Oil Chain-Length Effect on Wetting Transitions in Ternary Water + Oil + Surfactant Mixtures

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In the three-liquid-phase coexisting region of the system water + tetradecane + diethylene glycol monohexyl ether (C_6E_2), the middle surfactant-rich phase undergoes a sequence of wetting transitions comprising nonwetting → partial wetting → complete wetting at the interface of oil-rich and water-rich phases as the temperature is raised from its lower critical consolute temperature toward its upper critical consolute temperature (*J. Chem. Phys.* **1993**, *98*, 4830). In this study, the effect of oil chain length on the wetting transition in the system water + C_6E_2 + oil (dodecane, decane, and octane) is investigated by interfacial tension measurements. A sequence of wetting transitions, nonwetting → partial wetting → complete wetting, of the middle C_6E_2-rich phase is observed in all three systems while the system temperature increases. A decrease of the oil chain length in the system water + C_6E_2 + oil would make the three-liquid-phase body shrink and lead the system to approach a tricritical point. The effect of the system water + C_6E_2 + oil approaching its tricritical point on the wetting behavior of the middle C_6E_2-rich phase is discussed.

I. Introduction

The phase behavior of ternary water + oil + surfactant C_iE_j mixtures is well understood,[1,2] where C_iE_j stands for the nonionic surfactant $CH_3(CH_2)_{i-1}(OCH_2CH_2)_jOH$. Within a certain temperature range, a ternary system comprising water + oil + surfactant C_iE_j may separate into three coexisting liquid phases (i.e., an excess oil α phase and an excess water γ phase coexist with a middle β phase containing most of the surfactant C_iE_j and appreciable amounts of oil and water).
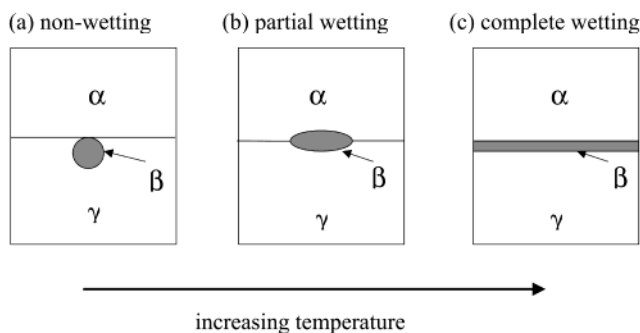
The wetting behavior of the middle β phase at the αγ interface has been an intensive research topic both experimentally[3−16] and theoretically[17] because of its particular importance in many industrial applications. In general, the wetting behavior of the middle β phase at the αγ interface can be classified into three categories according to its contact angle θ, as defined in Figure 1: (i) θ = 180° (i.e., the middle β phase does not wet the αγ interface, exhibiting nonwetting behavior), (ii) 0° < θ < 180° (i.e., the middle β phase partially wets the αγ interface, exhibiting partial-wetting behavior), and (iii) θ = 0° (i.e., the middle β phase spreads over the αγ interface, exhibiting complete-wetting behavior).

When the surfactant of these ternary systems has a long chain length,[18] for example, C_8E_3, the middle β phase almost always forms a lenticular drop floating at the αγ interface, as shown in Figure 2b. That is, the β phase always exhibits partial-wetting behavior. Whereas in the systems with a surfactant of short chain length,[18,19] for example, C_4E_1, the middle β phase always forms a thin film (i.e., complete-wetting behavior) separating the other two phases α and γ, as shown in Figure 2c. For medium chain-length surfactants,[3−16] for example, C_6E_j, the middle β phase exhibits a wetting transition between partial wetting and complete wetting.

In addition, it was found that the middle β phase of the system water + tetradecane + C_6E_2 exhibits a sequence of wetting
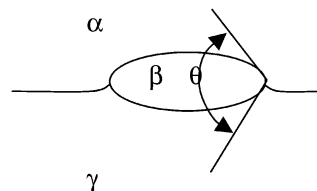

Figure 1. Definition of the contact angle θ in a three-phase coexisting system.

increasing temperature

Figure 2. Variation of the wetting behavior of the β phase in the system water + tetradecane + C_6E_2 as a function of temperature: (a) a nonwetting β phase, (b) a partial-wetting β phase, and (c) a complete-wetting β phase.

transitions, nonwetting → partial wetting → complete wetting, at the αγ interface by simply increasing the system temperature from its lower critical solution temperature ($T_{c,l}$) to its upper critical solution temperature ($T_{c,u}$),[8] as schematically shown in Figure 2. Note that the $T_{c,l}$ (or $T_{c,u}$) is the lowest (or highest) temperature where γ (or α) and β phases merge into a single phase. Moreover, this sequence of wetting transitions was also observed at the air−liquid interface in the two-liquid-phase coexisting regions of the system water + tetradecane + C_6E_2 by simply varying the system composition.[12]

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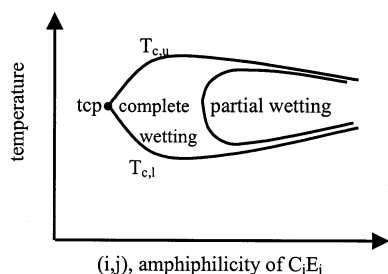
Figure 3. Schematic plot of the partial-wetting cusp within the three-liquid-phase temperature interval (between upper critical consolute temperature $T_{c,l}$ and lower critical consolute temperature $T_{c,u}$) of the system water + octane + C_iE_j by varying the amphiphilicity of C_iE_j.[14] ● stands for a tricritical point (tcp).

Figure 4. Schematic plot of the partial-wetting cusp within the three-liquid-phase temperature interval (between upper critical consolute temperature $T_{c,l}$ and lower critical consolute temperature $T_{c,u}$) of the system water + cyclohexane + C_iE_j by adding an alcohol.[15] ● stands for a tricritical point (tcp).

Consider the phase behavior of ternary systems of the type water + oil + nonionic surfactant C_iE_j. There exists a tricritical point (tcp), defined as the point at which three coexisting liquid phases simultaneously become identical, in this ternary mixture. In other words, the tricritical point results from the merger of upper and lower critical end points. Kahlweit and co-workers[14,20,21] pointed out that the tricritical point of the system water + oil + nonionic surfactant C_iE_j can be located by four different paths:

(1) varying the amphiphilicity of the surfactant within a homologous series;

(2) adding an appropriate electrolyte or alcohol;

(3) changing the hydrophobicity of the oil within a homologous series; and

(4) increasing the pressure.

Along path 1, Kahlweit and co-workers[13,14] observed that, on the basis of the variation of the amphiphilicity of C_iE_j, C_4E_1, C_5E_2, C_6E_3, and C_8E_4, in the system water + octane + C_iE_j the partial-wetting cusp is concluded and schematically shown in Figure 3. Near the tricritical point, the middle β phase is weakly structured and always completely wets the $\alpha\gamma$ interface in the entire three-liquid-phase temperature interval (between $T_{c,l}$ and $T_{c,u}$). As the amphiphilicity of surfactant C_iE_j, (i, j), is gradually increased (C_4E_1, C_5E_2, C_6E_3, and C_8E_4), the wetting behavior of the middle β phase changes from complete wetting to partial wetting.[14]

However, along path 2, Kahlweit and co-workers[15] also performed experiments on the wetting behavior of the middle β phase in two systems: water + cyclohexane + C_8E_4 and water + cyclohexane + $C_{10}E_5$. These systems were driven to approach their tricritical points by adding ethanol. These authors also found that an interfacial transition between partial wetting and complete wetting of the β phase always occurs at the $\alpha\gamma$ interface. The partial-wetting cusp in the system water + cyclohexane + C_iE_j + ethanol is schematically shown in Figure 4.[15] Again, near the tricritical point, the middle β phase completely wets the $\alpha\gamma$ interface in the entire three-liquid-phase temperature interval (between $T_{c,l}$ and $T_{c,u}$), similar to the case of varying the amphiphilicity of C_iE_j.[15]

Recently, Kahlweit and co-workers[16] also observed the variation of wetting behavior of the middle β phase in the system water + alkylbenzene + C_iE_j along path 3 by using different oil chain lengths and along path 1 by changing the amphiphilicity of surfactant C_iE_j. However, this study focuses only on the wetting behavior of the β phase at the mean temperature of the three-phase body. They consistently found that the β phase always exhibits a wetting transition from partial wetting to complete wetting as the system is driven to approach its tricritical point either by varying the oil chain length or by varying the amphiphilicity of C_iE_j.[16]
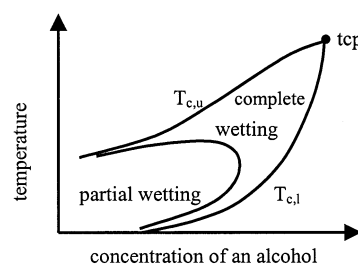
On the basis of Kahlweit and co-workers'[13−16] study of these three different paths, 1 to 3, of driving a water + oil + C_iE_j mixture to approach its tricritical point, one can conclude that the approach to the tricritical point is inevitably associated with a transition between partial wetting and complete wetting of the β phase that occurs at the $\alpha\gamma$ interface.

The purpose of this study is to explore the effect of the oil chain length in the water + oil + C_6E_2 mixture on the wetting transition. Path 3 was adopted to drive the system to approach its tricritical point by a decrease in oil chain length. In this article, we present experimental results on the phase diagram and the interfacial tensions for the following three systems: water + dodecane + C_6E_2, water + decane + C_6E_2, and water + octane + C_6E_2. The experimental procedures are described in the next section. The experimental results and further discussion are given in section III. The critical consolute temperatures of these three systems are determined from the fish-shaped phase diagram. According to the results for the interfacial tension, it is found that the β phase does exhibit a sequence of wetting transitions, nonwetting → partial wetting → complete wetting, for all three systems. Our result indicates that near the tricritical point the middle β phase *partially* wets the $\alpha\gamma$ interface in the entire three-liquid-phase temperature interval.

II. Experiments

All of the hydrocarbons—dodecane (99%), decane (99%), and octane (99%)—and the nonionic surfactant diethylene glycol monohexyl ether (C_6E_2) of 98% purity were products of Merck Chemical Co. The surfactant C_6E_2 was fractionally distilled under reduced pressure until a purity of >99.5% was attained, as determined by gas chromatography. Water was purified by a Millipore Milli-RO PLUS 10 and a Milli-Q system with a resistivity >18.2 MΩ cm.

The samples were prepared in a 1-cm diameter glass test tube at a fixed water/oil weight ratio (1/1) with varying surfactant concentration. The samples were then placed in a water bath for at least several hours or for sometimes up to several days to allow the system to reach equilibrium. The temperature stability of the water bath was better than ±0.005 K. To ensure thorough mixing, the samples were shaken vigorously several times before and during the equilibration process. After equilibrium was reached, the number of liquid phases for each sample was recorded at different temperatures. The phase boundary was systematically searched for each surfactant concentration by locating the temperature at which the number of liquid phases changed.

A spinning-drop tensiometer (Krüss, SITE 04, Germany) was used to measure the interfacial tensions, which were used to

locate a wetting transition when the relationship of three interfacial tensions switches between Antonow's rule[22] and Neumann's inequality.[23] To improve the accuracy of the tension measurement, an enhanced video-microscopy system was incorporated into the spinning-drop tensiometer to determine the radius of the spinning droplet. An image of the spinning droplet was taken directly from a B/W CCD camera (Sony, XC-77) through a traveling microscope and then digitized into 480 × 512 pixels by an image digitizer processor (Data Translation, DT2861) installed in a personal computer. Some interfacial tension results had been double-checked by our homemade pendant drop system.[24] The density for each liquid phase was measured by using a vibrating-tube densiometer (Paar DAM 58, Austria).

III. Results and Discussion

The experimental results on the fish-shaped phase diagrams of the three systems water + dodecane + C_6E_2, water + decane + C_6E_2, and water + octane + C_6E_2 are shown in Figure 5, where the symbols 3ϕ, 2ϕ, and 1ϕ stand for the three-, two-, and one-liquid-phase regions, respectively. The three-liquid-phase region is slightly enlarged as the oil chain length increases. The highest and the lowest temperatures of the three-liquid-phase region correspond to the upper ($T_{c,u}$) and the lower ($T_{c,l}$) critical consolute temperatures, respectively. Table 1 lists the upper and the lower critical consolute temperature of these three systems, which are consistent with the results of Kahlweit and Strey.[1] In this study, the interfacial tension measurements were restricted at temperatures within the three-coexisting-liquid-phase region of the system water + alkane + C_6E_2.

According to the Gibbs phase rule, there are only two degrees of freedom for a three-coexisting-liquid-phase ternary system. If one more system parameter, for example, the system pressure, is fixed, then there is only one degree of freedom left. In this study, all of our experiments were performed in the three-liquid-phase coexisting region of the ternary system water + alkane + C_6E_2 under atmospheric pressure. As a consequence, properties such as density and and interfacial tension as well as the wetting behavior uniquely depend on temperature. We therefore simply adjusted the system temperature to search for the wetting transition at liquid−liquid interfaces in the three-coexisting-liquid-phase region of the system H_2O + alkane + C_6E_2.

The experimental results of interfacial tension as a function of temperature for three systems, water + dodecane + C_6E_2, water + decane + C_6E_2, and water + octane + C_6E_2, are shown in Figure 6. The occurrence of a wetting transition[25] can be verified by switching the relationship of three interfacial tensions $\sigma_{\alpha\beta}(\diamond)$, $\sigma_{\alpha\gamma}(\bigcirc)$, and $\sigma_{\beta\gamma}(\triangle)$ between Antonow's rule[22] and Neumann's inequality.[23] When the system is approaching its upper critical consolute temperature, the β phase undergoes a wetting transition from partial wetting to complete wetting. That is, the relationship of three interfacial tensions $\sigma_{\alpha\beta}$, $\sigma_{\alpha\gamma}$, and $\sigma_{\beta\gamma}$ switches from $\sigma_{\alpha\beta} + \sigma_{\beta\gamma} > \sigma_{\alpha\gamma}$ to $\sigma_{\alpha\beta} + \sigma_{\beta\gamma} = \sigma_{\alpha\gamma}$. According to the experimental results of interfacial tension near $T_{c,u}$, as shown in Figure 6, the wetting transition temperatures for three systems H_2O + dodecane + C_6E_2, H_2O + decane + C_6E_2, and H_2O + octane + C_6E_2 are found to be 32.5, 22.9, and 13.8 °C, respectively. Since this wetting transition is close to its upper critical temperature, we therefore define this transition temperature as the upper wetting transition temperature, $T_{w,u}$.

It should be noted that the upper wetting transition temperature for the system H_2O + octane + C_6E_2 was determined by
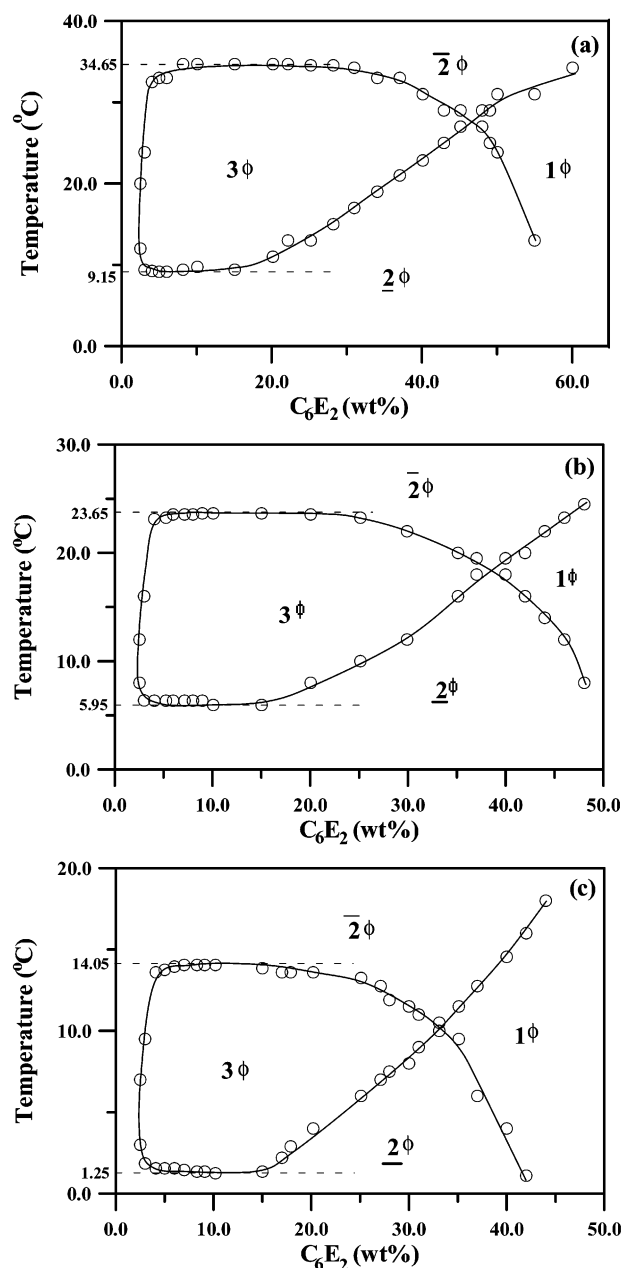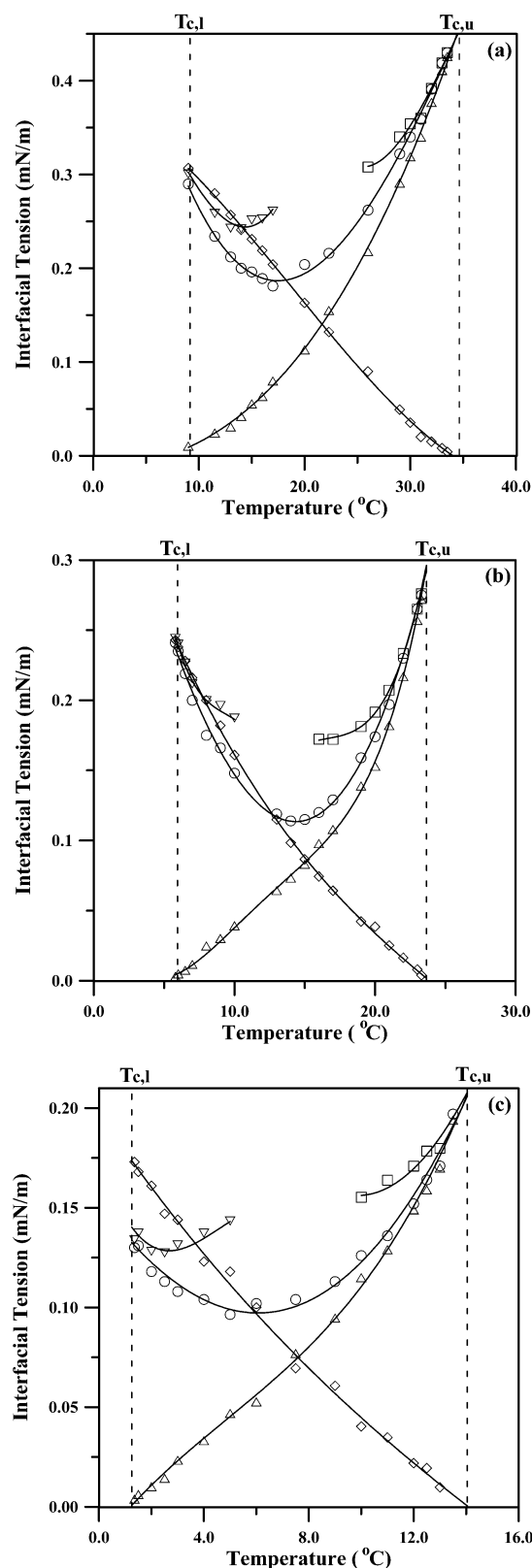

Figure 5. Fish-shaped phase diagrams at a constant water/oil weight ratio (1:1) as a function of temperature for three systems: (a) water + dodecane + C_6E_2; (b) water + decane + C_6E_2; and (c) water + octane + C_6E_2.

TABLE 1: Upper and the Lower Critical Consolute Temperatures of the Water + Alkane + C_6E_2 Systems

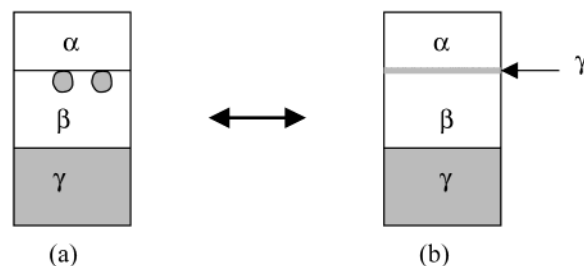| system	upper critical temp $T_{c,u}$ (°C)	lower critical temp $T_{c,l}$ (°C)
water + octadecane + C_6E_2[b]	75.73	a
water + hexadecane + C_6E_2[b]	60.34	a
water + tetradecane + C_6E_2[b]	46.23	9.86
water + dodecane + C_6E_2	34.65	9.15
water + decane + C_6E_2	23.65	5.95
water + octane + C_6E_2	14.05	1.25

[a] Lower critical consolute temperature does not exist. [b] Chen and Yan (1993).[8]

direct visual observation.[4] We were unable to use the spinning-drop tensiometer to measure the interfacial tension $\sigma_{\alpha\beta}$ for system temperature >13.5 °C simply because the system is too close to its upper critical consolute temperature of 14.05 °C.

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Figure 7. Schematic illustration of the γ-phase wetting transition. (a) Partial-wetting γ phase and (b) complete-wetting γ phase at the $\alpha\beta$ interface.

Obviously, this finding is consistent with the prediction of the critical-point wetting theory of Cahn[26] and Ebner and Saam.[27] That is, when a three-phase system is brought close to a critical end point, a transition from a nonzero contact angle (partial wetting) to a zero contact angle (complete wetting) must occur. The above results show that the wetting transition occurs as the temperature is increased toward the upper critical consolute temperature of the system. It is natural to ask whether another wetting transition occurs as the temperature is decreased toward the lower critical consolute temperature of the system.

As we mentioned above, for the system H_2O + tetradecane + C_6E_2, there does exist another wetting transition from partial wetting to nonwetting as the temperature decreases.[8] The most intriguing behavior is that this transition between partial wetting and nonwetting can also be identified as a γ-phase wetting transition. The γ-phase wetting transition is a transition between suspended beads of the γ phase at the $\alpha\beta$ interface and an intruding γ layer separating the α and β phases, as schematically illustrated in Figure 7. Again, this γ-phase wetting transition also follows the prediction of the critical-point wetting theory.[26,27]
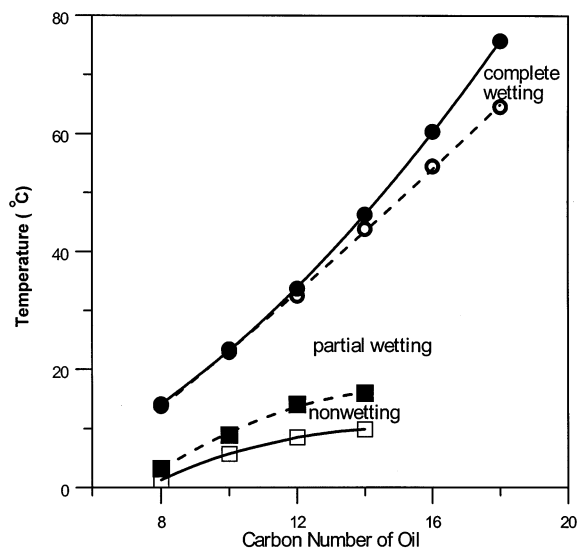
It is plausible to expect the occurrence of the wetting transition from partial wetting to nonwetting as the temperature decreases in all three systems H_2O + dodecane + C_6E_2, H_2O + decane + C_6E_2, and H_2O + octane + C_6E_2 since the system H_2O + tetradecane + C_6E_2 exhibits such a transition as the temperature decreases.

Alternatively, the γ-phase wetting transition can be interpreted in terms of the interfacial tension. When the β phase exhibits a wetting transition between partial wetting and nonwetting at the $\alpha\gamma$ interface, the relationship of the interfacial tension also demonstrates a transition between $\sigma_{\beta\gamma} + \sigma_{\alpha\gamma} > \sigma_{\alpha\beta}$ and $\sigma_{\beta\gamma} + \sigma_{\alpha\gamma} = \sigma_{\alpha\beta}$. According to our experimental results of interfacial tension, there indeed exists the wetting transition between the partial wetting and the nonwetting β phases for all three systems H_2O + dodecane + C_6E_2, water + decane + C_6E_2, and water + octane + C_6E_2, and the lower wetting transition temperatures ($T_{w,l}$) are, respectively, 14.05, 8.9, and 3.2 °C.

In summary, our experimental results for interfacial tension confirmed that the middle β phase of the systems water + dodecane + C_6E_2, water + decane + C_6E_2, and water + octane + C_6E_2 exhibits a sequence of interfacial phase transitions from nonwetting $\rightarrow$ partial wetting $\rightarrow$ complete wetting at the $\alpha\gamma$ interface as the temperature increases. The temperature difference between the upper critical consolute point and the transition temperature between the partial-wetting and complete-wetting β phases, $\Delta T = T_{c,u} - T_{w,u}$, decrease as the oil chain length decreases. However, the temperature difference $\Delta T = T_{c,l} - T_{w,l}$ also decreases as the oil chain length decreases, as shown in Figure 8.

If the oil chain length is further decreased, then the system is further driven to approach its tricritical point. When the oil

Figure 6. Variation of interfacial tension as a function of temperature for three systems: (a) water + dodecane + C_6E_2; (b) water + decane + C_6E_2; and (c) water + octane + C_6E_2. $\sigma_{\alpha\gamma}$, $\bigcirc$; $\sigma_{\alpha\beta}$, $\Diamond$; $\sigma_{\beta\gamma}$, $\triangle$; $\sigma_{\alpha\gamma}$ + $\sigma_{\beta\gamma}$, $\triangledown$; and $\sigma_{\beta\gamma}$ + $\sigma_{\alpha\beta}$, $\square$.

The reflectivity values of the α and β phases are too close to each other, which makes it impossible to distinguish any spinning drop of the α phase from that of the β phase in the tensiometer.

Figure 8. Wetting behavior of the β phase within the three-liquid-phase temperature interval (between $T_{c,l}$ and $T_{c,u}$) of the system water + alkane + C_6E_2 as a function of oil chain length. $T_{c,u}$, ●; $T_{c,l}$, □; $T_{w,u}$, ○; and $T_{w,l}$, ■.

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is replaced by heptane, its lower critical consolute temperature is below 0 °C. There is no lower critical consolute temperature for such a system since the aqueous phase freezes before its lower critical consolute temperature is reached. However, Figure 8 illustrates that the upper (or lower) wetting transition temperature is closer to its upper (or lower) critical consolute temperature as the oil chain length gets smaller. Moreover, there is a tendency for the upper (or lower) wetting transition temperature almost to merge into the upper (or lower) critical consolute temperature at small oil chain lengths. It is therefore believed that the middle β phase of the mixture water + C_6E_2 + alkane only partially wets the $\alpha\gamma$ interface near its tricritical point, if it exists. This finding is different from that of Kahlweit and co-workers,[13-16] who found a complete-wetting β phase near the tricritical point of water + C_iE_j + oil mixtures.