Wetting Transition at the Liquid−Air Interface of Methanol−Alkane Mixtures

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Wetting transition (T_w) and consolute (CT) temperatures close to the upper critical solution temperature (UCST) have been determined for methanol + n-alkane mixtures where $n = 6−12$. T_w and the CT were also measured for noninteger n values, i.e., for mixtures of methanol + a binary mixture of two normal alkanes. The liquid−vapor surface tension (σ_{LV}) and the liquid−liquid interfacial tension (σ_{LL}) were measured at 25 °C. For all mixtures studied the methanol rich-phase is denser than the alkane rich-phase. It is found that while the CT increases continuously, the T_w first increases and then decreases as a function of n. This is the first time that, for a homologous series of mixtures, this behavior has been found. For $6 \leq n \leq 8.25$ the observed wetting transition was from partial wetting to nonwetting (the alkane rich-phase intrudes between the methanol rich-phase and the vapor) while for $8.5 \leq n \leq 12$ the transition was from partial to total wetting (the methanol-rich phase intrudes between the alkane rich-phase and the vapor). Both the change of T_w and the inversion in the nature of the wetting phase with n are in qualitative agreement with the predictions of a recently developed mean-field model where a normalized parameter b, whose calculation involves σ_{LV} and σ_{LL}, plays the role of n in the experiments.

I. Introduction

For some systems, when three fluid phases α, β and γ coexist at equilibrium, it is possible to find different thermodynamic conditions where the wetting regimes depicted in Figure 1a are stable. The transit from a partial wetting regime to a total wetting regime, or vice versa, occurs at a temperature T_w and is called the wetting transition. Below T_w a droplet of the α phase with a finite contact angle may be formed at the interface between β and γ. Above T_w the contact angle is zero, but the thickness of the wetting film remains finite. In Figure 1a, the curvatures of the meniscus between α and β, β and γ, and those between α and β and the walls of the container are an schematic representation of those observed for the mixture methanol + dodecane. Since the pioneering work done by Cahn[1] and Ebner and Saam,[2] the existence and nature of such wetting transitions at fluid−fluid interfaces has been the subject of continued interest, from both the theoretical and experimental point of view. Experimentally, the most studied case is that where α and β are the immiscible liquid phases of a binary mixture as indicated in Figure 1b and γ is air,[3−11] although there are also several studies of wetting transitions on ternary[12−16] and quaternary[17,18] mixtures. Theoretically, several models of varying degrees of complexity have been proposed to describe wetting at fluid interfaces.[19] Among them, global analysis of possible wetting behaviors have been particularly fruitful[20−24] since they provide the relations between the structure of the phase diagram, the particular characteristics of the coexisting phases and the interfacial behavior. An example of such theoretical approaches has been presented recently[25] and constitutes the main motivation for the present work, viz., to test one of its predictions.

II. Brief Description of the Theoretical Framework

The model developed by Perez et al.[25] is a simple mean-field lattice model for binary mixtures for which the topology
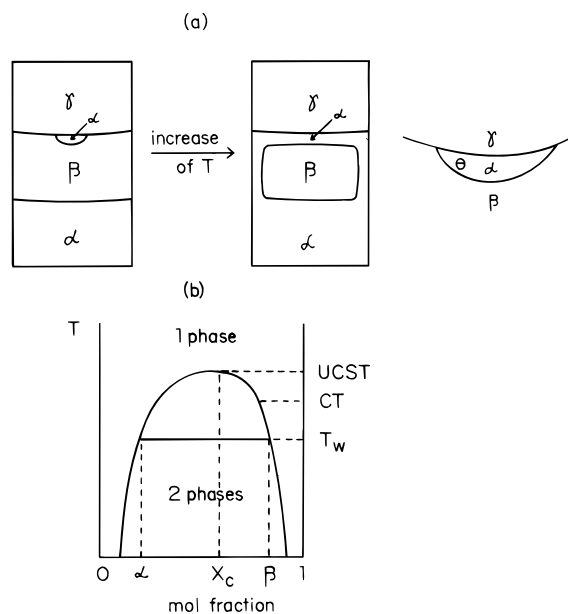

Figure 1. (a) Partial to total wetting transition in a three fluid phases α, β, and γ system; θ is the dihedral contact angle. In this work α and β were immiscible liquid phases and γ was air. The curvatures of the meniscus between α and β, β and γ and those between α and β and the walls of the container are a schematic representation of those observed for the mixture methanol + dodecane; (b) liquid−liquid coexistence curve for a binary mixture; T_w is the wetting transition temperature, CT is the consolute temperature where the two immiscible liquid phases become a one-phase liquid mixture and UCST (upper critical solution temperature) is the highest possible CT occurring at the critical concentration x_c.

and connectivity of bulk critical and wetting transition manifolds have been carefully studied. As with other models of the same type, the approximations introduced limit the description of all aspects of wetting behavior. However, one of its main virtues is that steaming for its particular way of treating and representing the interaction parameters involved, the model is capable of producing a set of easily visualized predictions which are both interesting and challenging to test experimentally. In particular,

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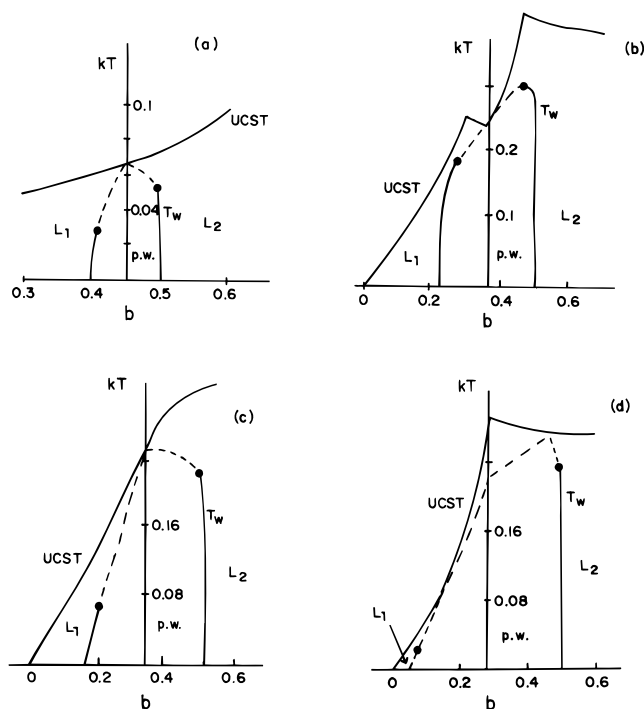
Figure 2. Field phase diagrams (*b*, *kT*) from ref 25 at four different constant *c* values, showing the evolution of the upper critical solution temperatures (UCST) and the wetting transition temperatures (*T*ₓ). *c* values are 0.1 in (a), 0.275 in (b), 0.33 in (c), and 0.45 in (d). Solid and dotted lines correspond to first- and second-order transitions, respectively. Partial wetting (pw) is to be found in the indicated regions. L₁ and L₂ indicate the nature of the intruding or wetting phase. Mixtures of perfluoromethylcyclohexane (2) + 1-alcohols (1)[9] follow the behavior in the middle section of (c) (*b* values from 0.4 to 0.45); mixtures of water (2) + *n*-alkanes (1)[11] and methanol (2) + *n*-alkanes (2)[11] display at 25 °C the change in the nature of the wetting regime indicated in (c) for 0.13 < *b* < 0.18 and in (a) for 0.4 < *b* < 0.5, respectively. The prediction in (a) is tested in this work.

the model describes the evolution of the upper critical solution temperature (UCST) and the wetting transition temperature T_w for a set of binary mixtures which share one common component while the other is changed within an homologous series (component 1). The description is done in terms of a normalized parameter *b* defined as

$$b = \sigma_{L1V}/(\sigma_{L1V} + \sigma_{L2V} + \sigma_{L1L2}) \qquad (1)$$

where σ_{L1V} and σ_{L2V} are the pure liquid−vapor (or air) surface tensions of components 1 and 2 of the binary mixture and σ_{L1L2} is the liquid−liquid interfacial tension between the liquid phases in equilibrium. As such, *b* is effectively the "reduced" tension of component 1. The particular behavior of the critical and the wetting temperatures as a function of *b* depends also on the value of the normalized parameter $c = \sigma_{L1L2}/(\sigma_{L1V} + \sigma_{L2V} + \sigma_{L1L2})$. Figure 2 illustrates the predictions of the model for four different values of the reduced interfacial tension c. The authors in ref 25 applied their model to the study of mixtures[9] of C_7F_{14} (perfluoromethylcyclohexane) and *n*-alcohols (component 1) finding a remarkable qualitative agreement with the observed experimental behavior. These mixtures correspond to the case $c \approx 0.33$ with *b* ranging from 0.4 to 0.45 and can be located in the middle section of Figure 2c. The model also predicts the change in the nature of the wetting regime experimentally observed at 25 °C in water + *n*-alkane (component 1) mixtures[11] ($c \approx 0.35$, 0.13 < *b* < 0.18 in Figure 2c) and methanol + *n*-alkane (component 1) mixtures[11] ($c \approx 0.05$, 0.4 < *b* < 0.5 in Figure 2a). This last case is of particular interest because the

model predicts a nonmonotonic behavior of the wetting temperature T_w as the UCST of the mixtures increases. Testing the behavior shown in Figure 2a, which has not been observed previously, was the main motivation of the present work. The model in ref 25 is perhaps not the only theoretical framework capable of predicting the behavior displayed in Figure 2. However, the fact that *b* values are easily accessible through the measurement of the surface and interfacial tensions involved opens the possibility of making a direct comparison, albeit qualitative, between theory and experiment; clearly, this makes the model in ref 25 quite attractive.

The prediction in Figure 2a has been corroborated here with the series of mixtures composed of methanol + an *n*-alkane (component 1). There are several reasons supporting the selection of this series of mixtures, namely, (i) it is known[11] that σ_{L1L2} is very small, producing a small *c* value, (ii) the surface tension of methanol is intermediate amongst the corresponding values for the series of *n*-alkanes; this, together with $\sigma_{L1L2} \approx 0$, produces a *b* value close to 0.5, (iii) the upper critical solution temperature (UCST), i.e., the CT at x_c (see Figure 1b), and T_w for these mixtures are relatively low and hence experimentally accesible, (iv) previous measurements[11] for *n* = 6 and 12 at 25 °C indicated an inversion in the nature of the wetting phase as predicted by the model,[25] and (v) given that mixtures of *n*-alkanes follow a corresponding states behavior,[26] it is possible to prepare "fractional" alkanes, i.e., those with a noninteger *n* value, mixing two normal alkanes. In this way, the *n* = 6.5 alkane is built mixing the same number of moles of hexane and heptane; this binary mixture possesses thermodynamic properties which are intermediate between those of hexane and heptane, i.e., it behaves as a pure alkane with *n* = 6.5. Working with both normal and "fractional" alkanes increases the number of possible methanol + alkane mixtures and hence of *b* values to be determined allowing a more detailed test of the prediction in Figure 2a.

III. Experimental Section

Materials. All *n*-alkanes used (*n* = 6−12) were from Aldrich Chemical Co. with at least 99+% purity. Methanol was from Merck Chemical Co. with a 99+% purity. All chemicals were employed without any further purification.

Procedure. *Sample Preparation.* Samples were prepared by weight (Mettler AT-250) as close as possible to x_c, the composition at the UCST (see Figure 1b), so that the difference (CT − T_w) would be as big as possible and increase the temperature range for the observation of the transition indicated in Figure 1a. For this purpose a correlation,[27] based on experimental data reported by many researchers, between x_c and *n* was used here for both integer and noninteger *n* values. The maximum difference between the mole fraction employed here and the critical one was 0.06; given the "flatness" on the liquid−liquid coexisting curve for the present mixtures,[27−28] the CT we determined is quite close to the UCST.

Determination of the T_w and CT. A glass cell with plane parallel walls separated 1 cm and a thermal jacket was used to determine the CT and T_w. The total sample volume (liquid) was approximately 2.5 cm³. Temperature was controlled within 0.01 °C using a Haake thermostat (Model D8-GH). Samples were prepared in the glass cell and placed at a temperature a few degrees below the T_w. Temperature was then increased in 0.1 °C steps stirring the sample to ensure proper mixing; after each temperature increase, upon reaching the desired temperature, the mixture was permitted to attain equilibrium stopping the stirring so either a pendant drop or a thin film of the lower α phase would spontaneously develop between the β phase and

TABLE 1: Wetting Transition Temperatures, Consolute Temperatures, Liquid−Air Surface Tension, and Liquid−Liquid Interfacial Tension for Methanol (2) + n-Alkanes (1)

n	x_2	T_w (°C)	CT (°C)[a]	UCST (°C)[b]	σ_{L1V}[c] (mN m^{-1})	σ_{L1L2}[c] (mN m^{-1})	b[d]
6	0.4996	7.1	34.4 (33.5)	33.7	18.1 (17.9)	0.26 (0.1)	0.447
6.25	0.5073	23.7	40.6				0.451
6.5	0.5269	31.0	43.5		19.0	0.48	0.455
6.75	0.5354	36.7	47.5				0.459
7	0.5820	47.0	51.9 (50.9)	51.0	19.5 (19.7)	0.56	0.463
7.25	0.5538	25.8	55.1				0.466
7.5	0.5714	57.0	59.1		20.4	0.82	0.469
7.75	0.5821	61.5	62.7				0.472
8	0.6008	65.0	66.0 (65.3)	65.8	21.0 (21.1)	0.98 (0.97)	0.475
8.25	0.6260	70.1	70.1				0.478
8.5	0.6175	72.5	72.9		21.6	1.33	0.480
8.75	0.6129	75.5	76.3				0.483
9	0.6570	77.2	78.3 (78.5)	79.0	22.4 (22.4)	1.47	0.485
9.25	0.6601	75.3	82.4				0.487
9.5	0.6637	75.0	85.2		23.2	1.64	0.489
9.75	0.6898	77.0	87.9				0.491
10	0.6869	75.7	90.4 (89.8)	91.0	23.2 (23.4)	1.70 (1.93)	0.493
10.25	0.7260	73.0	93.2				0.495
10.5	0.7324	66.3	96.0		23.6	1.77	0.497
10.75	0.7338	62.7	98.3				0.498
11	0.7660	61.3	100.4	102.1	23.7 (24.2)	2.0	0.499
11.25	0.7818	53.0	102.0				0.501
11.5	0.7827	47.5	105.1		24.4	2.03	0.502
11.75	0.7892	38.3	107.7				0.503
12	0.7989	12.8	110.0	111.5	25.1 (24.9)	2.26 (2.68)	0.504

[a] Values in parentheses are the CT at the concentration x_2 from ref 27. [b] From ref 27. [c] At 25 °C, values in parenthesis are from ref 30 for the liquid−air surface tension and from ref 11 for the interfacial tension. [d] From eq 1 using the polynomia in Table 2 for σ_{L1V} and σ_{L1L2}; for methanol σ_{L2V} = 22.2 mN m^{-1} (this work). The estimated errors for each property are given in the Experimental Section.

the γ phase. Typical observed pendant drops had a diameter of 2−3 mm so that the distance between the three-phase contact line and the glass walls of the container was 3.5−4 mm. The wetting regime was recorded (visual observation) after every temperature increase. Upon reaching T_w, the temperature was increased and decreased (several 0.1 °C steps in both directions) to ensure the reversibility of the transition. The CT was determined employing the same procedure described for T_w. The estimated uncertainty for both T_w and the CT is ±0.5 °C.

Determination of the Surface and Interfacial Tensions. The liquid−air surface tension for methanol and the n-alkanes (integer and noninteger n values) were determined at 25 °C ± 0.01 using a du Nouy Kruss (Model K8) tensiometer and employing the Harkins and Jordan correction.[29] The interfacial tension between the methanol- and n-alkane-rich phases were determined also at 25 °C ± 0.1 using a Kruss SITE 04 spinning drop tensiometer. The densities of each phase, necessary for the calculation of σ_{L1L2}, were measured at 25 °C employing a Sodev Inc. (Model 03D) vibrating cell densimeter. For these measurements, mixtures were prepared by weight and allowed to reach equilibrium at constant temperature (25 °C ± 0.01); samples of each phase were then carefully withdrawn to avoid concentration changes and their densities determined; here, the temperature was controlled within 0.001 °C using a Sodev Inc. thermostat (Model CT-L). The estimated errors are 5 × 10^{-5} g cm^{-3}, 0.2−0.25 and 0.1 mN m^{-1} for the densities, σ_{L1V} and σ_{L1L2}, respectively.

IV. Results and Discussion

The consolute temperatures CT and the wetting transition temperatures T_w for the 25 methanol + n-alkane mixtures studied are given in Table 1. For all mixtures studied the
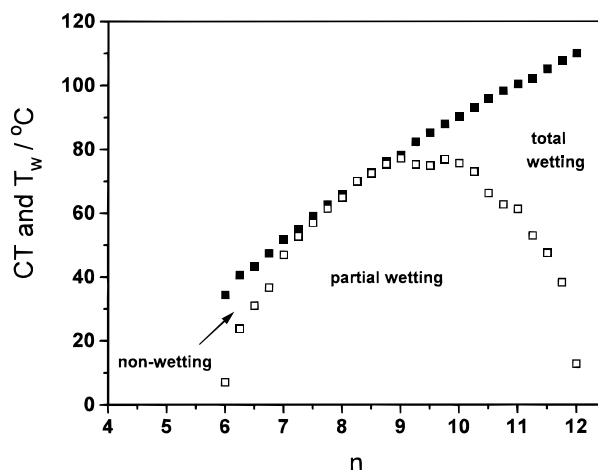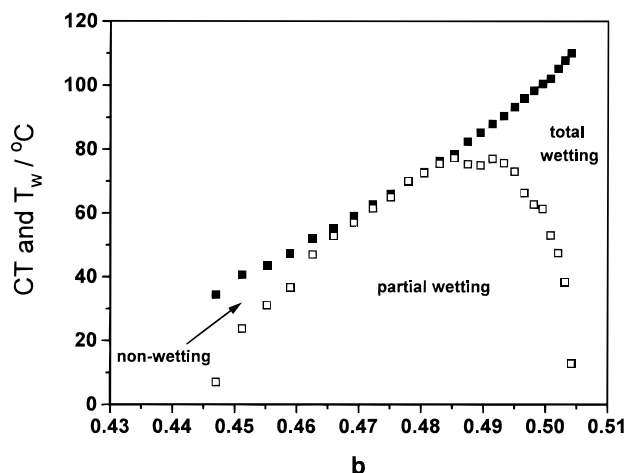

Figure 3. Consolute temperatures (■) and wetting transition temperatures (□) for methanol (2) + n-alkanes (1) as a function of n. The observed different wetting regimes are indicated. For all mixtures, the methanol rich-phase is the α or intruding phase in Figure 1a.

TABLE 2: Coefficients for the Second-Degree Polynomium $\sigma = \sum_i a_i n^i$ Fitted to the Experimental Pure n-Alkane Liquid−Air Surface Tension and the Liquid−Liquid Interfacial Tension at 25 °C[a]

	a_0	a_1	a_2	sd[b]
σ_{L1V}	5.128	2.69	−0.0875	0.23
σ_{L1L2}	−3.315	0.718	−0.0215	0.07

[a] For methanol σ_{L2V} = 22.2 mN m^{-1} (this work). [b] Standard deviation.

methanol-rich phase (L$_2$) is denser than the alkane-rich phase (L$_1$), i.e., it is the α or intruding phase in Figure 1a. The CT values at the concentrations employed here and the UCST both from ref 27 are also reported; the comparison between the two sets of CT clearly shows that the visual observation of the CT employed here is sufficient for the purposes of the present work. Also, Table 1 indicates that the CT measured here are quite close to the UCST allowing a direct comparison with the model predictions. In Figure 3, the CT are seen to increase monotonically with n; as expected, the corresponding states principle for n-alkanes[26] is followed, i.e., the binary mixture of two normal alkanes behaves as a pure liquid with a noninteger n value. In contrast with the variation of the CT with n, in Figure 3 the wetting transition temperatures T_w first increase and then decrease with n in close resemblance with the theoretical prediction in Figure 2a. To be able to display the CT and T_w data in terms of the model's language, the b values for all mixtures were calculated using eq 1 and are reported in Table 1. For this calculation polynomia of the form $\sigma = \sum_i a_i n^i$ were fitted to the liquid−air surface tension and to the liquid−liquid interfacial tension in Table 1; the resulting coefficients and the standard deviations are given in Table 2. For methanol σ_{L2V} = 22.2 mN m^{-1} which is in good agreement with the reported value of 22.07 ± 0.22 mN m^{-1} in ref 30. Both the surface and interfacial tensions in Table 1 follow the corresponding states principle as established a long time ago.[31] The evolution of the CT and T_w as a function of the model's parameter b is shown in Figure 4; the c parameter for these mixtures range from 0.01 to 0.045. Clearly, the theoretical prediction in Figure 2a is corroborated by the data in Figure 4. It appears then that the simple two order-parameter model of Perez et al.[25] is capable of producing excellent qualitative predictions; this is in contrast with one order-parameter models[1] which fail when dealing with multicomponent mixtures.[11] In Figure 2a, the highest T_w occurs where T_w = UCST curve while in Figure 4 the T_w curve goes through a maximum at a b value which is larger than that where

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Figure 4. Consolute temperatures (■) and wetting transition temperatures (□) for methanol (2) + *n*-alkanes (1) as a function of *b*, the reduced tension of the *n*-alkanes. The observed different wetting regimes are indicated. For these mixtures, the *c* parameter ranges from 0.01 to 0.045. For all mixtures, the methanol-rich phase is the α or intruding phase in Figure 1a.

$T_w \cong$ CT. This is not a failure of the model but rather the effect of a nonconstant *c* value. While in Figure 2a ($c = 0.1$) the maximum of the T_w curve occurs at $T_w =$ UCST, in Figure 2b ($c = 0.275$) this maximum is displaced toward higher *b* values; hence, the results in Figure 4 can be understood in terms of an increasing *c* value in going from $n = 6$ to $n = 12$.

As indicated in Figures 3 and 4, for $T < T_w$ the mixtures showed a partial wetting regime. For $T_w < T <$ CT the systems displayed different wetting regimes depending on the *n* or *b* value of the alkane, namely, (i) for $n = 6$ ($b = 0.447$) to $n = 8.25$ ($b = 0.478$) the observed transition was from partial wetting to a nonwetting regime, i.e., the alkane-rich phase intrudes between the methanol-rich phase and the vapor and (ii) for $n = 8.5$ ($b = 0.48$) to $n = 12$ ($b = 0.504$) the transition was from partial to total wetting, i.e., the methanol-rich phase intrudes between the alkane-rich phase and the vapor. In other words, at T_w the observed dihedral angle θ in Figure 1a reached a value of 180° for $6 \leq n \leq 8.25$ and a zero value (as in Figure 1a) for $8.5 \leq n \leq 12$. This inversion in the nature of the wetting phase is in agreement with that reported in ref 11 for methanol + *n*-hexane and + *n*-dodecane at 25 °C and with the prediction of the model[25] in Figure 2a. In general, we observed that the methanol-rich α phase wets the glass walls of the container better that the alkane-rich β phase, producing the meniscus curvatures displayed in Figure 1a; this causes for example that for $n = 12$ at $T > T_w$, the β phase is completely surrounded by the α phase. The model of Perez et al. predicts a change in the order of the wetting transition as the reduced tension of the alkanes *b* is increased. No attempt was made here to determine this order, and hence it is not possible to assert the performance of the model in this respect. However, given the approximations involved in the model, it is almost for sure that the order of the wetting transitions in Figure 4 are not correctly described; an indication that this might be the case is that for C_7F_{14} + 1-alcohol mixtures (middle section of Figure 2c), the model predicts second-order transitions while experimentally first-order transitions were found.[9] To what extent the predicted order of the transitions in Figure 2a are realistic or a mere artifact of the approximations used can be tested both experimentally and developing a more realistic theoretical approach. In particular, a semiempirical version of density functional theory where the intermolecular potentials are adjusted to match the surface tensions of the pure components and the interfacial tension between coexisting phases, is expected to be a better choice.

According to Figure 2a, there are *b* values for which binary mixtures can show either nonwetting or total wetting at all temperatures up to their UCST; this situation was not found here but from Figures 3 and 4 working with methanol + *n*-alkane mixtures with $n < 6$ and $n > 12$ would provide a test for this prediction. For $8.25 < n < 8.5$, the difference between the CT and the T_w would be less than 0.4 °C; hence, with our experimental setup for mixtures in this *n* range it is not possible to determine conclusively if the partial wetting regime will evolve to a nonwetting or to a total wetting regime before reaching the CT. Furthermore, it is possible that for $8.25 < n < 8.5$ a mixture would display a partial wetting regime up to the UCST as is predicted by the model (see Figure 2a). Testing this prediction and studying in more detail the structure of the liquid−air interface for *n*-alkanes with $8 \leq n \leq 9$ could be done using ellipsometry. Work on this direction is currently under way.

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