or suppressed. These observations can be interpreted as the interplay of short- and long-range substrate-liquid forces. When the two forces cooperate, complete wetting is promoted and a Cahn transition may be observed. When the two forces are opposed, incomplete wetting is maintained, and there is no Cahn transition below the critical point. The crucial assumption in our interpretation is that as the short-range force is reversed in sign due to changes in surface chemistry the sign of the long-range force remains the same. Since the mechanisms for the short- and long-range forces are different, this assumption is plausible but needs to be tested. The observed behavior is in agreement with the long-range substrate-liquid force exponent observed in wetting layer thickness measurements of the approach to complete wetting on an unaltered substrate. For example, the long-range force (when opposed to the short-range force) has a sufficiently large exponent to maintain the observed incomplete wetting up to the critical point. A determination of the long-range force operating in this system is greatly needed. Besides theoretical work, complementary experiments which are sensitive to the liquid-substrate potential are warranted. It would also be valuable to demonstrate the actual dependence of this interaction on surface preparation. Finally, quantitative characterization of the surface preparations used here is needed.

APPENDIX: SAMPLE PREPARATION

We discuss here the chemical techniques used to prepare specimens. There were three types of samples: hydroxylated, silylated A, silylated B, denoted by H, A, and B respectively. The groupings are according to functionality. As presented in the text, H type was always completely wet by N^*, A samples showed a wetting transition of incomplete to complete wetting by N^*, and B samples were always incompletely wet by C^*. As a further specification, we note the silylating reagent (TMCS or DMDCS silane compounds). Thus, the specification B-TMCS indicates type B, silylated with TMCS. The procedures for silylation always began with a hydroxylated specimen. The substrates were borosilicate glass capillaries[45] with inner radii of 134 ± 2 or 188 ± 2 μm. The preparation procedures are as follows. Unless specified, the temperature is room temperature.

1. Hydroxylation

(a) Preparation H-1 (Refs. 46 and 47)

Subjected to ultrasonic waves for ≥ 3 min each time in acetone, then methanol (at least twice). Rinsed, sonicated in distilled water at least three times. Dried in a mechanically pumped vacuum oven at 100 °C for 1 h. Cooled, exposed to ethylenediamine tetra-acetic acid (EDTA) solution[48] in a covered container for ≥ 10 h. Rinsed in distilled water several times, then subjected to sonic waves in distilled water. Dried in a vacuum oven at 100 °C for 1.5 h. Cooled, exposed to concentrated nitric acid in a covered container for ≥ 36 h. Rinsed eight times in distilled water. Dried in air or a vacuum oven. Stored in a dry atmosphere.

(b) Preparation H-2 (Ref. 49)

Subjected to sonic waves and rinsed in acetone, methanol, and distilled water as in H-1. Dried at 80 °C in an air oven. Exposed to chromic-sulfuric acid cleaning solution[50] at 80 °C for 15 min. Rinsed in several changes of distilled water. Boiled several times in distilled water.

Dried with an aeroduster[51] and stored in a dry atmosphere.

(c) Preparation H-3 (Ref. 46)

Subjected to sonic waves and rinsed in acetone and methanol as in H-1. Exposed to EDTA solution, subjected to sonic waves for 30 min. Exposed to EDTA for an additional 12 h. Rinsed in several changes of deionized water, dried, exposed to 70% nitric acid for 48 h, then subjected to sonic waves intermittently during this period for 2.5 h. Rinsed in deionized water several times. Subjected to sonic waves 30 min in deionized water with four changes. Dried in a vacuum oven.

2. Silylation

(a) Preparation A-DMDCS (Ref. 24)

Hydroxylated according to procedure H-1. Vacuum baked at 200 °C for 4 h. Cooled, transferred into DMDCS liquid[52] under argon atmosphere. Warmed to 35–80 °C for ≤ 4.5 h. Cooled, exposed to DMDCS under argon atmosphere for an additional 1–6 h. Transferred into clean glassware, subjected to sonic waves in methanol. Continued to expose to methanol for ≥ 17 h. Replaced methanol with hexane. Exposed for 2 h, while subjected to sonic waves intermittently for 30 min total. Removed hexane. Dried sample with aeroduster. Baked in vacuum oven at 80 °C.

(b) Preparation B-DMDCS (Ref. 53)

Hydroxylated according to Preparation H-2. Baked as in A-DMDCS. Exposed to DMDCS liquid while agitating for a total of 1.5 h. Continued to expose for an additional 24 h. Transferred into anhydrous methanol, agitated for one hour. Continued to expose to methanol for 20 h. Dried with an aeroduster, stored in dry atmosphere.

(c) Preparation B-TMCS (Refs. 22 and 54)

Hydroxylated according to H-3 above. Exposed to TMCS liquid[55] at 48 °C. The vapor was vented to the atmosphere, with a condenser recovering some of the silane. The exposure was maintained for 59 h. Sometime during the last four hours of exposure, about 0.8 ml of water was unintentionally added to the silane liquid (6 ml volume). Agitated in two changes of n-hexane, a drying agent, for 15 min each. Dried in a vacuum oven at 100 °C for 10 h.

3. Comments

Since bulk DMDCS polymerizes in the presence of water, we baked the tubes to remove physisorbed water and minimized exposure to atmospheric water while silylating with DMDCS. TMCS does not polymerize in this manner.[24]

4. Sample cell preparation

The glass sample cell was initially cleaned using chromic-sulfuric acid glass cleaning solution. In subsequent work, it was rinsed and subjected to sonic waves in acetone, methanol and distilled water. The Teflon valve used in the cell was cleaned similarly, omitting the acid-cleaning step. The capillary tube support structure inside the sample cell was made of Teflon and a Teflon-covered magnet. It was cleaned in soapy water, acetone, methanol, and distilled water. The sample cell was filled with 99 + % pure carbon disulfide and nitromethane[56] at the critical concentration. The samples were measured volumetrically with a precision of 0.03 ml to give an overall sample volume of 7 ml (typical). The samples were always in liquid-vapor coexistence. In some samples, molecular sieves[57] were used since they were found to stabilize T_c in other experiments, possibly by adsorbing water impurities. However, it was found that on one occassion, the sieves produced a colored sample, possibly due to the release of chromium ions.[58] This sample was abandoned, and the use of the sieves was discontinued.

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[1]John W. Cahn, J. Chem. Phys. 66, 3667 (1977).

[2]For recent excellent reviews of wetting theory and experiment, see, E. H. Hauge, in Fundamental Problems in Statistical Mechanics VI, edited by E. G. D. Cohen (North-Holland, Amsterdam, 1984), p. 65; D. E. Sullivan and M. M. Telo da Gama, in Fluid Interfacial Phenomena, edited by C. A. Croxton (Wiley, London, 1986), p. 45.

[3]J. W. Schmidt and M. R. Moldover, J. Chem. Phys. 79, 379 (1983).

[4]D. W. Pohl and W. I. Goldburg, Phys. Rev. Lett. 48, 1111 (1982).

[5]T and t denote temperature and reduced temperature, respectively.

[6]Pierre-Gilles de Gennes, C. R. Acad. Sci. (Paris), Ser. II 297, 9 (1983).

[7]P. Tarazona, M. M. Telo da Gama, and R. Evans, Mol. Phys. 49, 283 (1983).

[8]V. Privman, J. Chem. Phys. 81, 2463 (1984).

[9]M. P. Nightingale and J. O. Indekeu, Phys. Rev. B 32, 3364 (1985).

[10]C. Ebner and W. F. Saam, Phys. Rev. B 35, 1822 (1987).

[11]R. Pandit (private communication).

[12]See Fig. 1 of Ref. 1.

[13]J. S. Rowlinson and B. Widom, Molecular Theory of Capillarity (Clarendon, Oxford, 1982), p. 10.

[14]E. S. R. Gopal, R. Ramachandra, P. Chandra Sekhar, K. Govindarajan, and S. V. Subramanyam, Phys. Rev. Lett. 32, 284 (1974).

[15]A slight systematic difference was noticed between a preparation which used the EDTA chelating agent (as in H-1 and H-3) and a preparation in which chromic-sulfuric acid was used (H-2). However, these differences were insignificant compared to the variation between silylated and hydroxylated specimens, the focus of this report.

[16]Xiao-lun Wu, Mark Schlossman, and Carl Franck, Phys. Rev. B 33, 402 (1986).

[17]R. Lipowsky, Phys. Rev. B **32**, 1731 (1985).

[18]J. S. Rowlinson and B. Widom, *Molecular Theory of Capillarity*, Ref. 13, p. 265.

[19]A. Kumar, H. R. Krishnamurthy, and E. S. R. Gopal, Phys. Rep. **98**, 64 (1983).

[20]Lord Rayleigh, Proc. R. Soc. London, Ser. A **92**, 184 (1915).

[21]Mark Schlossman, Xiao-Lun Wu, and Carl Franck, Phys. Rev. B **31**, 1478 (1985).

[22]William J. Eakins, Ind. Eng. Chem. Proc. Des. Develop. 7, 39 (1968).

[23]B. Evans and T. E. White, in *Fundamental Aspects of Fiber Reinforced Plastic Composites*, edited by R. T. Schwartz and H. S. Schwartz (Interscience, New York, 1968), p. 177.

[24]R. E. Majors and M. J. Hopper, J. Chromatogr. Sci. **12**, 767 (1974).

[25]W. A. Zisman, in *Contact Angle, Wettability, and Adhesion*, edited by Fredrick M. Fowkes (American Chemical Society, Washington, D.C., 1964), Vol. 43, p. 8.

[26]D. Beaglehole, J. Phys. Chem. **87**, 4749 (1983).

[27]L. Sigl and W. Fenzl, Phys. Rev. Lett. **57**, 2191 (1986).

[28]Hisao Nakanishi and Michael E. Fisher, Phys. Rev. Lett. **49**, 1565 (1982).

[29]J. J. Kipling, *Adsorption from Solutions of Non-Electrolytes* (Academic, New York, 1965), p. 165.

[30]W. A. Schroeder, J. Am. Chem. Soc. **73**, 1122 (1951).

[31]Helmut Knozinger, in *The Hydrogen Bond: Recent Developments in Theory and Experiments*, edited by P. Schuster, G. Zundel, and G. Sandorfy (North-Holland, Amsterdam, 1976), Vol. 3, p. 1263.

[32]D. C. Jones and G. S. Mill, J. Chem. Soc. London **213**, (1957).

[33]Carl Franck and S. E. Schnatterly, Phys. Rev. Lett. **48**, 763 (1982).

[34]Janet A. Dixon, Mark Schlossman, Xiao-Lun Wu, and Carl Franck, Phys. Rev. B **31**, 1509 (1985).

[35]L. Peliti and S. Leibler, J. Phys. C **16**, 2635 (1983).

[36]I. E. Dzyaloshinskii, E. M. Lifshitz, and L. P. Pitaevskii, Adv. Phys. **10**, 165 (1961).

[37]This notion was pointed out to us by R. Lipowsky (private communication).

[38]Eq. (56) in J. N. Israelachvili and D. Tabor, Prog. Surf. Memb. Sci. **7**, 24 (1973).

[39]For the values of the low frequency permittivity of nitromethane, carbon disulfide, and borosilicate glass see *International Critical Tables of Numerical Data, Physics, Chemistry and Technology* (McGraw-Hill, New York, 1929), Vol. 6, pp. 83 and 76 and Vol. 2, p. 101, respectively.

[40]Bulk dispersion was incorrectly given as the interpretation in Ref. 16.

[41]R. F. Kayser, Phys. Rev. Lett. **56**, 1831 (1986).

[42]R. F. Kayser, Phys. Rev. B **34**, 3254 (1986).

[43]R. Lipowsky (private communication).

[44]Koreo Kinosita, in *Progress in Optics*, edited by E. Wolf, (North-Holland, Amsterdam, 1965), Vol. 4, p. 85.

[45]Fisher 21-164-2.

[46]D. Leckband (private communication).

[47]Gershon J. Shugar, Ronald A. Shugar, Lawrence Bauman, and Rose Shugar Bauman, *Chemical Technicians' Ready Reference Handbook* (McGraw-Hill, New York, 1981), p. 64.

[48]Ethylenediaminetetraacetic acid in an aqueous solution of sodium hydroxide giving a pH of 8.5.

[49]Fred Rosebury, *Handbook of Electron Tube and Vacuum Techniques* (Addison-Wesley, Reading, Mass., 1965), p. 5.

[50]Mallinckrodt 6622: 90–95 % sulfuric acid by weight.

[51]Miller-Stephenson MS220.

[52]Petrach Systems D5550.

[53]S. Bauer (private communication).

[54]Anil Menawat, Joseph Henry Jr., and Ranjani Siriwardane, J. Colloid. Interface Sci. **101**, 110 (1984).

[55]Petrach Systems T2951.

[56]Aldrich 15470-9 and 23073-1, respectively.

[57]Fisher M-564.

[58]J. Burlitch (private communication).