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Direct Observation of Phase Separation in Microemulsion Networks

A. Bernheim-Groswasser,† T. Tlusty,‡ S. A. Safran,‡ and Y. Talmon*,†

Department of Chemical Engineering, Technion-Israel Institute of Technology, Haifa 32000, Israel, and Department of Materials and Interfaces, Weizmann Institute of Science, Rehovot 76100, Israel

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Direct evidence by cryogenic temperature transmission electron microscopy shows the existence of networks in microemulsions near the two-phase closed loops. Networks formed by interconnected oil-swollen cylinders were observed in the water-rich regions of the phase diagram of the $C_{12}E_5$ /water/*n*-octane system. The coexisting phases within the loops were shown to be concentrated and dilute networks. Similar micellar networks were also found in the binary system. These observations substantiate the suggested theoretical link between the structural bicontinuity and the unique phase separation and criticality of microemulsions: All these regimes are governed by the entropic attraction between network junctions.

Introduction

Bicontinuous, multiply connected shapes are a widespread, almost generic feature of microemulsions (ME) and are associated with ultralow interfacial tensions. The typical spongelike microstructure of these phases consists of two-dimensional layers of amphiphiles separating oil and water domains that are both continuous.[1] These *dense symmetric sponges* (at almost equal volume fractions of oil and water) have been observed mainly in the vicinity of the inversion temperature ($\bar{T}$), where the preferred curvature of the amphiphile monolayer toward water or oil (the spontaneous curvature) is small.[2,3] The bicontinuity disappears at higher spontaneous curvatures, away from $\bar{T}$, where the monolayers tend to form disconnected globules containing water or oil surrounded by a continuous domain of the other component.[4−7]

Preliminary measurements by self-diffusion NMR and conductivity suggested the existence of connected structures at temperatures relatively far from $\bar{T}$, where one would have expected a phase of disconnected globules.[8,9] A recent theory predicted that those structures are *dilute, highly asymmetric networks* formed of interconnected semiflexible cylinders.[10] Moreover, it suggested a direct link between the structural bicontinuity and the unique thermodynamics of ME: The generic two-phase closed loops, their critical points, and the subsequent formation of the three-phase body (Figure 1A[1]) are all explained as a direct result of an effective entropic attraction induced by the network fluctuations. This attraction governs ME from dense sponges down to dilute (even *micellar)* networks; all these regimes can be understood as different limits of the same network picture.

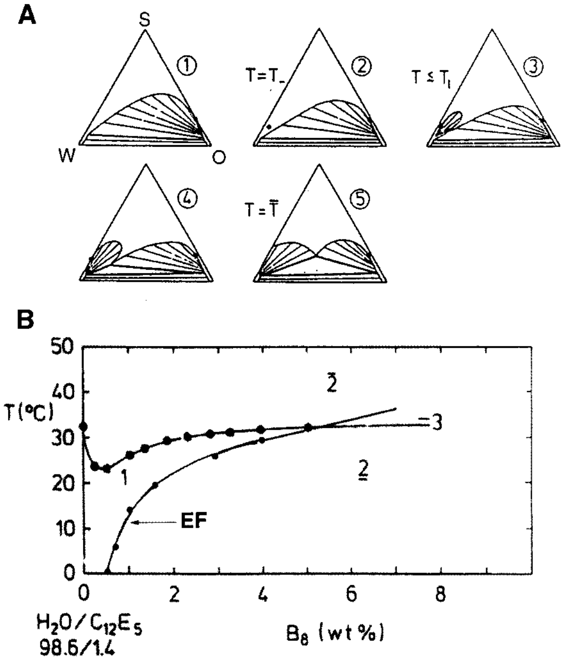

Figure 1. (A) Evolution of the three-phase triangles (water (W), oil (O), and surfactant (S)) with rising temperature, demonstrating the evolution of the isothermal closed loops, their critical points, and the subsequent formation of the three-phase body ($T = T_l$). (B) Evolution of the one-phase channel (1) defined by the EF line $(\underline{2})$ as we measured (small dots), and line of critical points $(\overline{2})$ (dots after Kahlweit et al.[1]), for fixed $C_{12}E_5$/water weight ratio of $\phi_s/\phi_w = 1.4/98.6$, as function of temperature and *n*-octane weight percent, ϕ_o.

Here we report the first direct evidence, by cryogenic temperature transition electron microscopy (cryo-TEM) imaging of the existence of these dilute, semiflexible networks in the nonionic, ternary ME, $C_{12}E_5$/water/*n*-octane, in the water-rich corner of the phase diagram. Disconnected spheres or even cylinders were indeed

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* To whom all correspondence should be addressed.

† Technion-Israel Institute of Technology.

‡ Weizmann Institute of Science.

(1) Kahlweit, M.; Strey, R.; Busse, G. *Phys. Rev. E* **1993**, *47*, 4197.

(2) (a) Scriven, L. E. In *Micellization, Solubilization and Microemulsion*; Mittal, K., Ed.; Plenum: New York, 1977. (b) De Gennes, P. G.; Taupin, C. *J. Phys. Chem.* **1982**, *86*, 2294.

(3) Kahlweit, M.; Strey, R.; Haase, D.; Kunieda, H.; Schmeling, T.; Faulhaber, B.; Borkovec, M.; Eicke, H.-F.; Busse, G.; Eggers, F.; Funck, Th.; Richmann, H.; Magid, L.; Söderman, O.; Stilbs, P.; Winkler, J.; Dittrich, A.; Jahn, W. *J. Colloid Interface Sci.* **1987**, *118*, 436.

(4) Strey, R. *Colloid Polym. Sci.* **1994**, *272*, 1005.

(5) Leaver, M. S.; Olsson, U.; Wennerström, H.; Strey, R. *J. Phys. II (France)* **1994**, *4*, 515.

(6) Strey, R.; Glatter, O.; Schubert, K. V.; Kaler, E. W. *J. Chem. Phys.* **1996**, *105*, 1175.

(7) Kahlweit, M.; Strey, R.; Sottmann, T.; Busse, G.; Faulhaber, B.; Jen, J. *Langmuir* **1997**, *13*, 2670.

(8) Strey, R. Unpublished.

(9) Lipgens, S.; Schübel, D.; Schlicht, L.; Spilgies, J. H.; Ilgenfritz, G.; Eastoe, J.; Heeman, R. K. *Langmuir* **1998**, *14*, 1041.

(10) Tlusty, T.; Safran, S. A.; Menes, R.; Strey, R. *Phys. Rev. Lett.* **1997**, *78*, 2616.

10.1021/la990301q CCC: $18.00

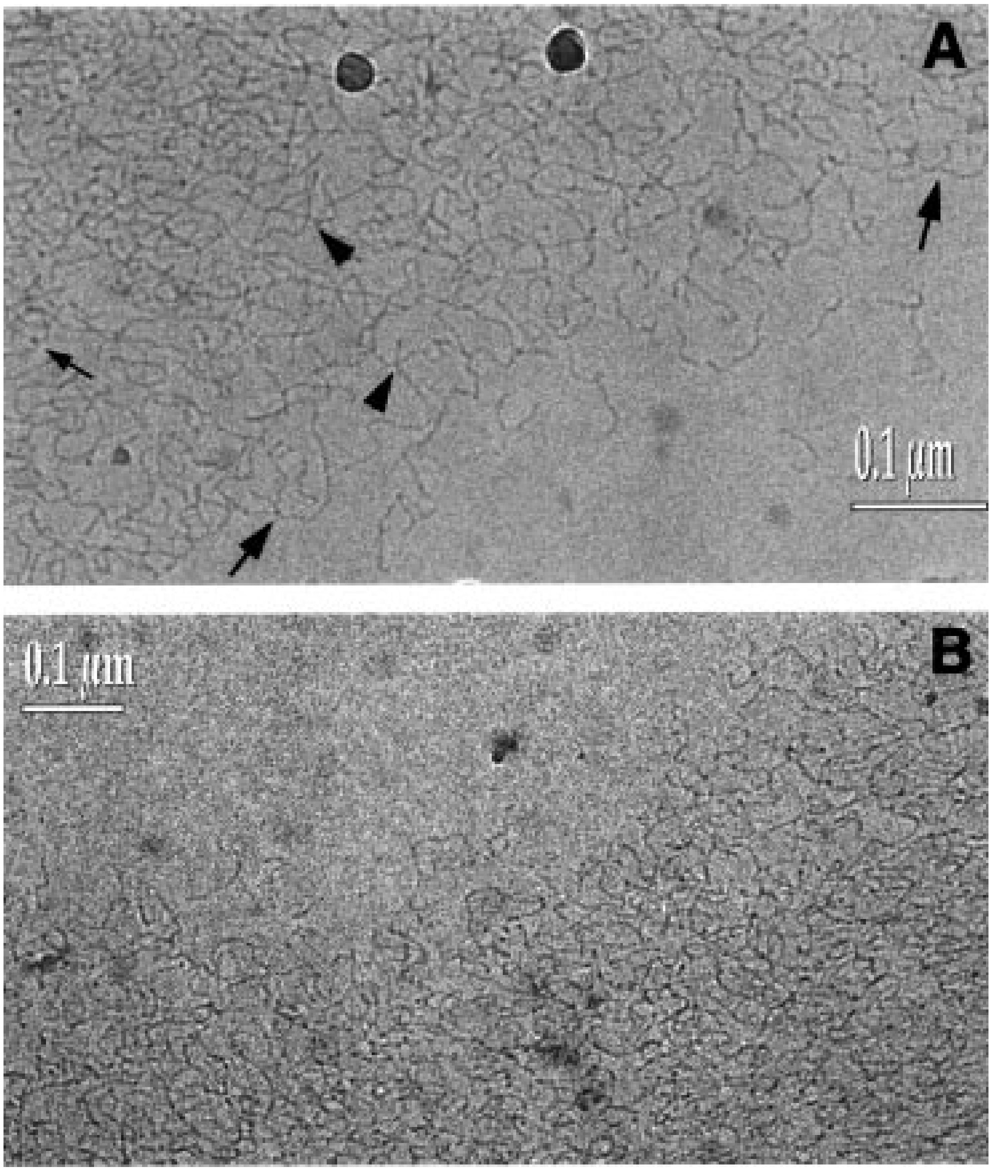

Figure 2. (A) Cryo-TEM image of a microemulsion at $\phi_o = 3\%$ and $T = 30$ °C showing swollen oil-in-water cylindrical tubes. One can identify 3-fold junctions (large arrows), entanglement points, or 4-fold junctions (arrowheads). Black dots indicate cylinder ends pointing outside the image plane or a folded thread (noted by a small arrow). (B) Cryo-TEM image of a microemulsion at $\phi_o = 0.7\%$ and $T = 23$ °C. The swollen oil-in-water cylindrical tubes are thinner in comparison to Figure 2A due to the lower oil content.

observed when lowering the temperature increased the spontaneous curvature. However, we find that all the important thermodynamic links between the symmetric, bicontinuous phase at temperatures close to $\bar{T}$ and those phases with finite spontaneous curvatures at temperatures relatively far from $\bar{T}$ occur via network topology. These networks are observed in the proximity of both the two-phase closed loop and the emulsification failure (EF) line, where they are in equilibrium with a rejected excess phase.[11] Moreover, the phase separation within the closed loop results in coexistence of concentrated and dilute networks. The three-phase equilibrium of the symmetric sponge ME with excess water/oil phases arises from the confluence of the EF instability and the two-phase loops,[10,12] both of which involve network structures. All these observations experimentally substantiate the theoretical link between ME phase separation, the entropic attraction, which leads to the formation of networks at temperatures away from $\bar{T}$, and the symmetric, bicontinuous phase at $\bar{T}$.[10] In the dilute limit, we observed similar network topology in the corresponding binary $C_{12}E_5$/water system.[13]

Experimental Section

Materials. We used $C_{12}E_5$ (Nikko, Japan) that had been stored under nitrogen atmosphere at about −20 °C, *n*-octane (Riedel-de Haën, Germany, 99% purity), and Millipore water. The solvents and the surfactant were used without further purification. Solutions were prepared at constant surfactant-to-water weight ratio of $\phi_s/\phi_w = 1.4/98.6$ at various *n*-octane contents ($\phi_o \leq 3\%$) and temperatures.

Cryo-TEM. Specimens were prepared in a controlled environment vitrification system (CEVS[14]), at controlled temperature and relative humidity to avoid loss of volatile components (water and *n*-octane). The microemulsion drop was placed on a TEM grid covered by a holey carbon film. The drop was then blotted with filter paper to form a thin liquid film on the grid, which was

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[11] Safran, S. A.; Turkevich, L. A. *Phys. Rev. Lett.* **1983**, *50*, 1930.

[12] Kahlweit, M.; Strey, R.; Busse, G. *J. Phys. Chem.* **1990**, *94*, 3881.

[13] Bernheim-Groswasser, A.; Wachtel, E.; Talmon, Y. To be submitted for publication.

[14] Bellare, J. R.; Davis, H. T.; Scriven, L. E.; Talmon, Y. *Electron Microsc. Technol.* **1988**, *10*, 87.

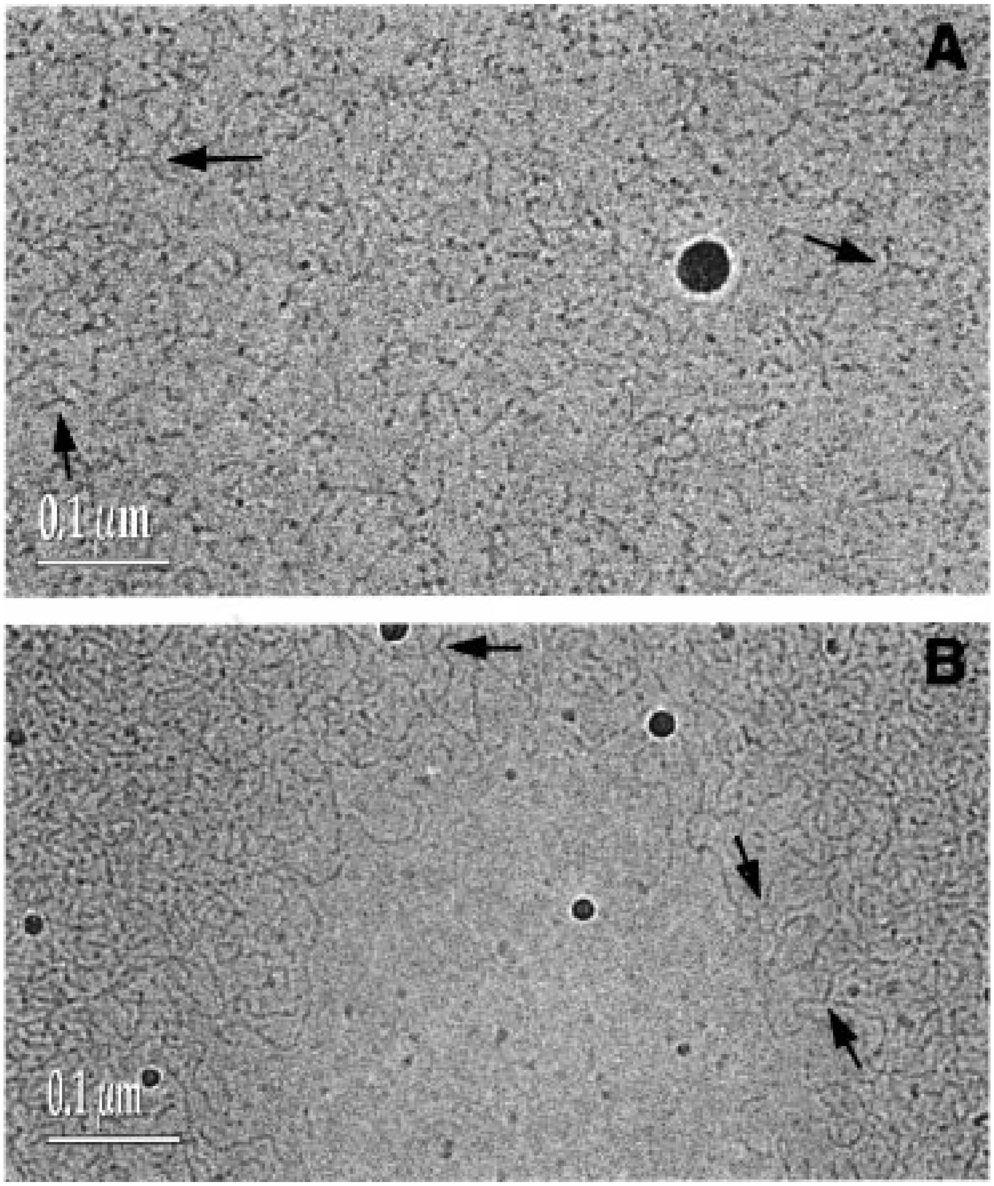

Figure 3. Cryo-TEM images of coexisting microemulsion networks at $T = 24.4$ °C: (A) dilute (high water content) and (B) concentrated (low water content) phase. In both images one can identify 3-fold junctions (arrows).

then immediately plunged into liquid ethane at its freezing temperature. The vitrified specimens were observed in a Philips CM120 transmission electron microscope at an accelerating voltage of 120 kV. The specimens were kept in the microscope at better than −175 °C by an Oxford Instruments cryo-specimen holder. Low-electron-dose images were digitally recorded by a Gatan MultiScan 791 CCD camera at about 4 μm underfocus to enhance phase contrast.

Results and Discussion

The ME network topology was observed by cryo-TEM in a large region that was probed in the one-phase channel defined by the EF line and the two-phase boundary as shown in Figure 1B[1]. Only at lower temperatures, where the spontaneous curvature is large, was a transition to disconnected globules observed. Following ref 1 we worked at a fixed $C_{12}E_5$/water weight ratio of $\phi_s/\phi_w = 1.4/98.6$, at various temperatures and *n*-octane weight percent, ϕ_o. Closed, two-phase coexistence loops are found[1] throughout the temperature regime where the upper phase boundary line ($\bar{2}$) is nonmonotonic. These loops first appear at the minimum of $\bar{2}$ (which we refer to as $T = T_{-}$) and then expand as temperature becomes higher. Their evolution as function of temperature is presented in Figure 1A, where the dotted line is a cut at fixed $C_{12}E_5$/water weight ratio. The width of the loop between its two critical points is approximately the difference in oil content ϕ_o, between the two branches of the $\bar{2}$ line. Another phase separation occurs at the EF line ($\underline{2}$) where the ME coexists with excess, almost pure oil, phase.[15] The single-phase channel bounded by these two lines shrinks as one increases the oil content and vanishes at the critical end point ($T_l = 31.8$ °C) where the two lines intersect to form the three-phase body.[12]

According to the network model,[10] this unique phase-behavior is intimately related to the interconnected structure of the ME in this region: The ternary system forms networks of oil-in-water cylindrical tubes (of radius $r \sim \phi_o/\phi_s$) connected by 3-fold junctions. The closed loops

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[15] This defines a plane through the phase prism that cuts the binodal surface ($\bar{2}$) close to the line of critical points. Throughout the temperature regime where the binodal line ($\bar{2}$) is nonmonotonic the isothermal cuts exhibit closed two-phase coexistence loops. These loops disappear at the double critical point located at the minimum of the binodal surface and the line of critical points. The EF surface located at the $\underline{2}$ line where the ME coexists with an excess phase, thus defining a single-phase channel.

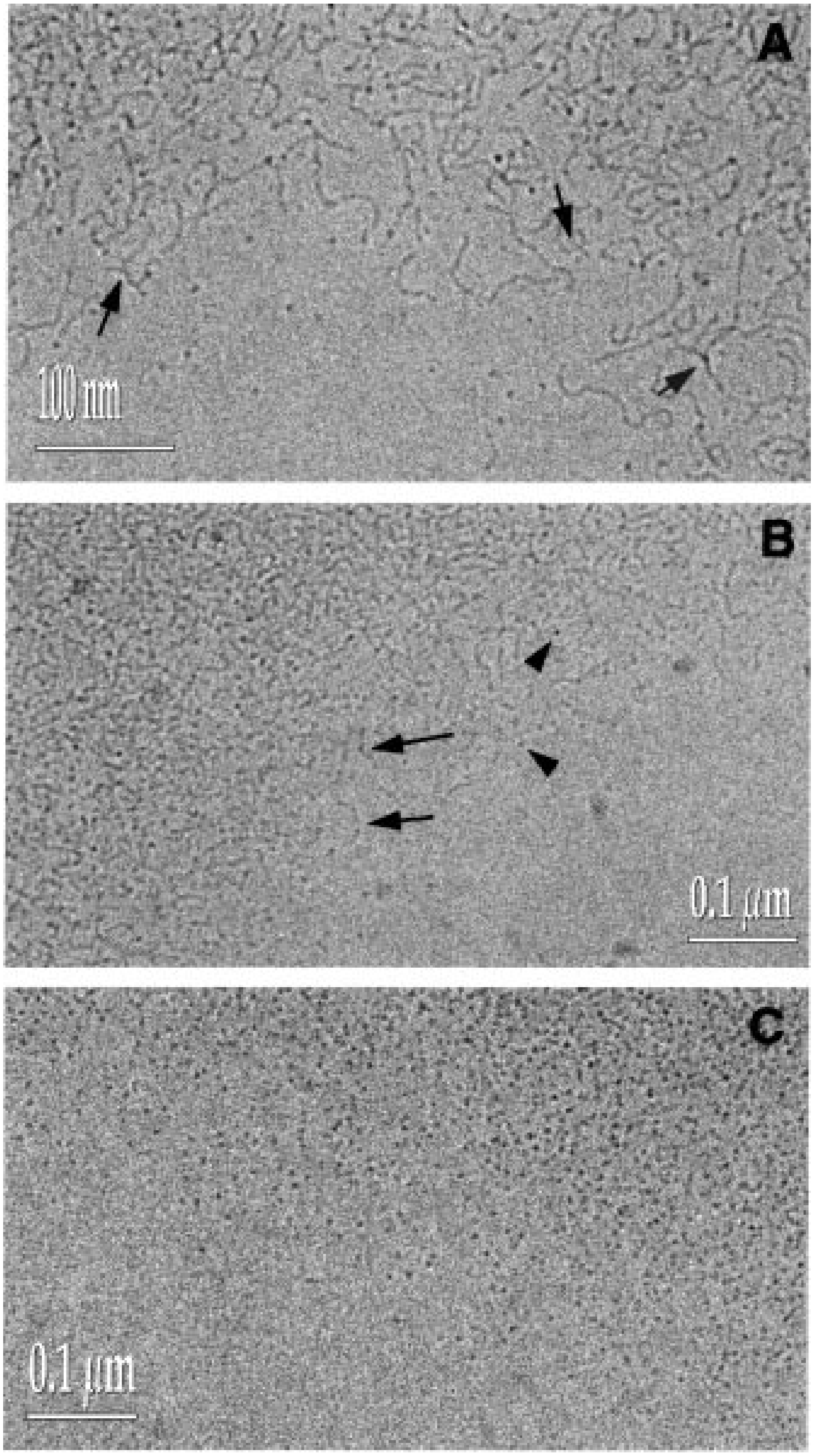

Figure 4. Cryo-TEM images of microemulsion micrsotructures along the EF line: (A) at $\phi_o = 3\%$ and $T = 26.5$ °C, where the structure is oil-swollen cylindrical micelles connected by 3-fold junctions (arrows); (B) the system at $\phi_o = 0.755\%$ and $T = 5$ °C is made of disconnected spherical oil-swollen globules (arrowheads) coexisting with relatively short (a few tens of nanometers) cylindrical threads (arrows); (C) at a very low temperature of $T = 2$ °C and at $\phi_o = 0.613$ the observed microstructure is that of monodisperse oil-swollen spheres.

are a direct consequence of an effective attraction within the ME networks due to the translational entropy of the junctions. This attraction is proportional to the number density, ρ, of the junctions which scales exponentially with their curvature energy, ϵ, like $\rho \sim \phi_o^{3/2} e^{-\epsilon/T}$. The ME separates into two network phases when the junction curvature energy is below a critical value $\epsilon_c \sim 2$ corresponding to a critical junction density $\rho_c \sim 0.03$ (in units of $1/r^3$), where attraction first overcomes the repulsion between neighboring fluctuating cylinders. Due to the

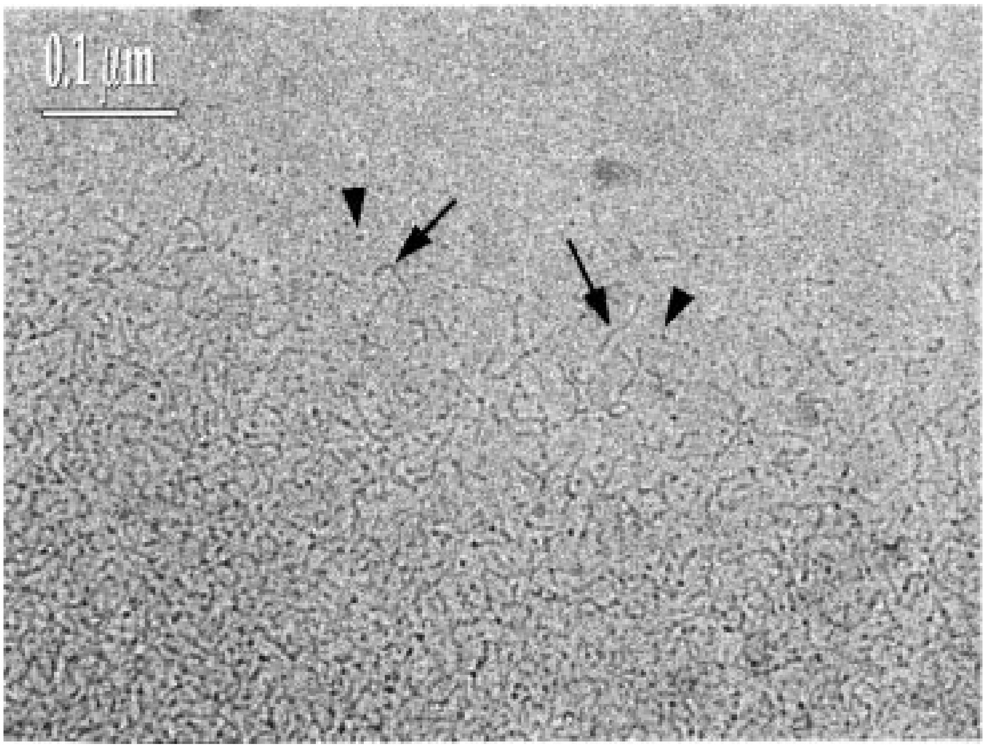

Figure 5. Approaching the binary micellar system ($\phi_o = 0.028$) at $T = 2$ °C, the system is comprised of cylindrical structures (arrows) in coexistence with spheres (arrowheads), as seen by cryo-TEM.

nonmonotonic dependence of the curvature energy $\epsilon(r)$ on the cylinder radius, r (which scales such as $r \sim \phi_o/\phi_s$), the resulting phase separation region is a closed loop bounded by two critical points.[10]

Consistent with this picture, we observe ME networks along the $\overline{2}$ line from the critical end point (Figure 2A at $\phi_o = 3\%$, $T = 30$ °C) through the double critical point (Figure 2B, at the minimum in Figure 1B, $\phi_o = 0.7\%$, $T = 23$ °C) toward a binary solution. A typical cryo-TEM micrograph of network phase is shown in Figure 2A: swollen oil-in-water cylindrical tubes describe the local structure. One can easily identify many 3-fold junctions (large arrows) connecting these semiflexible tubes, thus forming a network. The typical length of the tubes (distance between neighboring junctions) is a few tens of nanometers with a rather broad distribution, in accord with the exponential distribution suggested by theory. The radius of the tubes is about 5 nm, close to the theoretical value determined by volume and surface conservation. The tubes in the picture are semiflexible with a persistence length of about 10−20 nm. Although much less numerous, one can find disconnected network fragments that may be related to shearing during specimen preparation. The few four-way "crossroads" mark entanglement points or the rare 4-fold junctions (arrowheads). The black dots indicate cylinder ends pointing outside the image plane or a folded thread (noted by a small arrow). Following the $\overline{2}$ line to lower oil content (Figure 2B) the topology of local cylindrical structures connected by 3-fold branching points is unchanged. Note that the cylinders are now thinner due to lower oil content. Since the planar cut defined by the constant weight ratio is close to the line of critical points, the number density of the junctions along the $\overline{2}$ line is expected to scale as the critical value, $\rho_c r^{-3} \sim \rho_c(\phi_s/\phi_o)^3$. This is qualitatively supported by the measurements that indicate denser networks as we approach the binary system ($\phi_o \rightarrow 0$).

Within the two-phase closed loop, the predicted coexistence into concentrated (upper) and dilute (lower) network phases was indeed observed. This continuous phase separation occurs close to the double critical point, T_-, where the closed loop is relatively small (the minimum of $\overline{2}$). Figure 3 shows the coexisting ME networks of a system whose temperature is slightly above this double critical point, at $T = 24.4$ °C and $\phi_o = 0.76\%$. In both cryo-TEM micrographs of the lower (Figure 3A) and the upper (Figure 3B) phases one can identify the network topology formed of 3-fold junctions (arrows) interconnecting the oil-in-water cylindrical tubes. As predicted, the two networks in Figure 3 are of equal cylinder radius, r, and differ only in their junction density, ρ. At higher temperatures, where the closed loop has already widened, the network topology was observed in both concentrated and dilute phases, but in the dilute phase we also found disklike shapes. If the temperature is further increased, a three-phase body is formed. In the dilute (lower) phase, we found only disconnected structures, due to their higher entropy. Their shapes range from spherical to disklike shapes due to the small spontaneous curvature. Similar bicontinuous ME networks were observed even along the EF line, where previous theoretical studies predicted a discontinuous topology of spherical droplets.[11] The EF of networks, as manifested experimentally by observation of networks coexisting with an excess phase, agrees with the prediction of the network model: It suggests that the same mechanism leading to the rejection of excess phase by droplets at their optimal curvature, far from $\overline{T}$, induces EF also in a ME network. The model shows that EF results from the optimization of the local geometry (i.e., the mean curvature of the surfactant monolayers) and is therefore insensitive to the global geometry of disconnected globules or connected network.[16] Figure 4A shows a typical cryo-TEM image in the one-phase channel slightly above the EF line at $\phi_o = 3\%$ and $T = 26.5$ °C. The structure is similar to that of Figure 2, with oil-swollen cylindrical

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(16) Tlusty, T.; Safran, S. A.; Strey, R. To be submitted for publication.

micelles connected by 3-fold junctions (arrows). Similar networks were observed down to $T = 9$ °C where the EF line is at $\phi_o = 1\%$ (Figure 1B).

Following the EF line to lower temperatures induces a topological transition: Figure 4B shows the microstructure of the ME on the EF at $T = 5$ °C and $\phi_o = 0.755\%$; the system is comprised of disconnected spherical oil-swollen globules (arrowheads) coexisting with relatively short (a few tens of nanometers) cylindrical threads (arrows). This is in qualitative agreement with theory that predicts a network breakup in regions where the higher entropy of the disconnected cylinders overcomes the higher curvature energy of their end-caps relative to the network junctions.[16] Finally, when we further decreased the temperature to $T = 2$ °C (at $\phi_o = 0.613$) the observed structure is that of rather monodisperse oil-swollen spheres (Figure 4C) as predicted by comparison of their curvature energy to that of the cylinders.[16,17] This is in accord with previous experimental studies of EF using freeze-fracture electron microscopy,[4] NMR,[5] small angle neutron scattering (SANS),[6] and light scattering.[7] Approaching the binary micellar system (by decreasing the oil content down to $\phi_o = 0.028\%$) while keeping the same temperature as in Figure 4C ($T = 2$ °C), we return to cylindrical structures (arrows) in coexistence with spheres (arrowheads) (Figure 5) as observed in the pure binary system.[13] In the binary system, networks were observed at higher temperatures, below the two-phase separation curve (with critical temperature $T_c = 31.5$ °C). This roughly locates a connected/disconnected topological transition line departing from the EF line at a temperature between 5 and 8 °C and increasing with T as oil content is lowered (Figure 1B).

Conclusions

The theoretical model predicts that the same physics of entropic interactions within semiflexible networks that govern swollen ME may also determine the structure and phase behavior of certain binary micellar solutions. Our study supports this prediction experimentally by the observation of network topology in the vicinity of the binary critical point. In contrast to past theories that explained phase separation and criticality as resulting from increasing attraction between growing micelles,[18] we suggest an explanation within the same context of ME networks:[19] The binary critical point and the phase separation are naturally described as the $\phi_o \rightarrow 0$ limit of the ME critical point and two-phase coexistence region.

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(17) NMR and SANS measurements indicate a cylinder to sphere transition at higher temperatures, but still below the loops (Strey, R.; Glatter, O. Private communication).

(18) Blankschtein, D.; Thurston, G. M.; Benedek, G. B. *J. Chem. Phys.* **1986**, *85*, 7268.

(19) Drye, T. J.; Cates, M. E. *J. Chem. Phys.* **1992**, *92*, 1367.