Wetting transition of a binary liquid due to suppression of electrostatic forces

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When a phase-separated mixture of carbon disulfide and nitromethane is put in contact with borosilicate glass, a thick nitromethane-rich wetting layer generally results. The long-range force responsible for this layer is believed to be electrostatic in nature and caused by ionization of hydroxyl groups on the glass surface. We have used a capillary-rise experiment to examine the effect on the state of wetting of suppressing this force through the addition of a soluble salt, tetrabutylammonium iodide. We find that for small salt concentrations ($< 0.1M$) the glass appears to remain completely wet to within at least 40 K of T_c, but that for larger concentrations ($> 0.2M$) the glass is incompletely wet for temperatures $T < (T_c - 25$ K$)$. At $T \approx (T_c - 25$ K$)$ the system undergoes a wetting transition from incomplete to complete wetting. The appearance of this wetting transition seems to result from the complete removal of the long-range electrostatic interaction.

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I. INTRODUCTION

Much of the current interest in wetting phenomena dates to 1977, when Cahn [1] predicted that two-fluid systems at coexistence might undergo surface phase transitions from incomplete to complete wetting on approach to their bulk critical points. This early work stressed the importance of short-range, contact interactions between fluid and substrate, and was soon confirmed by the experimental discovery of such wetting transitions in binary liquid mixtures at liquid-vapor [2] and liquid-solid [3] interfaces. Subsequent work showed, however, that considering short-range forces alone was not sufficient for a thorough understanding of wetting and wetting transitions; long-range intermolecular forces can also play important roles even near critical points [4]. Indeed, it is the interplay between short- and long-range forces that has accounted for much of the rich variety of behavior observed in wetting systems [5].

One system in which this is true is the binary liquid carbon disulfide and nitromethane, whose wetting properties against borosilicate glass have been studied extensively using capillary-rise [6, 7] and reflectivity [8, 9] techniques. When the glass is cleaned so as to produce a maximally hydroxylated surface, it preferentially adsorbs nitromethane; a thick nitromethane-rich wetting layer generally forms on the substrate if the liquid is at two-phase coexistence. Capillary-rise measurements [7] indicate the situation is one of complete wetting even far below ($\approx$ 40 K) the critical consolate temperature T_c. However, by chemically treating the glass so that surface hydroxyl groups are replaced by methyl groups, one can alter the wetting picture substantially—even to the point of producing complete drying by the carbon disulfide-rich phase, to cite an extreme example [10].

Durian and Franck [7] reacted glass capillary tubes with hexamethyldisilazane in such a way that the glass was completely wetted by the nitromethane-rich phase within a few degrees of T_c, but incompletely wetted at lower temperatures; the temperature location of the wet-

ting transition depended on how long the reaction had been allowed to run. The data obeyed very well scaling predictions derived by considering short-range interactions only, showing the power of Cahn's original assumption. At the same time, other parts of the data set indicated the presence of a long-range liquid-substrate interaction favorable to wetting by nitromethane, a result which had also been reached by earlier experiments [6, 8]. Such a long-range force would help to explain the very thick ($\approx$ 500 nm) nitromethane-rich wetting layers observed in reflectivity data [8].

Initially, this long-range force was thought to be a dispersion force, due to induced-dipole interactions. This was an obvious choice given that such forces are ubiquitous. However, Kayser [11] soon showed that dispersion forces could not be used to account for nitromethane wetting. In a careful numerical calculation, he demonstrated that, in this system, such forces favor wetting by carbon disulfide, not nitromethane. Instead, he suggested that the sought-after long-range force was electrostatic in nature and caused by ionization of hydroxyl groups on the glass surface. Expanding on an idea due to Langmuir [12], Kayser argued that, since nitromethane is polar while carbon disulfide is nonpolar, counterions removed from the now negatively charged surface would tend to distribute themselves in the nitromethane-rich wetting layer in accordance with the Poisson-Boltzmann equation. The concentration of ions at the liquid-liquid interface would then determine the vapor pressure of the wetting layer and would tend to push the interface away from the substrate. A wetting layer stabilized by such an electrostatic force could in principle be much thicker than one stabilized by dispersion forces.

Kayser's idea received strong confirmation in a reflectivity experiment of Ripple *et al.* [9]. In an effort to screen the electrostatic interaction, they added a small amount of a salt, tetrabutylammonium iodide, to the mixture and found that the thickness of the resulting wetting layer was indeed substantially depressed. The effect was so striking that it raised the question of whether, through

screening, one could not only reduce the layer thickness, but also change the state of wetting, moving the system from complete to incomplete wetting [13].

That question motivated the experiment described in this paper. We added various amounts of tetrabutylammonium iodide to a phase-separated mixture of nitromethane and carbon disulfide and measured the capillary rise of the nitromethane-rich phase against a hydroxylated glass substrate. Capillary rise provides an indirect measure of the contact angle the liquid-liquid interface makes with the substrate and, therefore, of the state of wetting [14]. At small salt concentrations ($< 0.1M$), the glass appeared to remain completely wet to within at least 40 K of T_c, but at higher concentrations ($> 0.2M$), it was incompletely wet for temperatures $T < (T_c - 25$ K$)$. At $T \approx (T_c - 25$ K$)$, these samples underwent a wetting transition from incomplete to complete wetting. We believe the appearance of this transition resulted from the total elimination of the long-range electrostatic force.

The remainder of this paper is organized as follows. Section II describes the sample preparation and experimental procedure. Section III presents the bulk of our results, including evidence of the observed wetting transitions. Section IV argues that the binary liquid plus salt may be considered a quasibinary system and analyzes the transitions in detail. Section V discusses our results in light of earlier work on this chemical system and of a similar experiment on a different system by Sigl and Fenzl [15].

II. EXPERIMENTAL MATERIALS AND PROCEDURE

The materials and equipment used here are similar to those described in Ref. [6]. The sample cell consisted of a 12-cm-long glass cylinder of inner diameter 0.9 cm. The bottom of the cylinder was fused shut and the top could be sealed with a Teflon stopcock. Temperature control for the cell was provided by an insulated water bath, kept stable to within 0.3 mK.

The sample cell contained six capillary tubes which had been cut from borosilicate glass micropipets. These tubes had inner radii of 0.190 or 0.300 mm and lengths of 4-5 cm. They were held and manipulated inside the cell by a cylindrical Teflon holder which contained a Teflon-encapsulated magnetic stir bar (see Fig. 2 of Ref. [6]). The cleaning process for the capillaries was meant to produce maximally clean, hydroxylated surfaces. It began with sonication in several changes of acetone, methanol, distilled water, and ethylenediamine tetra-acetic acid (EDTA). The tubes were then rinsed with distilled water, sonicated in nitric acid, sonicated again in distilled water, and finally dried in vacuum.

The cell was filled with 6.5-ml samples of carbon disulfide and nitromethane [16] at compositions ranging between $\phi = 0.6$ and 0.8 volume fraction of carbon disulfide. Amounts of tetrabutylammonium iodide [17] were added to produce overall salt molarities c between $0M$ and $0.8M$. A pure mixture of carbon disulfide and nitromethane has a normal coexistence curve with an upper critical temperature at $T_c \approx 64\,°$C. One effect of the

salt was to shift T_c upward, by as much as 30 $°$ for the highest concentration. We estimated T_c for each sample from the capillary-rise measurements themselves, by extrapolating to zero rise. To avoid problems due to aging, all samples were studied within three or four days of preparation.

For a given sample, the procedure was to begin making capillary-rise measurements 40–60 K below T_c and then to raise the temperature toward T_c, making new measurements every 2–4 K. To check for aging problems, measurements at lower temperatures were subsequently repeated. Before making each measurement, the liquid sample was mixed thoroughly by raising and lowering the capillary tubes and their holder repeatedly through the length of the cell. Sufficient time was then allowed to pass to ensure that the sample had equilibrated, leaving two clear coexisting phases — the top phase rich in nitromethane (the less dense liquid), the bottom phase rich in carbon disulfide. After this equilibrium had been established, the capillary tubes were slowly raised through the liquid-liquid interface. Within a few minutes, the capillary menisci had attained stationary positions below the level of the bulk meniscus, and a cathetometer of resolution 0.02 mm was used to measure these values. (Note that what we measured might more precisely be termed capillary depression than capillary rise.) Several measurements were taken at each temperature.

Capillary rise h, the height difference between the capillary and bulk menisci, depends on the interfacial tension σ and the density difference $\Delta\rho$ between the two bulk liquid phases, the capillary radius r, and the contact angle θ that the liquid-liquid interface makes with the solid substrate. Generally, h is given by the well-known formula, valid for $h \gg r$ [14],

$$h = \frac{2\sigma}{\Delta\rho g r} \cos\theta, \tag{1}$$

where g is the gravitational acceleration. One notes that it is possible, in principle, to extract θ from rise measurements, and, hence, to determine the state of wetting. When the contact angle is finite, one has what is called incomplete wetting; when it is zero, one has complete wetting.

III. WETTING TRANSITIONS

Hydroxylated glass in contact with a pure mixture of nitromethane and carbon disulfide is known to be completely wetted by the nitromethane-rich phase over a temperature range that extends well below T_c [7]. This can be seen in measurements of capillary parameter $a^2 = hr$ versus temperature (Fig. 1). According to Eq. (1), when $\theta = 0$, a^2 should be directly proportional to $\sigma/\Delta\rho$. Both these quantities scale with reduced temperature $t \equiv (T_c - T)/T_c$ as power laws in the neighborhood of the critical point. So, for the case of complete wetting, the capillary parameter should also scale with t as a power law:

$$a^2 = a_0^2 |t|^{\mu-\beta}. \tag{2}$$

The numerical value of $\mu - \beta$ is 0.94 [18]; we expect there-
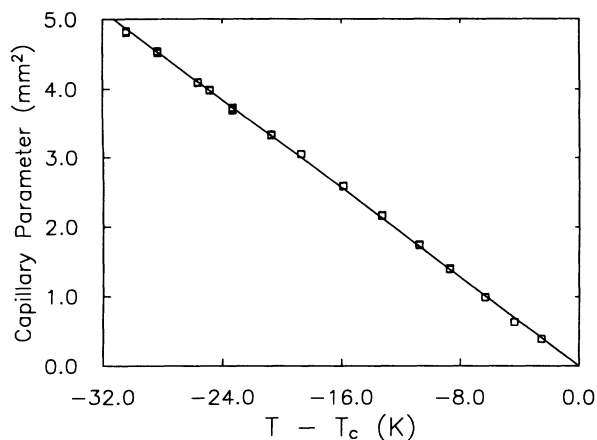
FIG. 1. Capillary parameter a^2 vs temperature for a pure mixture of carbon disulfide and nitromethane. The sample was prepared at the critical composition of $\phi_c = 0.60$ volume fraction of carbon disulfide. The critical temperature was $T_c \approx 64\,°C$.

fore that a^2 should very nearly be linear in temperature if θ is zero. As Fig. 1 shows, this is the case. The deviation from linearity that would be the sign of incomplete wetting is not present.

Given the absence of unusual behavior (e.g., a reentrant phase transition [19] or a tricritical point [20]) in this system and the relatively small T_c shifts [21], we expect that the same scaling relation, Eq. (2), that pertains to the pure mixture should hold for salted mixtures. And, indeed, graphs of capillary parameter versus temperature for samples with salt concentrations less than about $0.1M$ are also quite linear. We can see no sign of incomplete wetting in them even 40 K below T_c.

However, for larger concentrations ($> 0.2M$), the situation is very different. Consider the data for a sample with carbon disulfide volume fraction $\phi = 0.8$ and overall molarity $c = 0.4M$, for hydroxylated glass capillaries (Fig. 2, open squares). The relationship between a^2 and T here is certainly not compatible with Eq. (2). Near T_c the curve is approximately linear, as would be expected for complete wetting, but farther away there is a definite change in slope as the curve flattens out. From Eq. (1), this means that the glass cannot be completely wet over the entire temperature range, but that, at lower values of T, the contact angle θ must be finite. This suggests that the slope change evident in the data is a signature of a wetting transition from incomplete to complete wetting as the critical temperature is approached.

One point about which we were initially uncertain was the question of whether the glass was indeed completely wet near T_c. The linearity of the a^2 vs T curve at high temperatures suggested that this was the case, but, in order to get stronger confirmation, we performed a control experiment in which we compared the capillary rise measured in hydroxylated glass capillaries with that measured in silylated glass capillaries. These latter tubes had first been cleaned as described in Sec. II, but had then been exposed to a 1% solution of octyltrichlorosilane in
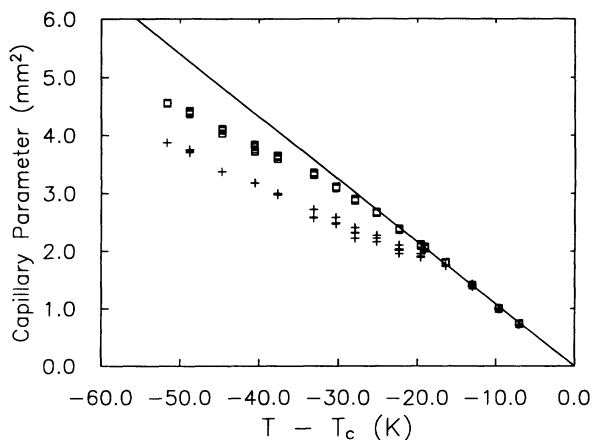

FIG. 2. Capillary parameter a^2 vs temperature for a salted mixture of carbon disulfide and nitromethane. Sample had carbon disulfide volume fraction $\phi = 0.80$ and overall salt molarity $c = 0.4M$. The critical temperature was estimated to be $T_c \approx 83.9\,°C$. Open squares are for hydroxylated glass capillaries and indicate distance of capillary meniscus below bulk meniscus; crosses are for silylated glass capillaries and indicate distance of capillary meniscus above bulk meniscus. Note the two sets of data collapse onto each other on approach to T_c.

dicyclohexyl [22]. Durian [10] found that this treatment resulted in substrates that were completely dry when in contact with the pure mixture to within at least 20 K of T_c; that is, the capillaries were completely wetted by the other phase, the carbon disulfide–rich phase. The capillary depression measured in the hydroxylated tubes had the same magnitude as the capillary rise measured in the silylated tubes: one had $\theta = 0$, the other had $\theta = \pi$. When such silylated capillaries were placed in the salted solution, the result was the cross data of Fig. 2. Both types of glass substrates were incompletely wet (or dry) at low temperatures, but closer to T_c the two curves came together, giving the same value of the capillary parameter, though with different sign. It is exceedingly unlikely that two very different substrates would produce the same capillary rise at a significant distance from T_c unless they were both completely wetted by their preferred phases. The convergence of the two sets of data in Fig. 2 therefore gives us strong confidence that, near T_c, the hydroxylated system has become completely wet. (It may be noted in passing that the silylated substrates apparently undergo what might be called drying transitions when in a salted sample. These are interesting in their own right, but we have not studied them extensively and will not comment on them further here.)

Since the control experiment has indicated complete wetting near T_c while the violation of the nearly linear relation of Eq. (2) has indicated incomplete wetting well away from T_c, it follows that a wetting transition has taken place a finite distance from T_c in Fig. 2, at the position marked by the change in slope. We measured several such transitions in a variety of samples, varying both the salt concentration and the relative amounts of car-
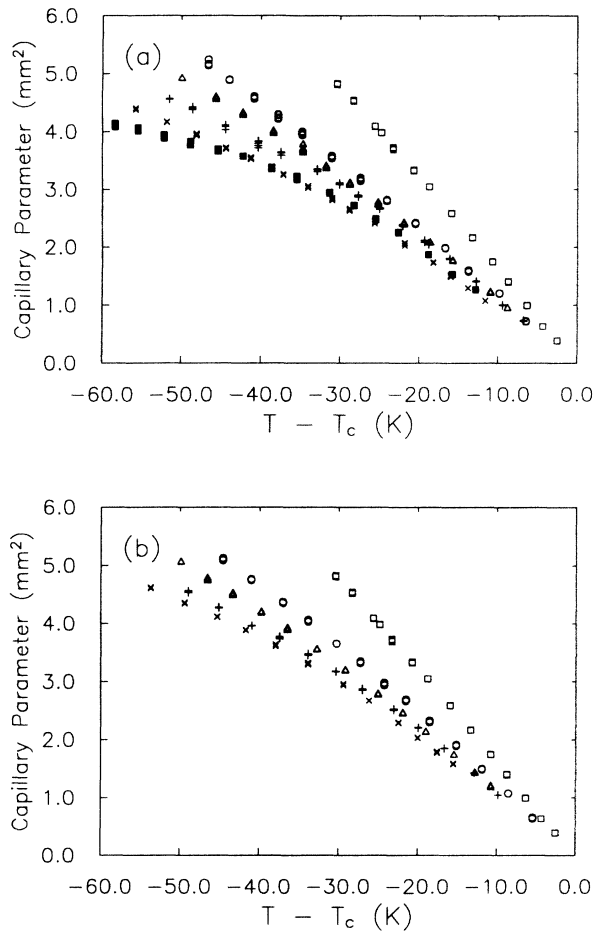
FIG. 3. Capillary parameter a^2 vs temperature for samples with various salt concentrations and liquid compositions. In both graphs, open squares represent data from a pure, unsalted liquid mixture with carbon disulfide volume fraction $\phi = 0.6$. (a) The salted samples in this graph all had $\phi = 0.8$. The overall salt concentrations c were $0.2M$ (circles), $0.3M$ (triangles), $0.4M$ (plus signs), $0.6M$ (multiplication signs), and $0.8M$ (closed squares). (b) These salted samples all had $\phi = 0.7$. The overall salt concentrations c were $0.3M$ (circles), $0.45M$ (triangles), $0.6M$ (plus signs), and $0.8M$ (multiplication signs). Note that the salted data generally cannot be described as linear; the slopes well below T_c are clearly different from those near T_c.

bon disulfide and nitromethane. The results are shown in Fig. 3. We note that as salt is added, not only does T_c shift upwards, but the amplitude of the capillary parameter a_0^2 becomes smaller, presumably because the salt lowers the surface tension.

IV. ANALYSIS

Figure 3 demonstrates that the results depend on both the overall salt molarity c and the carbon disulfide volume fraction ϕ. One might think, however, that we ought to be able to characterize samples by a single parameter, since only one new component has been added to the pure

mixture. A very likely candidate for such a parameter is the number of moles of salt per liter of nitromethane,

$$C \equiv \frac{c}{1 - \phi}. \tag{3}$$

The idea is that the salt so strongly prefers to dissolve in nitromethane, a polar liquid, over carbon disulfide, a nonpolar one, that the salted samples ought to be considered quasibinary. That is, they may effectively be treated as two-component mixtures, with one component being carbon disulfide and the other nitromethane doped with a certain amount of salt. To test whether this notion is reasonable, one can examine whether the mixture's bulk properties can be characterized by C. Figure 4 shows how the critical temperature T_c and the ratio of the amplitudes of the surface tension and density difference $\sigma_0/\Delta\rho_0$ ($= ga_0^2/2$) are affected by varying salt concentration and carbon disulfide fraction. From that
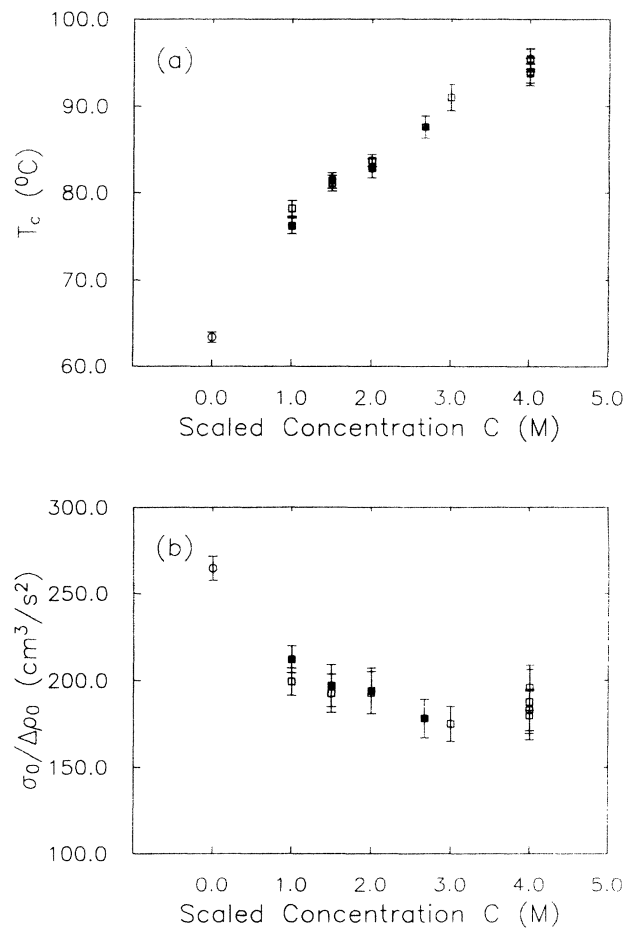

FIG. 4. (a) Critical temperatures for salted mixtures. (b) Ratio of surface tension and density difference amplitudes for salted mixtures. The scaled concentration C given on the horizontal axes is the number of moles of salt per liter of nitromethane. For both graphs, open squares represent data from samples with liquid composition $\phi = 0.8$ volume fraction of carbon disulfide. Closed squares represent data from samples with $\phi = 0.7$. The open circles are from an unsalted liquid mixture with $\phi = 0.6$.

figure, it does seem that C is a useful number in describing the data; we will use it in presenting our analysis of the wetting transitions.

First, let us consider how the wetting transition temperature T_w is affected by the amount of salt added to the mixture (Fig. 5). The way we have measured T_w for each sample is by estimating where the curves of Fig. 3 change slope. This is a difficult task; the slope changes are not so sharp that the wetting transitions can be placed very precisely. Consequently, the measurement uncertainty is great, as is reflected by the size of the error bars on the data points of Fig. 5. Nevertheless, a pattern clearly emerges: all of the wetting transitions we have measured occur at roughly 25 K below the critical temperature. Varying C produces no readily apparent change in $(T_c - T_w)$. This suggests that the high salt concentrations have put us in a saturation regime, where adding more salt has no effect on the wetting behavior, but only serves to shift T_c.

This raises the question of what is happening at lower salt concentrations, ones below the saturation value. The pure mixture appears to be completely wet even 40 K below T_c; if it does have a wetting transition, then $(T_c - T_w) > 40$ K. One would expect a smooth crossover between the behavior at $C = 0$ and that at $C > 1.5$; that is, one would expect wetting transitions at temperatures between 25 and 40 K below T_c for samples with scaled concentrations less than $C = 1.5$ but greater than $C = 0$. We were not able to detect such transitions. This very well may be because our technique is not sensitive enough. The transitions may exist but a less crude method must be used to find them.

Now, let us examine the nature of the wetting transitions we did observe. In particular, we can ask if they are first-order or critical phase transitions. A very useful test for the order of a wetting transition is provided by the temperature dependence of the contact angle θ in the incompletely wet regime [5]. If we define a re-

duced temperature with respect to the wetting temperature, $t_w \equiv (T_w - T)/T_w$, then the cosine of the contact angle is expected to go as

$$1 - \cos\theta = a|t_w|^{2-\alpha}, \qquad (4)$$

where a is a temperature-independent amplitude. The value of the exponent α depends on the transition's order. For the case of first-order wetting, α is expected to be equal to 1. For critical wetting, α should be less than or equal to 0, depending on the kind of forces responsible for wetting in the system. Applying this test to our data is somewhat difficult because it involves estimating both $\cos\theta(T)$ and T_w, and the uncertainty in these quantities is very large. However, even taking the uncertainties into account, the test strongly indicates that all of the wetting transitions that we measured were first order. No matter how we adjusted our estimates of contact angle and wetting temperature, we were never able to obtain an exponent α less than 0.8 from any of our data. All of the data were consistent with a value for α of 1; none were consistent with $\alpha \leq 0$.

Finally, we can attempt to characterize the wetting behavior in the incompletely wet regime. A convenient way of doing this is provided by the amplitude a in Eq. (4). Assuming that $\alpha = 1$, we extracted values for a for the samples which exhibited wetting transitions; these are shown in Fig. 6, where the error bars were obtained by considering extreme but plausible values of T_w and $\cos\theta(T)$ for each sample. Within the precision of the observation, the scaled concentration C appears to be an appropriate parameter. Clearly, the amplitude increases with increasing salt concentration; one can see this directly from Fig. 3 by noting how much more dramatically the heavily salted samples seem to bend over as T is lowered away from T_c. To understand why this might be, consider $\cos\theta$ expressed in terms of $V(l_{eq})$, the
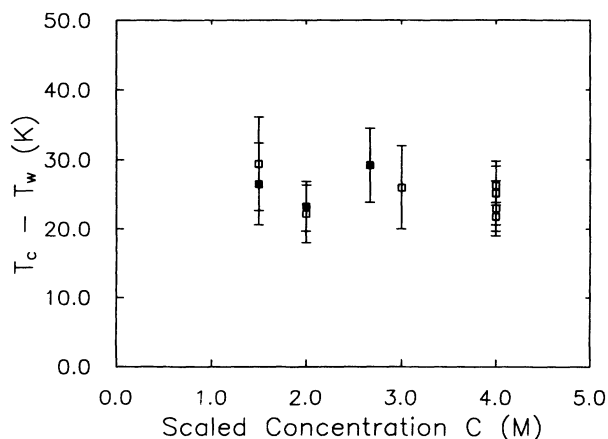

FIG. 5. Difference between critical and wetting transition temperatures for salted mixtures. Scaled concentration C is number of moles of salt per liter of nitromethane. Open squares have carbon disulfide volume fraction $\phi = 0.8$; closed squares have $\phi = 0.7$.
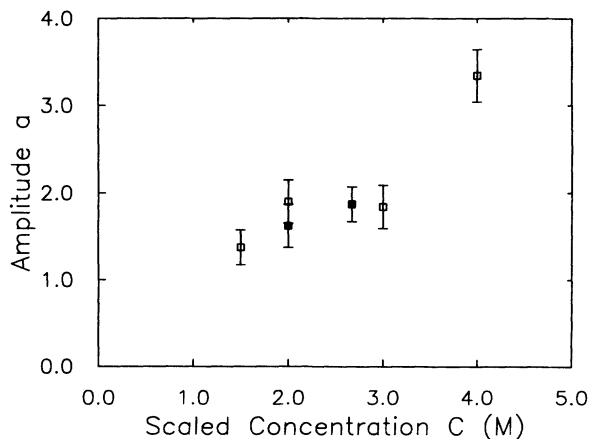

FIG. 6. Wetting amplitude a in incompletely wet regime for salted mixtures which exhibit wetting transitions. Equation (4) defines a, with α assumed to be 1. Scaled concentration C is number of moles of salt per liter of nitromethane. Open squares are from samples with $\phi = 0.8$; closed squares are from samples with $\phi = 0.7$.

free energy associated with a wetting layer of equilibrium thickness l_{eq} [23]:

$$\cos\theta = 1 + \frac{V(l_{eq})}{\sigma}. \tag{5}$$

Complete wetting is the case when $V(l_{eq}) = 0$; incomplete wetting is when $V(l_{eq}) < 0$. At a given distance from a wetting transition t_w, samples with more salt have lower values of $\cos\theta$. One possibility is that the additional salt decreases $V(l_{eq})$—makes the system more incompletely wet by making the free energy cost of a wetting layer greater. A second possibility is that $V(l_{eq})$ is the same for all of the salted samples, but that the effect on $\cos\theta$ is more pronounced in the most heavily salted cells because the surface tension σ is considerably less in these cells, as Fig. 4(b) demonstrates. We cannot test this idea stringently because the uncertainties in our estimates of a and σ are too large. Nevertheless, this second explanation seems more likely because the insensitivity of $(T_c - T_w)$ to salt concentration (Fig. 5) suggests we are looking at a saturation regime in which additional salt has unimportant effects and because, as we will show in the next section, calculations of the electrostatic contribution to $V(l_{eq})$ indicate that it is almost negligible for the salt concentrations we have used.

V. DISCUSSION

The intermolecular forces responsible for wetting in this system have been studied in considerable detail [6–11], and it should be possible to understand the observed wetting transitions in terms of these forces. Three are thought to be most important: hydrogen bonding, dispersion forces, and electrostatic forces.

The significance for wetting transitions of the short-range interaction due to hydrogen bonding is almost indisputable. As was mentioned earlier, experiments in which the glass surface was chemically modified in order to produce a transition [7] showed that the phenomenon obeyed scaling relations derived by assuming a short-range, contact force, while ignoring any effects of long-range forces. In particular, the chemical modification could be described as being equivalent to tuning a surface field h_1. More generally, one must expect that an interaction that decays exponentially from the surface (with the correlation length as the characteristic length) must become increasingly important on approach to the critical point.

Much less clear is the role played by long-range forces. One such force which is present to some extent in all wetting systems is dispersion, due to induced-dipole interactions [24]. Kayser [11] employed the theory of dispersion forces developed by Dzyaloshinskii, Lifshitz, and Pitaevskii [25] (DLP) to calculate numerically the strength of this interaction for a pure mixture of carbon disulfide and nitromethane in contact with borosilicate glass. He found that the force always favored wetting by the carbon disulfide–rich phase. However, adding salt changes the picture substantially because the presence of impurity ions can screen the zero-frequency contribution to the dispersion interaction [24]. For the high salt concentrations of these measurements, we expect that the static term should more or less disappear. In the absence of this term, the nature of the dispersion force becomes much more ambiguous. Using Kayser's numerical results, one finds that the force can change sign with temperature and wetting layer thickness—favoring carbon disulfide wetting in one regime, nitromethane wetting in another. Moreover, the functional form of the disjoining pressure associated with dispersion becomes quite complicated; it certainly cannot be modeled by an algebraic term. Simply put, in the presence of screening ions, it is neither clear that dispersion opposes nitromethane wetting nor that it can properly be called "long range." As a result, available theoretical models [4] based on assumptions about purely short-range (exponential) and purely long-range (algebraic) interactions, or that do not require a second-order transition in the absence of a nonalgebraic long-range force, become untenable if dispersion is an important force for the wetting phenomena that we have observed.

But is dispersion an important force affecting our results? One way to answer this question is by estimating the contribution it can be expected to make to the free energy $V(l_{eq})$. Our techniques were such that deviations of $\cos\theta$ from unity of 10% or more should have been readily measurable. From Eq. (5), it follows that, in order to affect $\cos\theta$ in a way that would be detectable by this capillary-rise experiment, a contribution to $V(l_{eq})$ must be within at least an order of magnitude of the surface tension σ. The size of the dispersion contribution V_{disp} for the salted samples may be estimated from the numerical work of Kayser, if one takes care to omit the zero-frequency term [26]. Doing so, we find that dispersion can be expected to have hardly any effect on $\cos\theta$ in the temperature range examined here. This is true even if we make overly generous assumptions about its sign and functional form. For example, at $(T_c - T) = 35$ K, the magnitude of the dispersion energy should be no greater than $|V_{disp}| \approx 10^{-6}$ J/m^2. By comparison, the surface tension is nearly three orders of magnitude larger, $\sigma \approx 10^{-3}$ J/m^2 [7]. We can conclude, therefore, that dispersion forces cannot affect in a significant way the wetting transitions that our experiment has measured.

By a very similar argument, we can show that electrostatic forces also cannot be significant to the wetting behavior once salt has been added. Again from the work of Kayser [11], we know that the electrostatic contribution to $V(l_{eq})$ decays exponentially with l_{eq} for the salt concentrations we employed. The decay length is given by the Debye screening length [27]. For an overall molarity of $c \approx 0.1M$, the Debye length can be no more than a few angstroms—smaller than the correlation length even 50 K below T_c. Consequently we expect the effect of the electrostatic interaction to be negligible for all of the salted samples which showed wetting transitions.

Of the three intermolecular forces thought to be important for wetting by the pure binary liquid, it appears that only one, the short-range interaction due to hydrogen bonding, can have a significant effect on the salted samples we have studied. This suggests a scenario to explain

the appearance of a wetting transition once sufficient salt has been added: Short-range forces acting alone would produce a wetting transition in this system roughly 25 K below T_c. However, in the pure mixture, the presence of a long-range electrostatic force favorable to nitromethane wetting suppresses this transition, or at least makes it very difficult to detect. Adding sufficient salt effectively shuts down the electrostatic force and allows the short-range-mediated wetting transition to reveal itself. This scenario, if correct, would help to explain the saturation behavior suggested by Fig. 5. Amounts of salt smaller than the amounts we added to our cells might be enough to eliminate the electrostatic force and produce a wetting transition; additional salt then has little additional effect.

This explanation is lent a certain credence by experimental and theoretical work of Ripple et al. [9]. They used a reflectivity technique to measure the growth of a nitromethane-rich wetting layer in samples with and without added salt as the temperature was lowered from the single-phase region of the phase diagram toward the coexistence curve. The thickness of the wetting layer was substantially smaller in the salted sample. In an effort to examine their result quantitatively, they developed a mean-field description of wetting in this system which incorporated both critical adsorption effects and surface ionization forces. By making plausible assumptions about surface charge and sample purity, they found that they could explain the data reasonably well. In particular, their theoretical model suggested that the growth of the layer, as coexistence was approached 1.2 K below T_c, was dominated by critical adsorption; the addition of the impurity ions had rendered the effect of electrostatic forces relatively unimportant.

It should be noted that our experiment is similar to and may be compared with one of Sigl and Fenzl in which they altered the wetting properties of 2,6-lutidine and water against Pyrex glass by adding potassium chloride. The pure system undergoes a wetting transition 15 K away from T_c [3], but, by adding increasing amounts of salt, Sigl and Fenzl were able to move the transition smoothly down to T_c itself. This result is in sharp contrast to our own in that we found that every wetting transition we measured occurred at $(T_c - T) \approx 25$ K; there was no smooth behavior with increasing salt concentration. It is difficult to say why the two results are so different—partly because the wetting behavior of 2,6-lutidine and water against various kinds of glass is still a point of some ambiguity [28]—but clarifying further how impurity ions affect wetting and wetting transitions would appear to be a valuable next step.

VI. CONCLUSIONS

Short- and long-range forces can both profoundly affect wetting phenomena, and understanding the interplay between them is crucial to understanding the range of behavior possible in wetting systems. The carbon disulfide–nitromethane binary liquid exposed to borosilicate glass is one system in which a short-range interaction (due to hydrogen bonding) and a long-range interaction (due to surface ionization) are believed to be present. Both favor wetting of the glass by nitromethane and, in the pure system, the substrate is completely wet even far below T_c. But, by adding screening ions, we have found that it is possible to drive the system through a wetting transition at $(T_c - T) \approx 25$ K. We have also found that a quasibinary description of the liquid system via a scaled salt concentration variable C is appropriate for bulk critical properties and possibly also for wetting phenomena. In light of what is known about the intermolecular forces in this binary liquid, we have argued that the appearance of the wetting transition results from the complete elimination of the long-range electrostatic force. The transition then apparently depends on the short-range interaction and the interface fluctuations associated with bulk criticality [5] alone.

ACKNOWLEDGMENTS

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