

Continued exploration of the wetting phase diagram

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Measurements are presented of the state of wetting of a binary liquid mixture on heavily silylated glass, which are believed to probe a new region of the wetting phase diagram. We find unusual temperature dependence and the first experimental evidence of a possible "partial drying" transition recently predicted by Ebner and Saam for the case of strong short-range substrate-liquid forces opposed by a weak long-range force.

INTRODUCTION

In a recent paper by Durian and Franck¹ (DF), we report capillary-rise measurements of the state of wetting of the carbon disulfide + nitromethane binary liquid mixture at coexistence on chemically altered borosilicate glass substrates. We find that hydroxylated substrates are always completely wet by the nitromethane-rich (N^*) phase; capillaries lightly silylated with hexamethyldisilazane (HMDS) are less attractive to N^* and exhibit a transition from partial to complete wetting, by N^* , as the temperature is increased toward the liquid-liquid critical demixing point T_c . In the course of the experiment several substrates were produced with such heavy silylation as to become attractive to the carbon disulfide-rich (C^*) phase. These substrates gave data with unusual temperature dependence but were not included in DF because of unacceptable errors arising from bulk-meniscus mislocation. In this report we present data on similar heavily silylated capillaries which have been corrected for this systematic error. It should be noted that Abeysuriya, Wu, and Franck² (AWF) have published observations for similar substrates; however, improved sample-preparation technique permits great enough precision that previously unnoticed features are now observed.

PROCEDURE

All sample cells used were similar to those of AWF and DF. They were filled in an Ar atmosphere to have 0.601 ± 0.015 volume fraction carbon disulfide, approximately the critical composition.³ The initial critical temperatures were within $T_c = (63.052 \pm 0.011)^\circ\text{C}$ and were found to drift, typically, by $+5$ mK/day. The positive drift and $T_c > T_c^3$ indicate increasing presence of impurities which are preferentially dissolved in one of the two liquid phases.⁴

The starting point of the work to be reported here is the data shown in Fig. 1 for heavily silylated tubes with a net attraction to the opposite phase from the hydroxylated control. It is believed that hydroxylated surfaces produce both short-range and long-range forces attractive to N^* . Furthermore, one can hypothesize that by changing the glass surface chemistry only the short-range force is

affected.⁵ If this is true, our heavily silylated substrates can be used to test the theoretical predictions of Nightingale and Indekeu,⁶ and Ebner and Saam⁷ for the wetting behavior of surfaces with a short-range force weakly opposed by a long-range force. The predictions are, briefly, that complete drying will occur continuously at T_c , and that if the short-range surface field h_1 is strong enough there will be a "partial drying" transition between two states of incomplete drying. We follow Ebner and Saam in referring to wetting by N^* as "wetting," and wetting by C^* as "drying."

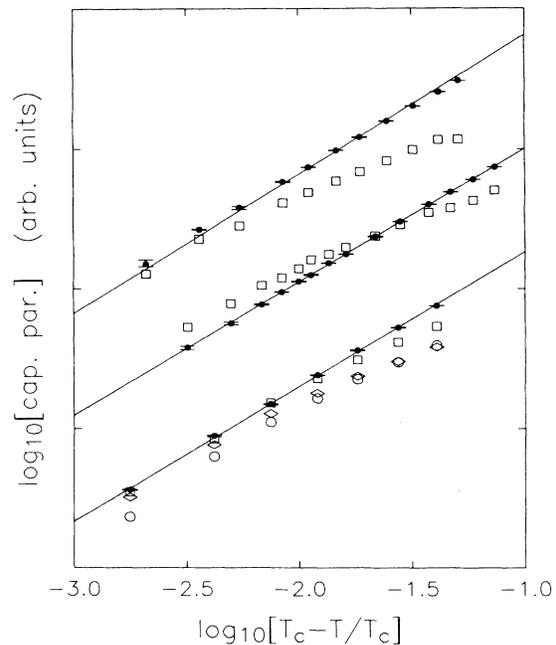


FIG. 1. Preliminary capillary parameter (rise times inner radius) vs reduced temperature. In each of the three data sets (displaced vertically for clarity) the solid symbols represent completely wet, hydroxylated, capillaries. The open symbols, having error bars comparable to the hydroxylated data, represent heavily silylated capillaries which are incompletely dry. From top to bottom, the HMDS exposures were 48 h at 8 mm Hg, then 67, 707, 226, and 130 h at 2.4 mm Hg. Vertical-axis tick marks indicate successive decades.

Three sets of preliminary data are shown in Fig. 1. The open symbols denote the capillary parameter (rise times inner radius) of heavily silylated capillaries; the solid symbols (fit by power law) denote the absolute capillary parameter of completely wet hydroxylated capillaries. All capillaries have identical radii, 0.188 mm. The capillary-rise formula,⁸

$$a^2 = \frac{2\sigma_{\alpha\beta}}{\Delta\rho g} \cos\theta, \quad (1)$$

predicts that the capillary parameter will have the same (maximum) magnitude for both complete wetting, $\cos\theta = -1$, and complete drying, $\cos\theta = 1$. Here a^2 is the capillary parameter, $\sigma_{\alpha\beta}$ is the interfacial surface tension, $\Delta\rho$ is the liquid-liquid mass density difference, g is the gravitational acceleration, and θ is the contact angle coexisting liquid phases made with the substrate. Equation (1) is valid only for rise much greater than radius; this condition is satisfied by all observations presented in this report. Note that large systematic errors are present in these data: The silylated capillary of the middle data set in Fig. 1 attains a rise near T_c greater than the depression of the completely wet hydroxylated capillary. This behavior corresponds to $\cos\theta > 1$ and is unphysical; our explanation is that mislocation of the bulk meniscus is responsible. Nevertheless, the following statements can be made with certainty. Far from T_c all silylated capillaries are incompletely dry. Even near T_c the two least heavily silylated capillaries of the bottom data set are incompletely dry because their rises are less than that of the most heavily silylated capillary in the sample cell. All data show evidence of a possible discontinuity in slope which could be interpreted as either a first-order drying transition or a partial-drying transition. To determine which, we need to understand and eliminate the bulk-meniscus location error in further experiments; this we now present.

Due to the curvature of the bulk meniscus at the sample cell walls and around the capillary tubes, it is not possible to measure capillary rise relative to the bulk without systematic error. This is especially troublesome for heavily silylated capillaries because their menisci lie on the opposite side of the bulk meniscus thereby preventing direct comparison with the completely wet hydroxylated control. In particular, there is little systematic error in calculating the contact angle by $\cos\theta = (\text{silylated rise})/(\text{hydroxylated rise})$ for lightly silylated tubes near complete wetting, but there would be an unacceptably large error in doing the same for heavily silylated capillaries near complete drying (as we have just seen in Fig. 1).

We attempt to eliminate the bulk-meniscus location error by using data from three hydroxylated capillaries of different inner radii (0.134, 0.188, and 0.300 mm) to estimate the effective position of the bulk meniscus. To do this, we rely on the property that capillary rise is inversely proportional to radius. For each position of the capillaries through the bulk meniscus, we measure the rise r_k in the hydroxylated tubes, radii a_k , and for each distinct pair compute $x_{i,j}$ such that

$$(r_i + x_{i,j})a_i = (r_j + x_{i,j})a_j. \quad (2)$$

The correction $x = \langle x_{i,j} \rangle$ is then added to the measured

rises of all capillary tubes. As expected, this correction becomes smaller as $T \rightarrow T_c$ due to decreasing bulk-meniscus curvature. As a mild check on our correction, we plot the average corrected hydroxylated capillary parameter versus reduced temperature, $t = (T - T_c)/T_c$ with T and T_c in K, as solid symbols in Fig. 2 for the two sample cells studied. The error bars represent both statistical variation from values at different positions through the bulk meniscus and variation in x . Based on the capillary-rise formula, the predicted behavior is $a^2 = a_0^2 |t|^{\mu-\beta}$ with⁹ $\mu - \beta = 0.935 \pm 0.015$. We find $\mu - \beta = 0.943 \pm 0.010$ and $a_0^2 = 50 \pm 1 \text{ mm}^2$ and include this fit in Fig. 2 for both data sets. We observe the correlation $x_{0.134,0.188} < x_{0.300,0.134} < x_{0.188,0.300}$ at all temperatures in both sample cells; this indicates an unknown systematic error and is reflected in the indicated uncertainties.

In each of the two sample cells there were three silylated capillaries with identical radii, 0.188 mm, in addition to the hydroxylated capillaries discussed above. All capillaries were cleaned together according to the procedures described in DF. Degrees of silylation were varied, as in DF, by length of exposure to hexamethyldisilazane vapor at 2.4 mm Hg.

After liquid equilibration, the capillary rises were measured with a cathetometer at four different positions of the tubes through the bulk meniscus. By "equilibration" we mean allowing the temperature to stabilize while mixing the liquids, giving the liquids a final thorough mixing, then waiting for the upper and lower phases to become entirely clear. As in DF, the capillaries were raised so that the silylated tubes, being partially wet by the lower (C^*)

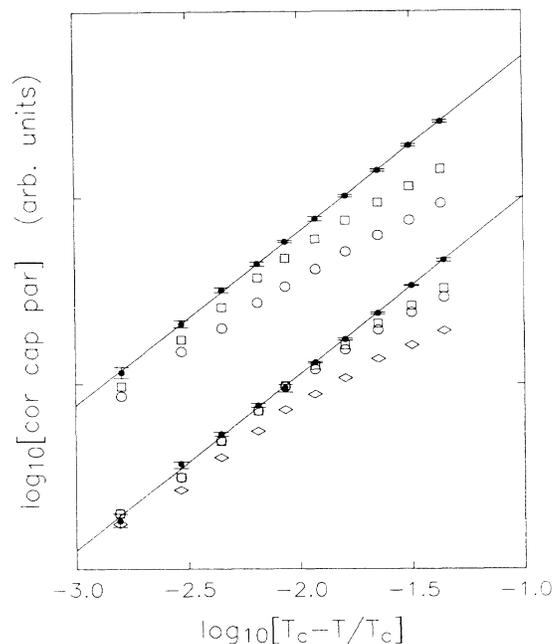


FIG. 2. Corrected capillary parameter vs reduced temperature. The correction eliminates systematic error due to bulk-meniscus mislocation. From top to bottom, the HMDS exposures were 573, 227, 2733, 573, and 227 h at 2.4 mm Hg. Vertical-axis tick marks indicate successive decades.

phase, had receding menisci.¹⁰ Consequently, the hydroxylated tubes, being completely wet by the upper (N^*) phase, had advancing menisci; however, we measure the hydroxylated rises to be identical for advancing and receding menisci. No systematic dependence of rise on position indicates that the capillary tube surface chemistry was uniform over its length.

A possible source of systematic error that must be noted is an aging effect in which the silylated surface is attacked by the liquid mixture. As pointed out in DF, the HMDS silyl coatings can be entirely removed by our liquids, given sufficient time. To minimize this effect, all data presented here were taken within a 16-h period. Also, data for the first sample cell were taken at a monotonically decreasing sequence of temperatures; data for the second were taken at a monotonically increasing sequence of temperatures. No difference is seen in the resulting data sets. We feel that negligible error was introduced by this aging effect for two other reasons. In DF data were obtained on incompletely wet silylated substrates by similar manner which gave an understandable power law without noticeable systematic error. Secondly, no position dependence of capillary rise was observed to develop during the experiment (as might be expected from different parts of the tube being exposed to different liquid composition as it is raised and held through the bulk meniscus). We believe, however, that the next generation of experiments on chemically altered substrates must squarely face this issue.

RESULTS

The bulk-meniscus correction was applied and the results are shown in Fig. 2. Error bars for silylated tubes are again comparable to the hydroxylated error bars. The upper data set shows tubes exposed to HMDS for 573 and

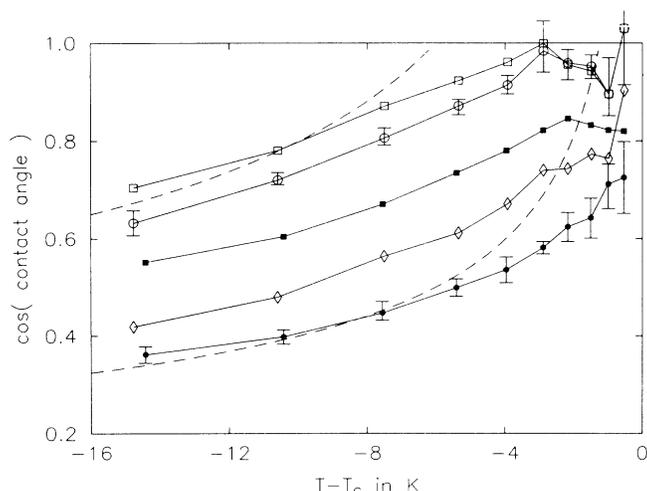


FIG. 3. Contact angle vs temperature computed from the corrected capillary parameter data of Fig. 2. Note that capillaries appear incompletely dry at all temperatures studied and cannot be described by a power law with exponent $\beta_1 - \mu$ (dashed curves). Indicated uncertainties are typical for all data.

227 h. (Data from a 419-h silylated capillary are omitted due to their unusually large random scatter. This tube was prepared identically with others; we speculate that a piece of Teflon became lodged in the tube during insertion into the holder.) The lower data set shows tubes exposed to HMDS for 2733, 573, and 227 h. The data of Fig. 2 share many features with the preliminary data of Fig. 1; the main difference being that now we can compute the contact angle and make statements about the state of drying.

All silylated tubes remain incompletely dry at the temperatures studied. This assertion may be questioned for the most heavily silylated capillary of the lower data set because its error bars strongly overlap those of the hydroxylated capillaries as $T \rightarrow T_c$. All others are definitely incompletely dry either because there is no such overlap or because there is a silylated capillary in the same sample cell which shows a greater rise. In Fig. 3 we present the contact angles for both the upper and lower data sets (solid and open symbols, respectively). This is the most informative way of presenting our data; unfortunately, however, it magnifies the error bars, especially near T_c where the rises are small.

The temperature dependence of the incompletely dry state is different from that of the incompletely wet state reported in DF. There we observe that the incompletely wet rise is proportional to $|t|^{\beta_1 - \beta}$, or equivalently $\cos\theta$

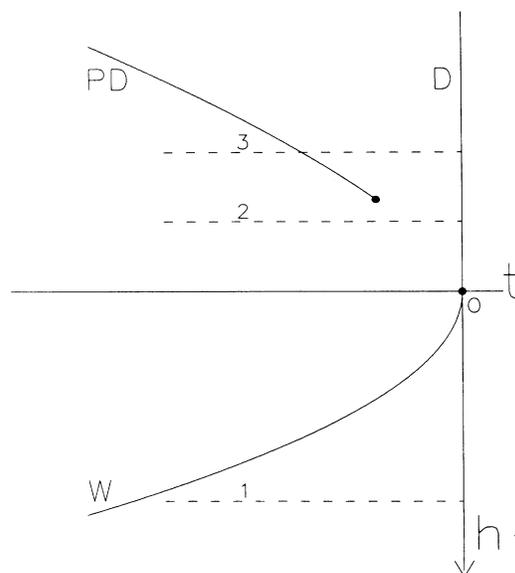


FIG. 4. Wetting phase diagram of Ebner and Saam. W is the locus of first-order transition to complete wetting (by "liquid", e.g., N^*), D is the locus of continuous drying transitions (i.e., to complete wetting by "vapor", e.g. C^*). They meet as the so-called ordinary point O. PD is the locus of first-order partial-drying transitions. This is for the case of negative surface enhancement and a weak long-range force which favors the wetting phase N^* independently of the short-range force h_1 . Trajectory 1 is for hydroxylated capillaries which are completely wet at all temperatures studied. Trajectories 2 and 3 summarize possible predicted behavior of the heavily silylated capillaries of this report.

$\propto |l|^{1-\mu}$, as predicted from short-range force scaling arguments. The two examples of this power law, included as dashed lines in Fig. 3, clearly show that the temperature dependence of the incompletely dry state is not of this form. If a long-range substrate attraction to N^* is indeed responsible for preventing a drying transition below T_c then the expected behavior is as follows. The free energy per unit area to have the β phase at infinity with a layer of the α phase, l_a thick, adjacent to the wall is $\sigma_{\beta W} = \sigma_{\alpha W} + \sigma_{\alpha\beta} + \Delta V(l_a)$, where $\Delta V(l_a)$ is the work done by the long-range force in attracting the α - β interface from infinity to l_a . If the long-range force can be modeled by a contribution to the free-energy density of $-h_{LR}(z)m(z)$, where $h_{LR}(z) = A/z^\omega$ and $m(z)$ is the bulk order parameter at distance z from the wall, then $\Delta V(l_a) \propto (m_\alpha - m_\beta)l_a^{1-\omega}$. According to Nightingale and Indekeu,⁶ the long-range force will thin the drying layer to thickness $l_a \approx \xi$ at which the attraction is balanced by the repulsion due to the interface fluctuations; ξ is the bulk correlation length. The predicted temperature dependence of the state of partial drying for this case is therefore

$$1 - \cos\theta = -\frac{\Delta V(l_a)}{\sigma_{\alpha\beta}} \sim |l|^{1-\mu-\nu(1-\omega)} \quad (3)$$

It is, in principle, possible to test this formula by capillary-rise experiments. However, the large uncertainty in our data prevents quantitative comparison. It should be noted that Fig. 3 is consistent with the prediction $\cos\theta \rightarrow 1$ as $T \rightarrow T_c$, whereas the data of AWF on related substrates are not.

A qualitative trend suggested by both Figs. 2 and 3 is that there is a difference in the temperature dependence near and far from T_c . Our data are consistent with there being either a discontinuity in slope or a rounding between these two regions. A discontinuity would be interpreted as the "partial drying" transition of Ebner and Saam⁷ in

which the partial-drying layer thickness jumps discontinuously. This case corresponds to trajectory 3 of our reproduction of Ebner and Saam's wetting phase diagram, Fig. 4. A rounding would be interpreted as corresponding to trajectory 2, which does not intersect the partial-drying transition line. Stable surfaces are needed to obtain enough data in the region of interest if the existence of the partial-drying transition is to be addressed further by the capillary rise method.

CONCLUSIONS

Heavily silylated capillary tubes have been produced and used in experiments which are the first to confidently explore a new region of the wetting phase diagram. The capillaries remain incompletely dry at all temperatures studied but do not have temperature dependences arising from weak short-range force scaling only, as was seen in DF for incomplete wetting. In contrast with the work of AWF, our data are consistent with there being complete drying only at T_c . We notice a possible discontinuity in the slope of capillary rise versus temperature. This is the first experimental evidence of the "partial-drying" transition predicted by Ebner and Saam for the case of short-range substrate-liquid attraction weakly opposed by a long-range force.

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⁵See Ref. 2 for discussion of these points.

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⁸See, for example, A. W. Adamson, *Physical Chemistry of Surfaces* (Wiley, New York, 1982)

⁹See, e.g., J. S. Rowlinson and B. Widom, *Molecular Theory of Capillarity* (Clarendon, Oxford, 1982), p. 265, for values of bulk critical exponents.

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