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Patterns of Phase Behavior in Ternary Ethoxylated Alcohol-*n*-Alkane-Water Mixtures

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Certain ternary mixtures of ethoxylated alcohols, *n*-alkanes, and water at 25 °C separate at equilibrium into three liquid phases. The development of an amphiphile-rich middle phase is sensitive to alcohol molecular weight, alkane carbon number (ACN), and temperature. A middle phase arises when all three variables are adjusted such that the alcohol has no preference to partition into either an oleic or aqueous phase. A change in one of these variables yields a sequence of ternary phase diagrams in which the range of the three phases is from one critical tie line to a second. There are two distinct patterns, however, in which the critical tie lines arise. With a low molecular weight ethoxylated alcohol, both critical tie lines lie in the miscibility gap between water-rich and alkane-rich phases. With larger ethoxylated alcohols, however, one of the critical tie lines arises from the fusion of that miscibility gap with the critical point on a second one between water-rich and alcohol-rich phases. Both patterns are modeled well by modifying the Flory-Huggins equation of state to account for the tendency of amphiphile to concentrate between water-rich and alkane-rich domains, thereby attenuating or screening the enthalpic repulsion between water and alkane. The screening is expressed by a factor which is exponential in amphiphile concentration. The type of three-phase equilibria which arises from fusion of two miscibility gaps requires a pair of screening factors. Other available thermodynamic models appear incapable of approximating this second pattern of three-phase equilibria.

Introduction

Knickerbocker et al.^{1,2} have found that the phase behavior of monohydric alcohol-hydrocarbon-brine mixtures qualitatively mimics phase splits and compositions observed in surfactant-hydrocarbon-brine mixtures. These investigators also discovered that a generic field variable-composition phase diagram could be used to understand the basic phase behavior patterns reported for ternary and pseudoternary mixtures of alcohol-hydrocarbon-water-salt. As amphiphiles, the lower-molecular-weight monohydric alcohols can be considered to be protosurfactants, or surfactant precursors, even though they form neither micelles nor liquid crystals in aqueous solutions.³ The lower molecular weight ethoxylated alcohols resemble small alcohols in being modest solubilizers of oil and water and do not form micelles or liquid crystals. The polyethoxylated long-chain alcohols, however, are excellent solubilizers of oil and water.^{4,5} Moreover, with oil and water, the higher-molecular-weight ethoxylated alcohols form the microstructured fluids, namely liquid crystals,⁶⁻⁹ micellar solutions,¹⁰⁻¹⁴ and microemulsions,^{4,9,15,16} expected of a true surfactant. Thus, by increasing the lengths of the hydrocarbon and the ethoxy moieties of the ethoxylated alcohols one can study the patterns of phase behavior as the ethoxylated alcohols go from simply associating amphiphiles to microstructure-forming surfactants.

The purpose of this paper is to investigate the patterns of phase behavior as the alcohol increases in size from a mere amphiphile to a full-fledged surfactant. We concentrate on the behavior of water-hydrocarbon-ethoxylated alcohol at 25 °C, although we present some results at different temperatures. Five ethoxylated alcohols and six normal alkanes are studied. The observed patterns of phase behavior are viewed in the light of the generic field variable-composition diagram of Knickerbocker et al.^{1,2} Also, we employ the screened Flory-Huggins solution model^{17,18} to shed light on the molecular origins of the observed phase behavior. In a subsequent paper, we will report an experimental study of fluid microstructure in these mixtures.¹⁹

Thermodynamic Theory of Ternary Phase Behavior

In seeking water-hydrocarbon-surfactant formulations useful for enhancing oil recovery, a generic pattern of ternary and pseudoternary phase behavior has been identified.^{1,2,20-22} Knickerbocker et al.^{1,2} have shown that this pattern results from translations, truncations, or fusions of the basic field variable-

composition diagram shown in Figure 1. A field variable is an intensive thermodynamic variable and takes on equal values in all phases in equilibrium.²³ Temperature, pressure, and chemical potential of a solution component are generally recognized, continuous field variables. However, the carbon number of a homologous alkane series or a sequence of molecular moieties of an amphiphile also qualifies as a field variable, albeit a discretely varying rather than a continuously varying one.

The search for a surfactant formulation for enhancing oil recovery, or the search for a tricritical point in a four-component amphiphile-oil-water-salt mixture,^{24,25} generally involves the

- (1) Knickerbocker, B. M.; Pescheck, C. V.; Scriven, L. E.; Davis, H. T. *J. Phys. Chem.* 1979, 83, 1984.
- (2) Knickerbocker, B. M.; Pescheck, C. V.; Davis, H. T.; Scriven, L. E. *J. Phys. Chem.* 1982, 86, 393.
- (3) Laughlin, R. G. *Adv. Liq. Cryst.* 1978, 3, 41.
- (4) Shinoda, K.; Kunieda, H. *J. Colloid Interface Sci.* 1973, 42, 381.
- (5) Friberg, S.; Buraczewska, I.; Ravey, J. C. In *Micellization, Solubilization, and Microemulsions*, Vol. 2, Mittal, K. L., Ed.; Plenum: New York, 1977; p 901.
- (6) Corkill, J. M.; Goodman, J. F. *Adv. Colloid Interface Sci.* 1969, 2, 297.
- (7) Harusawa, F.; Nakamura, S.; Mitsui, T. *Colloid Polym. Sci.* 1974, 252, 613.
- (8) Lang, J. C.; Morgan, R. D. *J. Chem. Phys.* 1980, 73, 5849.
- (9) Bostock, T. A.; McDonald, M. P.; Tiddy, G. J. T. In *Surfactants in Solution*, Mittal, K. L., Lindman, B., Eds.; Plenum: New York, 1984.
- (10) Corkill, J. M.; Goodman, J. F.; Ottewill, R. H. *Trans. Faraday Soc.* 1961, 57, 1627.
- (11) Balmbra, R. R.; Clunie, J. S.; Corkill, J. M.; Goodman, J. F. *Trans. Faraday Soc.* 1964, 60, 979.
- (12) Balmbra, R. R.; Clunie, J. S.; Corkill, J. M.; Goodman, J. F. *Trans. Faraday Soc.* 1962, 58, 1661.
- (13) Corti, M.; Degiorgio, V. *J. Phys. Chem.* 1981, 85, 1442.
- (14) Triolo, R.; Magid, L. J.; Johnson, J. S., Jr.; Child, H. R. *J. Phys. Chem.* 1982, 86, 3689.
- (15) Friberg, S.; Lapeczynska, I. *Prog. Colloid Polym. Sci.* 1975, 56, 16.
- (16) Bostock, T. A.; McDonald, M. P.; Tiddy, G. J. T.; Waring, L. *Surface Active Agents, a Symposium*; Society of Chemical Industry: London, 1979; p 181.
- (17) Rossen, W. R.; Brown, R. G.; Davis, H. T.; Prager, S.; Scriven, L. E. *Soc. Pet. Eng. J.* 1982, 22, 945.
- (18) Kilpatrick, P. K.; Scriven, L. E.; Davis, H. T. *Soc. Pet. Eng. J.* 1985, 25, 330.
- (19) Kilpatrick, P. K.; Davis, H. T.; Miller, W. G.; Scriven, L. E. *J. Colloid Interface Sci.* submitted.
- (20) Robbins, M. L. In *Micellization, Solubilization, and Microemulsions*, Vol. 2, Mittal, K. L., Ed.; Plenum: New York, 1977; p 713.
- (21) Reed, R. L.; Healy, R. N. In *Improved Oil Recovery by Polymer Flooding*, Shah, D. O., Schechter, R. S., Eds.; Academic: New York, 1977, p 383.
- (22) Healy, R. N.; Reed, R. L. *Soc. Pet. Eng. J.* 1974, 14, 491.
- (23) Griffiths, R. B.; Wheeler, J. C. *Phys. Rev. A* 1970, 2, 1047.
- (24) Bennett, K. E.; Phelps, C. H. K.; Davis, H. T.; Scriven, L. E. *Soc. Pet. Eng. J.* 1981, 21, 747.

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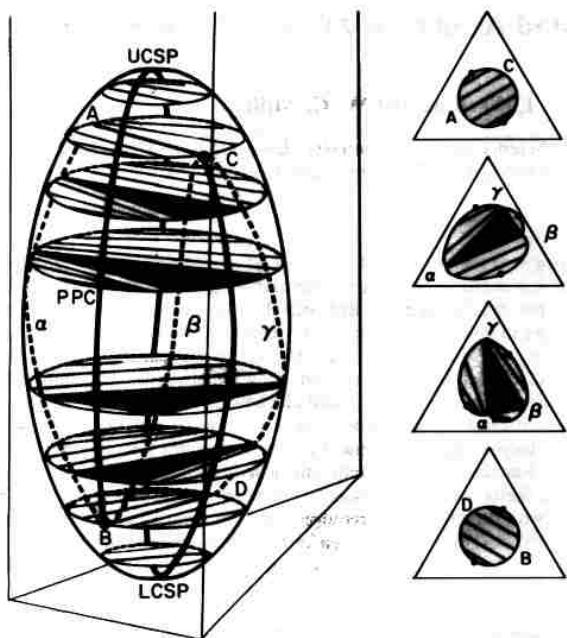


Figure 1. Representation of multiphase equilibria in prismatic field variable-composition coordinates for a ternary mixture (from Knickerbocker et al.²).

scanning of at least two field variables (among which common choices are salt chemical potential, temperature, hydrocarbon chain length, alkane chain length of the hydrocarbon moiety of the surfactant, and the chemical potential of a cosurfactant or amphiphile) to find conditions under which an isotropic, surfactant-rich middle phase (a microemulsion) will exhibit ultralow tension against coexisting oil-rich and water-rich phases. In the context of the theory of Knickerbocker et al.,^{1,2} such a search is successful because amphiphile-hydrocarbon-water mixtures exhibit the generic pattern of phase behavior shown in Figure 2. As field variable 1 (e.g. salt chemical potential or temperature) increases from a low value, a middle or third phase appears, the third phase arising from a critical endpoint (CEP) tie line of the 2-phase system. (The number-overbar-underbar notation is that of Knickerbocker et al.^{1,2} Here, the number denotes the number of equilibrium liquid phases in a system, an underbar signifies that amphiphile partitions predominantly in a lower or water-rich phase, and an overbar signifies that amphiphile partitions predominantly in an upper or oil-rich phase. A 3 denotes a three-phase system in which amphiphile partitions predominantly into a middle phase which incorporates significant amounts of oil and water.) With increasing field variable 1, the middle phase progresses from water-rich to increasingly oil-rich until the tie triangle collapses into another critical endpoint (CEP) tie line of the 2-phase system. As field variable 2 (e.g., temperature or activity of a cosurfactant) increases, the two CEP's move together, i.e. the range of field variable 1 between the 2-3 and 3-2 transitions decreases. At sufficiently large field variable 2, the two CEP's collapse into a tricritical point (TCP).

Robbins²⁰ and Reed and Healy^{21,22} were early to identify the generic 2-3-2 pattern of phase sequences in salinity and temperature scans. Bennett et al.²⁴ have observed the trends displayed in Figure 2 with a pure and a commercial alkyl aryl sodium sulfonate surfactant with salinity and hydrocarbon chain length as field variables. Knickerbocker et al.^{1,2} made similar observations in monohydric alcohol-hydrocarbon-water mixtures. Kahlweit and co-workers²⁶⁻²⁹ have reported the same trends in four-

six-carbon ethoxylated alcohol-hydrocarbon-water mixtures and have devised an extrapolation technique for determining the tricritical composition and temperature. In what follows we shall demonstrate that the new experimental results reported here fit the trends shown in Figure 2. Slightly at variance with the 2-3-2 sequence in Figure 2 is the 2-3-2 sequence reported by Kunieda and Friberg³⁰ for a temperature scan of C_8E_3 -n-decane-water mixtures. However, this pattern can be accounted for by an appropriate fusion of the thermodynamic ovoid of Knickerbocker et al.^{1,2} Moreover, we show that the pattern can be predicted by the screened Flory-Huggins equation of state that has previously been shown to be capable of producing the 2-3-2 patterns of Figure 2.^{17,18}

Experimental Section

Materials. The hydrocarbons used were either Aldrich Gold Label (99+%) or Philips pure-grade (99+%) products. They were stored in glass vials or bottles and used without further purification. Distilled water was drawn through a Millipore four-stage cartridge system which reduces conductivity to less than 1 $\mu\text{S}/\text{cm}$. This water was stored in polyethylene plastic ware to eliminate ion leaching from glass. The shorter ethoxylated alcohols— C_4E_1 , C_4E_2 , and C_6E_2 —were obtained from Union Carbide in varying states of purity. C_4E_1 was 99.99% pure by gas-liquid chromatography (glc). C_4E_2 and C_6E_2 were considerably less pure and were fractionally distilled under vacuum until a purity greater than 99% was attained as determined by glc.

C_8E_3 and $C_{10}E_4$ were synthesized by a Williamson ether reaction, a route first used to prepare pure ethoxylated alcohols by Chakhovskoy,³¹ Gingras and Bayley,³² and Mulley.³³ Use of the method has been widespread and is reviewed by Mulley.³⁴ The synthesis produces a monodisperse alcohol in about 50 to 70% yield. Elimination byproducts, alkali halide, and diether resulting from addition of two alkyl halides to the parent glycol are also produced. Workups of the product in the past have usually involved filtration of the alkali halide and subsequent fractional distillation under vacuum. We found the separation was expedited by extracting the unreacted glycol from the reaction product by dissolving the reaction mixture in equal volumes of aqueous methanol and hexane. A similar procedure was reported by Lang and Morgan.⁸ C_8E_3 and $C_{10}E_4$ partition preferentially into the hexane phase while unreacted polyethylene glycol partitions into the aqueous phase. After extraction, the ethoxylated alcohol was distilled from the low-boiling impurities: water, hexane, methanol, unreacted alkyl halide, and the elimination byproduct, 1-alkene. The ethoxylated alcohol was repeatedly fractionated until a heart-cut of purity greater than 99%, as indicated by glc, was obtained. Upon isolation of pure product, C_8E_3 and $C_{10}E_4$ were positively identified by mass spectrometry and ^{13}C NMR spectroscopy. Ammonia chemical ionization mass spectra revealed parent peak ions of molecular weight 17 daltons greater than theoretical, corresponding to ammoniated ethoxylated alcohol. ^{13}C NMR spectra were consistent with the expected molecular structures; resonance assignments agreed with those of Ribeiro and Dennis.³⁵ More details of the synthesis and purification are given by Kilpatrick.³⁶

Methods. Samples were prepared either in 10–15-mL screw-cap vials with Teflon inserts or in 10–20-mL sealed glass ampules. In the former case, evaporative loss was negligible. Changes in phase volumes were not detected over the time frame of the experiments (5–20 days). The samples were shaken thoroughly and allowed to equilibrate in either a water bath or an air bath,

- (29) Kahlweit, M.; Lessner, E.; Strey, R. *J. Phys. Chem.* 1983, 87, 5032.
- (30) Kunieda, H.; Friberg, S. *Bull. Chem. Soc. Jpn.* 1981, 54, 1010.
- (31) Chakhovskoy, N.; Martin, R. H.; Van Nekel, R. *Bull. Soc. Chim. Belg.* 1956, A/III 65, 453.
- (32) Gingras, B. A.; Bayley, C. H. *Can. J. Chem.* 1957, 35, 599.
- (33) Mulley, B. A. *J. Chem. Soc.* 1958, 2065.
- (34) Mulley, B. A. In *Nonionic Surfactants*, Schick, M. J., Ed.; Dekker: New York, 1967; Chapter 13, p 421.
- (35) Ribeiro, A. A.; Dennis, E. A. *J. Phys. Chem.* 1977, 81, 957.
- (36) Kilpatrick, P. K. Ph.D. Thesis, University of Minnesota, 1983.

(25) Lang, J. C.; Widom, B. *Physica* 1975, 81A, 190.

(26) Kahlweit, M.; Lessner, E.; Strey, R. *J. Phys. Chem.* 1984, 88, 1937.

(27) Herrmann, C.-U.; Klar, G.; Kahlweit, M. *J. Colloid Interface Sci.* 1981, 82, 6.

(28) Kahlweit, M. *J. Colloid Interface Sci.* 1982, 90, 197.

WATER - AMPHIPHILE - HYDROCARBON PHASE DIAGRAMS

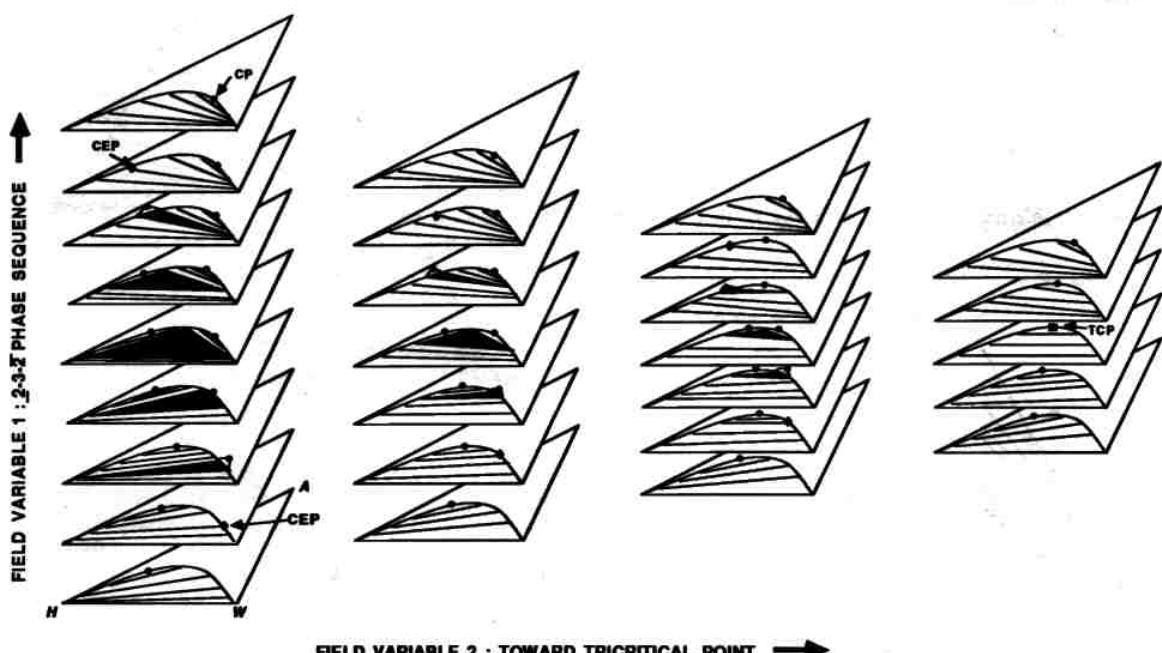


Figure 2. Generic sequence of ternary phase diagrams in water-amphiphile-hydrocarbon mixtures as two field variables are changed. Field variable 1 induces a 2-3-2 critical endpoint to critical endpoint sequence of three-phase equilibria while field variable 2 drives the three-phase region toward a tricritical point.

each kept at a constant temperature of 25.00 ± 0.05 °C. With C_4E_1 , C_6E_2 , C_8E_3 , and $C_{10}E_4$, equilibrium was usually reached within minutes and was accompanied by sharp, mirrorlike interfaces. Equilibration to the same phase volumes following repeated mixing and thermodynamic consistency of the phase diagrams were taken as evidence that equilibrium was reached. With $C_{10}E_4$, opaque emulsions formed at several concentrations, some of which remained stable for more than 4 years. Only those samples which settled to give clear phases and sharp interfaces were used to obtain phase data. Following equilibration, microliter aliquots from each phase were analyzed by glc in conjunction with systematic visual observations to determine ternary phase splits and compositions. Single-phase samples of known composition were used to calibrate the instrument in the composition range of interest. Replicate analyses indicated a precision of $\pm 1\%$ in the concentration of each component.

A Hewlett-Packard Model 5730A gas chromatograph with a Model 3380A integrator was used. A 5 ft by $3/4$ in. aluminum column of silicone oil SE-30 on acid-washed Chromosorb W was used to obtain ethoxylated alcohol peaks of excellent symmetry. A Poropak P column was used to analyze water and *n*-alkane peaks. Mass spectra were taken on a Finnigan 4000 spectrometer. ^{13}C NMR spectra were obtained with a Varian XL-100-15 spectrometer.

Results

Hydrocarbon chain length strongly affects partitioning of an ethoxylated alcohol between coexisting aqueous and oleic phases, particularly with the small and delicately balanced amphiphiles. The smallest ethoxylated alcohol examined— C_4E_1 —partitions nearly equally between aqueous and oleic phases below an amphiphile concentration of about 10 wt %; above this concentration the amphiphile partitions preferentially into the oleic phase when *n*-hexane and *n*-octane are the oils and into the aqueous phase when *n*-tetradecane is the oil (Figure 3). Binary mixtures of C_4E_1 with water and with all *n*-alkanes studied at 25 °C are miscible in all proportion. When only two phases are present, therefore, there is a critical point at an amphiphile composition greater than 10 wt %. In the cases of *n*-nonane and *n*-decane, C_4E_1 prefers neither the aqueous nor the oleic phase at high concentrations,

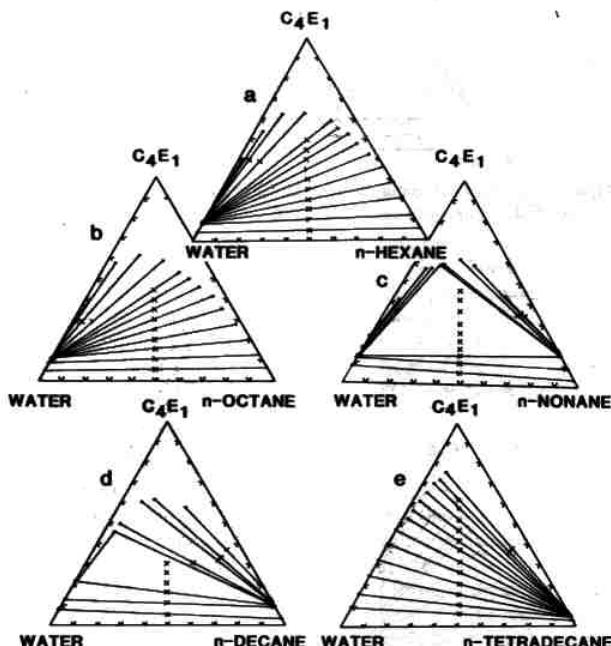


Figure 3. Ternary phase diagrams of C_4E_1 -*n*-alkane-water systems at 25 °C and ambient pressure. In these and subsequent diagrams, compositions are given on a weight percent basis, X's denote mixpoints, and •'s denote equilibrium compositions determined by glc.

but instead forms an amphiphile-rich third phase which incorporates substantial quantities of *n*-alkane and water. In these two phase diagrams, there are now two critical points—one water-rich and one oil-rich. Several mixpoints throughout the ternary C_4E_1 -water-*n*-undecane system indicated that this *n*-alkane forms a 2 system with C_4E_1 and water at 25 °C (Table I).

We also examined the effects of a 5 °C temperature increment on the ternary phase behavior of the C_4E_1 -water-*n*-nonane and C_4E_1 -water-*n*-decane systems. The ternary phase diagrams for

TABLE I: Classification of Types of Ternary Phase Equilibria at 25 °C Exhibited by Mixtures of Ethoxylated Alcohols, *n*-Alkanes, and Water

	alkane carbon number										
	6	7	8	9	10	11	12	13	14	15	16
C ₄ E ₁	2	2	3	3	2 ^a				2		
C ₆ E ₂	2		2	2	3 ^a	3			3 ^a	3 ^a	
C ₈ E ₃	2 ^a		2 ^a	2 ^a	3		3 ^a		3 ^a	3	
C ₁₀ E ₄			2 ^a	2 ^a	2 ^a	2 ^a		3 ^a	3 ^a	3 ^a	

^aPhase behavior inferred from several mixpoints; no tie lines were determined.

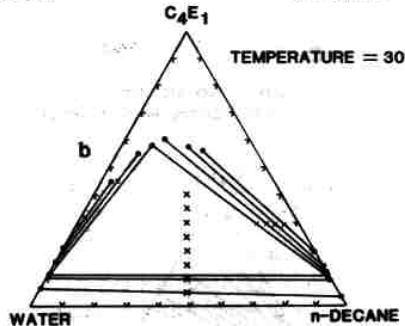
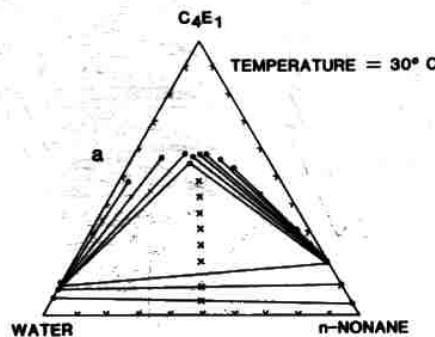


Figure 4. Ternary phase diagrams at 30 °C of (a) C₄E₁-n-nonane-water and (b) C₄E₁-n-decane-water.

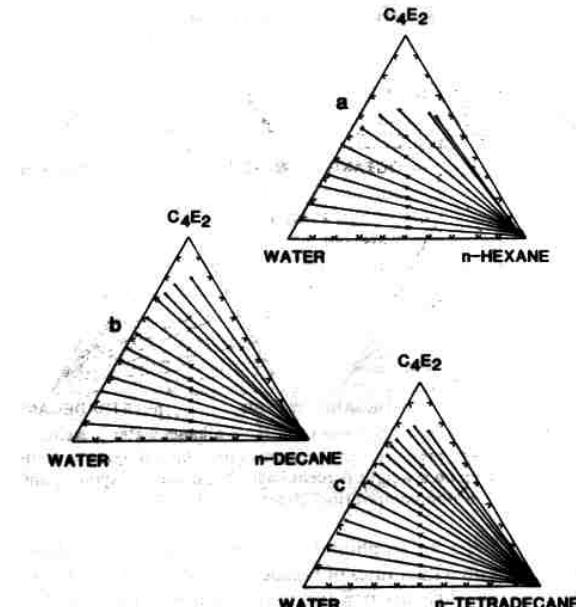


Figure 5. Ternary phase diagrams of C₄E₂-n-alkane-water systems at 25 °C and ambient pressure.

these two systems at 30 °C are shown in Figure 4. In both cases, increasing temperature shifted the apex of the three-phase tie triangle to lower water contents and higher *n*-alkane contents.

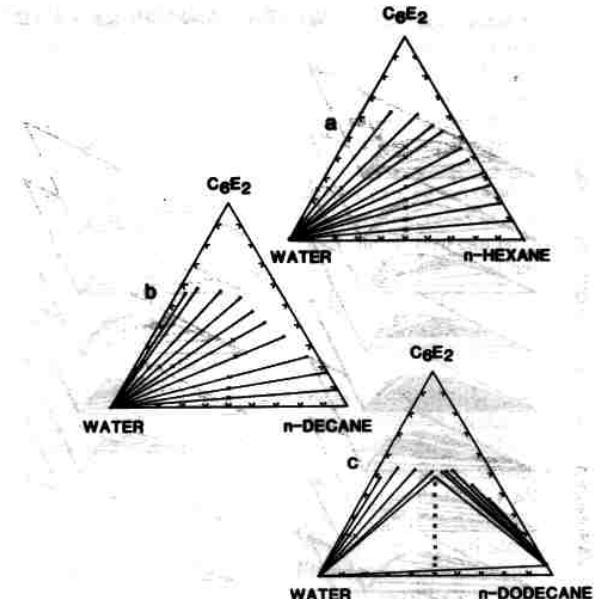


Figure 6. Ternary phase diagrams of C₆E₂-n-alkane-water systems at 25 °C and ambient pressure.

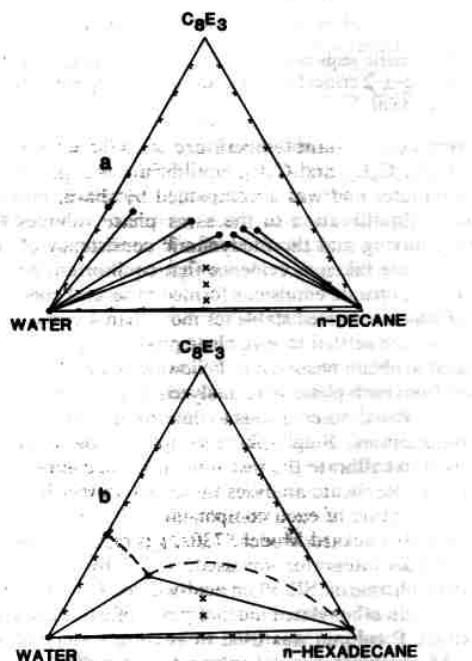


Figure 7. Ternary phase diagrams of C₈E₃-n-alkane-water systems at 25 °C and ambient pressure.

The partitioning of C₄E₂ at 25 °C between aqueous and oleic phases is fairly insensitive to *n*-alkane chain length (Figure 5). With all three *n*-alkanes studied, C₄E₂ partitions into an aqueous phase; three-phase formation is not observed.

Ternary mixtures of C₆E₂, *n*-alkane, and water at 25 °C give three-phase equilibria over a range of hydrocarbon size. With *n*-hexane and *n*-decane, there are only two-phase equilibria and the amphiphile partitions into the oleic phase (Figure 6). At 25 °C, there is a miscibility gap along the water-amphiphile edge. As a consequence, the two-phase region fans from the *n*-alkane-water edge to the amphiphile-water edge with no critical point. In the case of *n*-dodecane, a large three-phase region dominates the ternary phase diagram (Figure 6). Although phase diagrams were not determined for *n*-tetradecane and *n*-hexadecane as oils, ternary mixtures of these *n*-alkanes with C₆E₂ and water

were observed to form three liquid phases at 25 °C (Table I). Ternary phase diagrams at 25 °C of C_8E_3 and water with *n*-decane and *n*-hexadecane are shown in Figure 7. Both show three-phase equilibria and both require about 30 wt % amphiphile to solubilize equal masses of *n*-alkane and water. The ternary C_8E_3 -water-*n*-hexane, -*n*-octane, and -*n*-nonane systems show only two-phase equilibria, whereas *n*-dodecane and *n*-tetradecane systems give three-phase equilibria (Table I).

$C_{10}E_4$ forms three liquid phases with water and *n*-tetradecane, *n*-pentadecane, and *n*-hexadecane at 25 °C. Samples of 45 vol % water, 45 vol % *n*-alkane, and 10 vol % $C_{10}E_4$ with the *n*-alkanes octane, nonane, decane, and dodecane produced two liquid phases; whether these ternary mixtures exhibit three-phase equilibria at 25 °C is not known.

The ternary phase equilibria of the ethoxylated *n*-alkanols in the series $C_4E_1-C_6E_2-C_8E_3-C_{10}E_4$ with water and *n*-alkanes at 25 °C are summarized in Table I. Given there are the maximum number of phases in each phase diagram and the phase into which the amphiphile preferentially partitions.

Discussion

Patterns of Experimental Phase Equilibria. The sequence of ternary phase diagrams generated by varying alkane carbon number with water and C_4E_1 fits the generic 2-3-2 sequence shown in Figure 2, with carbon number serving as field variable 1. Of course, owing to the discreteness of this field variable the critical endpoints which bound the extent of the three-phase region are missed in the carbon number scan.

Temperature has the reverse effect to alkane carbon number on relative partitioning of C_4E_1 between oil-rich and water-rich phases. A small temperature increment (5 °C) shifts the amphiphile-rich phase composition in C_4E_1 -*n*-alkane-water mixtures by more than 10 wt % (Figure 4), with either *n*-nonane or *n*-decane as the oil. This sequence of phase equilibria can also be represented by Figure 2, an increase in field variable 1 corresponding to a decrease in temperature. With C_4E_1 -*n*-decane-water, we traverse only a portion of the three-phase region in making a temperature increment of 5 °C. However, Kahlweit et al.²⁸ have shown that, in the C_4E_1 -*n*-decane-water system, the critical endpoints occur at temperatures of about 23 and 50 °C. Thus we have truncated the lower and upper portions of the three-phase region in Figure 2 by examining only the temperature interval from 25 to 30 °C.

A small addition of NaCl to the C_4E_1 -*n*-decane-water system has an effect similar to that of temperature. The salt occupies the water-rich phase almost exclusively and drives the amphiphile into an alcohol- or an oil-rich phase. Although the mixtures with salt are strictly four-component systems, they can be approximately represented in prismatic coordinates with salt as the pseudo-field variable. Kilpatrick et al.¹⁹ have determined pseudo-ternary phase behavior in the C_4E_1 -*n*-decane-water system. With an increase in salt concentration from pure water to 0.2 M in the aqueous phase, the apex of the three-phase region shifts by about 10 wt % in amphiphile concentration (Figure 8). As with a small temperature increment, this corresponds to a small portion of the generic phase diagram in Figure 2.

With C_6E_2 -water-*n*-alkane mixtures at 25 °C, only the upper portion of the generic prismatic diagram in Figure 2 is traversed in increasing *n*-alkane chain length from *n*-hexane to *n*-tetradecane. Apparently, the addition of one ethoxy moiety to C_4E_1 makes the resulting amphiphile excessively hydrophilic and causes it to partition exclusively into the water-rich phase at all carbon numbers examined. The experimental sequence of ternary phase diagrams in Figure 5 thus corresponds to only a portion of the 2-phase region in Figure 2.

At temperatures higher than 25 °C, Kahlweit et al.²⁹ found three-phase equilibria in the C_4E_2 -water-*n*-alkane mixtures. Increasing the length of the hydrophilic head group makes the amphiphile more water soluble but this imbalance can be counteracted by increasing temperature which makes the amphiphile less water soluble. The system can also be balanced by decreasing the alkane carbon number of the oil. Kahlweit et al.²⁹ found that changing from octane to cyclohexane decreased the temperature

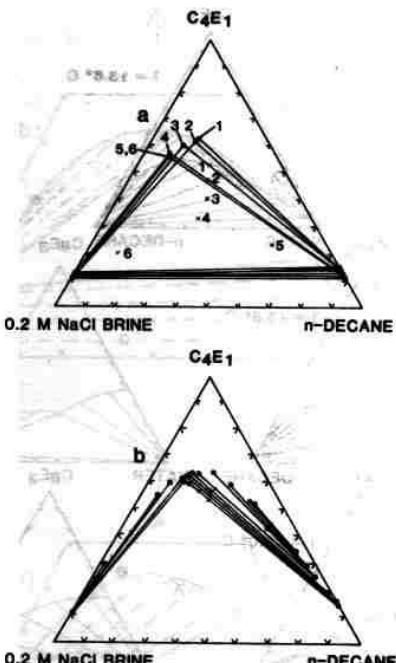


Figure 8. Pseudoternary phase diagram of C_4E_1 -*n*-decane-0.2 M NaCl brine at 25 °C showing (a) three-phase tie triangles as a function of mixpoint and (b) two-phase tie lines as a function of mixpoint.

range over which three liquid phases form by about 25 °C. The range of three-phase equilibria from one critical tie line to another can thus be shifted by any molecular or thermodynamic variable which affects the partitioning tendency of the amphiphile. In the small ethoxylated alcohol systems— C_4E_1 and C_4E_2 —critical tie lines emerge from and collapse into the same two-phase region projected from the water-alkane edge of the ternary phase diagram.

In the C_6E_2 -water-*n*-alkane mixtures at 25 °C, increasing alkane carbon number from *n*-hexane to *n*-hexadecane corresponds to a traversal of the 2-phase region, across the oil-rich critical endpoint, and into part of the three-phase region. The miscibility gap along the C_6E_2 -water edge truncates the 2-phase binodal, thus cutting off the water-rich critical point shown in the generic phase diagram (Figure 2) and observed in the C_4E_1 systems.

The portion of the generic phase diagram of Figure 2 which the C_8E_3 -water-*n*-alkane mixtures at 25 °C trace out is the same as with the C_6E_2 -water-*n*-alkane systems at 25 °C, i.e., the 2-phase region and a portion of the three-phase region. Again, the water-rich critical point in the generic diagram has been truncated by the water- C_8E_3 miscibility gap. At 25 °C, we cannot further increase the tendency of C_8E_3 to partition into the water-rich phase by increasing alkane carbon number because *n*-octadecane is a solid at this temperature. However, a different field variable 1 can be used to induce the phase transition through the water-rich critical endpoint. Kunieda and Friberg³⁰ have examined C_8E_3 -*n*-decane-water as a function of temperature. Their results are reproduced in Figure 9. At temperatures below 13.6 °C, there are two distinct miscibility gaps with their respective critical points. The unusual feature of the phase diagram of Figure 9a is that, although there is a miscibility gap on the C_8E_3 -water edge and complete miscibility between *n*-decane and C_8E_3 , the addition of a small amount of *n*-decane to an immiscible water- C_8E_3 mixture results in a one-phase sample. Moreover, in the ternary oil-water miscibility gap at this temperature, C_8E_3 partitions preferentially into the water-rich phase. This pattern of three-phase equilibria in the C_8E_3 -water-*n*-decane system with temperature is qualitatively different from that with the smaller amphiphiles C_4E_1 and C_4E_2 .

By representing the C_8E_3 -water-*n*-decane phase behavior pattern in prismatic coordinates, the manner in which it differs

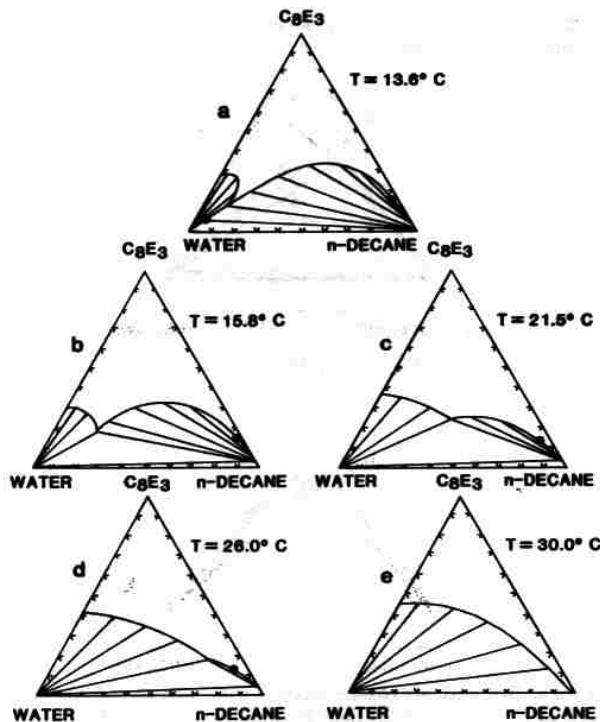


Figure 9. Ternary phase diagrams of C_8E_3 - n -decane-water mixtures as a function of temperature (from Kunieda and Friberg³⁰).

from the generic sequence in Figure 1 becomes clear (see Figure 10). We see that the two-phase region which abuts the water-rich portion of the three-phase region near the water-rich critical endpoint has bulged out and jutted below in field variable value the water-rich critical tie line. The consequence of this alteration is that, for values of field variable below that at the water-rich critical tie line, two separate miscibility gaps exist in the ternary phase diagram, but both ultimately belong to the same multiphase region.

The pattern of three-phase equilibria in which the tie lines all lie in the same water-alkane miscibility gap can be qualitatively modeled by any regular solution-like equation of state. For quantitative prediction of the amount of oil and water which can be cosolubilized by amphiphile, however, a modification of the random binary enthalpic interactions in regular solution which accounts for amphiphilic "screening" of oil-water repulsion must be incorporated into the model. The second pattern of three-phase formation in which a ternary water-amphiphile and a ternary water-oil miscibility gap pinch off at a water-rich critical endpoint requires both amphiphilic screening of water-oil repulsion and oleic screening of water-amphiphile repulsion. We now describe the modeling of both types of three-phase formation.

Equation of State Modeling. The low concentration at which amphiphile solubilizes oil and water cannot be predicted by a thermodynamic equation of state which is based on only pairwise interactions of randomly distributed molecules.^{17,37} The situation can be improved somewhat by assuming weak ordering and interaction of pairs of molecules with each other, as in the quasi-chemical solution model.³⁸ A thermodynamic description which can quantitatively model effective solubilization by amphiphile requires ternary interaction of oil, water, and amphiphile, i.e. specific enthalpic contributions which reflect the amphiphile's nature to interact simultaneously with oil and water. A model which can predict three-phase equilibria with equal amounts of oil and water and small amounts of amphiphile is the exponentially

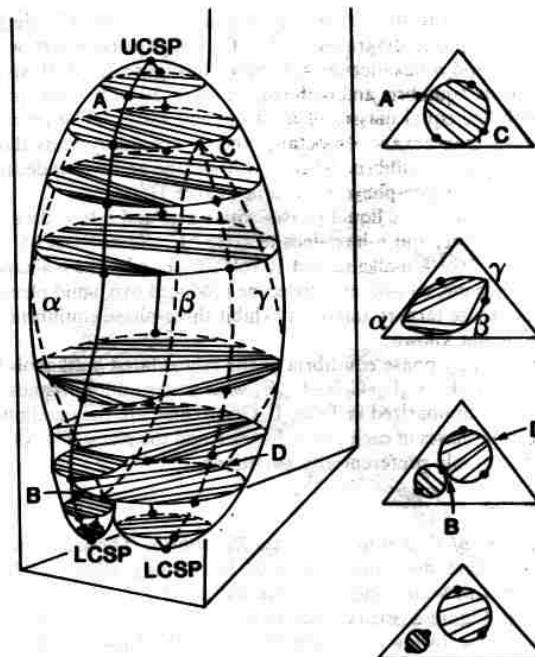


Figure 10. Emergence of three-phase equilibria by fusion of two miscibility gaps.

screened Flory-Huggins (ESFH) model.^{17,18} The model is the Flory-Huggins equation of state for polymer solutions in which the repulsive binary interaction between oil and water is "screened" by a term which depends exponentially on amphiphile concentration:

$$g^* = \frac{n_w g}{RT} = \phi_w \ln \phi_w + (m_w/m_o)\phi_o \ln \phi_o + (m_w/m_a)\phi_a \ln \phi_a + \alpha_{wo}\phi_w\phi_a + \alpha_{oa}\phi_o\phi_a + \alpha_{wo} \exp(-\beta_a\phi_a)\phi_w\phi_o \quad (1)$$

Here, g^* and g are dimensionless and dimensional molar Gibbs free energy of mixing; ϕ_w , ϕ_o , and ϕ_a are volume fraction of water, oil, and amphiphile; m_w/m_o and m_w/m_a are aggregate molecular weight ratios for statistically weighting athermal entropy of mixing; α_{wo} , α_{wa} , and α_{oa} are binary enthalpic interaction parameters representing the net difference between i-i, j-j, and i-j interactions; and β_a is the screening parameter.

A value of α_{wo} of 4.8 yields a large miscibility gap on the oil-water edge. A molecular weight ratio m_w/m_o of unity makes this miscibility gap symmetric. The amphiphile-water and amphiphile-oil edges are completely miscible for values of α_{wa} and α_{oa} less than 0.7 when the molecular weight ratio m_w/m_a is 0.1. A screening parameter β_a of 0.3 or greater yields three-phase tie triangles which are symmetric about the equal oil-water axis. By varying either α_{wa} or α_{oa} from this symmetric case, the three-phase tie triangle can be forced to collapse into a critical tie line with either an oil-rich or water-rich critical endpoint. Such a variation in α_{oa} with all other parameters fixed is equivalent to varying alkane carbon number in C_4E_1 - n -alkane-water mixtures at 25 °C. Ternary phase diagrams with $\alpha_{wa} = 0.55$, $m_w/m_o = 0.1$, $\alpha_{wo} = 4.8$, $\beta_a = 0.3$, $m_w/m_o = 1$, and α_{oa} varying from 0.55 to 0.61 are shown in Figure 11. This phase behavior progression and the corresponding 2- and 1-phase diagrams at values of α_{oa} below 0.47 and above 0.62 come quite close to quantitatively modeling C_4E_1 -alkane-water ternary phase equilibria at 25 °C as n -alkane is varied from n -hexane to n -tetradecane. A least-squares regression of the parameter values to the experimental data could undoubtedly yield a more quantitative match of experiment and theory; we made no attempt to do so, however. Similar progressions in phase behavior are obtained for larger values of β_a with correspondingly smaller amounts of amphiphile in middle phase. Such an increase in cosolubilization with increasing β_a

(37) Meijering, J. L. *Philips Res. Rep.* 1950, 5, 333. *Philips Res. Rep.* 1951, 6, 183.

(38) Larson, R. G.; Scriven, L. E.; Davis, H. T. *J. Chem. Phys.* 1985, 83, 2411.

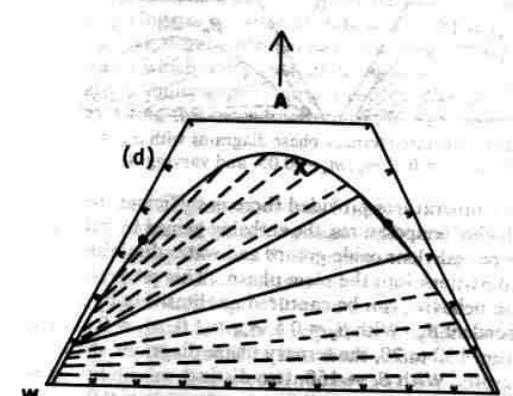
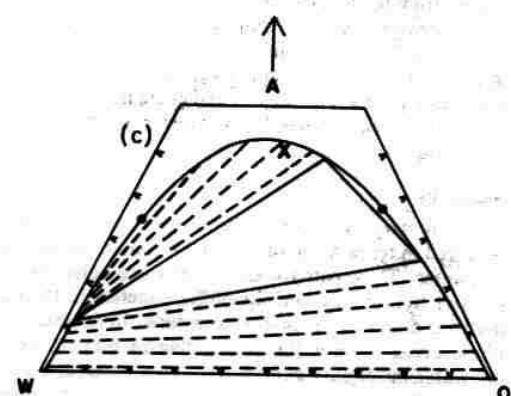
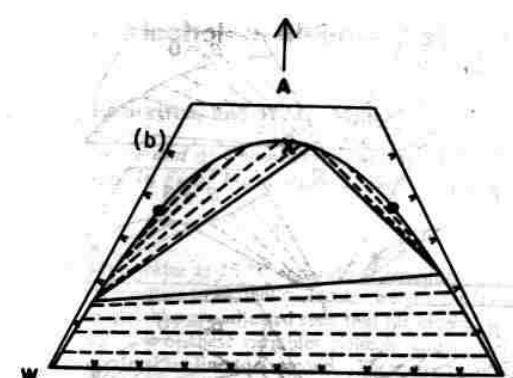
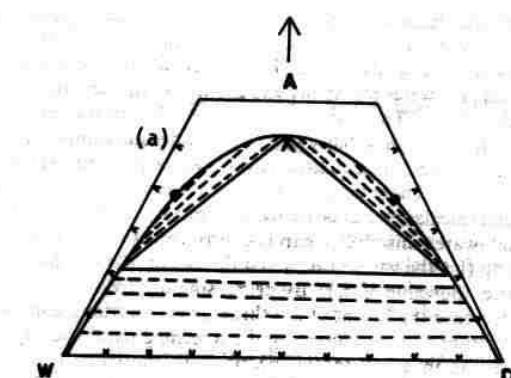


Figure 11. Exponentially screened Flory-Huggins (ESFH) model-generated ternary phase diagrams with $\alpha_{wo} = 4.8$, $\alpha_{os} = 0.55$, $m_w/m_o = 0.1$, $\beta_a = 0.3$, and varying α_{wa} : (a) $\alpha_{wa} = 0.55$, (b) $\alpha_{wa} = 0.57$, (c) $\alpha_{wa} = 0.59$, (d) $\alpha_{wa} = 0.61$. Critical points are given by filled circles, and tie lines by dashed lines. (Reproduced with permission from ref 18). Copyright 1985, Society of Petroleum Engineers of AIME.

equivalent to increasing amphiphile size in the experimental systems.¹⁸

The phase behavior progression in Figure 9 for C_8E_3 -*n*-decane-water mixtures as a function of temperature cannot be generated with the ESFH model as written in eq 1. The difficulty is in producing the unusual partitioning behavior of Figure 9a. Here, even though water and amphiphile are immiscible from $\phi_a = 0.01$ to $\phi_a = 0.25$, the addition of from 5 to 10% *n*-decane produces a one-phase mixture. Moreover, addition of more *n*-decane produces a 2 system in which C_8E_3 partitions preferentially into the water-rich phase. This is surprising because one would conclude, based on the binary amphiphile-water and amphiphile-*n*-decane phase behavior, that C_8E_3 should preferentially partition into an oil-rich rather than a water-rich phase. With α_{wa} positive and sufficiently large to yield a binary water-amphiphile miscibility gap and with α_{os} less than the positive value which yields an oil-amphiphile miscibility gap, the ternary phase behavior derived from eq 1 always predicts that amphiphile will partition into the phase with most oil when the mixpoint lies in the multiphase region. Figure 9 indicates that the addition of small amounts of oil attenuate water-amphiphile repulsion just as small amounts of amphiphile attenuate oil-water repulsion. Equation 1 does not explicitly account for this oleic "screening" of water and amphiphile but can be made to do so.

The ESFH model which includes both oil-water screening by amphiphile and amphiphile-water screening by oil is

$$g^* = \phi_w \ln \phi_w + (m_w/m_o)\phi_o \ln \phi_o + (m_w/m_o)\phi_a \ln \phi_a + \alpha_{wo} \exp(-\beta_a \phi_o) \phi_w \phi_o + \phi_{os} \phi_o \phi_s + \alpha_{ws} \exp(-\beta_w \phi_a) \phi_w \phi_s \quad (2)$$

The oleic screening parameter can be interpreted in a structural way. In the absence of oil, amphiphile cannot effectively isolate its lipophilic groups from water by micellizing and so phase separation occurs. In the presence of small amounts of oil, however, amphiphile organizes to form swollen micelles of apparently lower free energy than the phase-separated amphi-

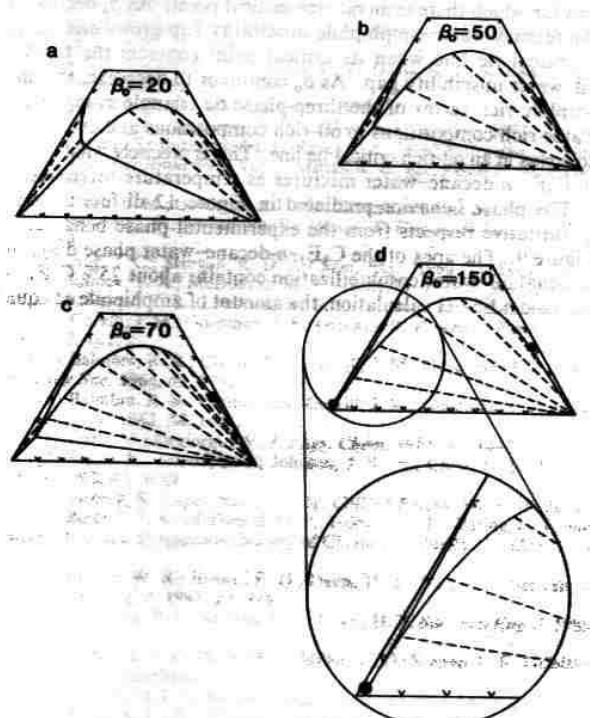


Figure 12. ESFH generated ternary phase diagrams incorporating oleic screening term with $\alpha_{wo} = 4.8$, $\alpha_{ws} = 1.0$, $\alpha_{os} = 0.65$, $\beta_a = 0.5$, $m_w/m_o = 0.1$, and varying β_o .

phile-rich solution. Even though amphiphile is completely miscible with *n*-decane in all proportions, C_8E_3 partitions into a water-rich

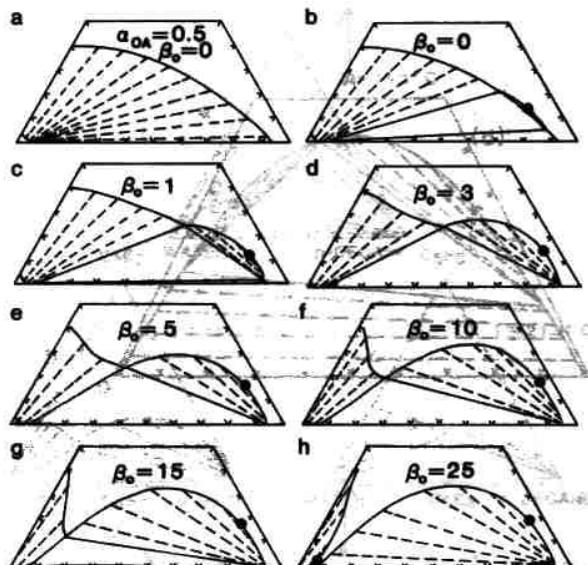


Figure 13. ESFH generated ternary phase diagrams with $\alpha_{wo} = 3.0$, $\alpha_{wn} = 0.8$, $\alpha_{oo} = 0.54$, $\beta_s = 0.3$, $m_w/m_n = 0.05$, and varying β_o .

phase at low temperatures provided there is sufficient *n*-decane present. At higher temperatures, the enthalpy gained by hydrogen bonding between ethylene oxide groups and water diminishes and amphiphile partitions into the oleic phase. This progression of ternary phase behavior can be captured qualitatively by a temperature-dependent β_o . With $\beta_s = 0.5$, $\alpha_{wn} = 1.0$, $\alpha_{oo} = 0.65$, and β_o varying from 150 to 20, the ternary phase diagrams shown in Figure 12 result. With $\beta_o = 150$, two distinct miscibility gaps exist: an amphiphile–water miscibility gap from $\phi_a = 0.04$ to $\phi_a = 0.56$ and extending into the ternary diagram to an oil volume fraction of about 0.015, and an oil–water miscibility gap which extends into the ternary diagram to a value of ϕ_a of about 0.55 and for which there is an oil-rich critical point. As β_o decreases, the ternary water–amphiphile miscibility gap grows and forms a critical tie line when its critical point contacts the ternary oil–water miscibility gap. As β_o continues to decrease, the amphiphile-rich vertex of the three-phase tie triangle swings from water-rich compositions to oil-rich compositions and eventually collapses in an oil-rich critical tie line. This is precisely what occurs in C_8E_3 –*n*-decane–water mixtures as temperature increases.

The phase behavior predicted in Figure 12 differs in some quantitative respects from the experimental phase behavior of Figure 9. The apex of the C_8E_3 –*n*-decane–water phase diagram at equal oil–water cosolubilization contains about 25% C_8E_3 ; in the model ESFH calculation, the amount of amphiphile at equal

cosolubilization is about 46%. The binary C_8E_3 –water miscibility gap decreases in extent with temperature and at 13.6 °C is about 24 wt % in width; the ESFH model calculation predicts an amphiphile–water miscibility gap extending from less than 1% to more than 57%. The water-rich critical point on the ternary amphiphile–water miscibility gap has an *n*-decane composition of about 5%; the ESFH calculation gives a water-rich critical point of only 1.2% oil. These three quantitative differences between experiment and calculation can be corrected somewhat. The size of the ternary oil–water miscibility gap is controlled by the binary miscibility gap (i.e. the value of α_{wo}) and the extent of amphiphilic screening (i.e. the value of β_o). By decreasing α_{wo} from 4.8 to 3.0, we can decrease the height of the three-phase tie triangle in the ternary mixture without increasing the screening parameter β_o . This also results in a substantial decrease in the value of β_o , the oleic screening parameter, at the water-rich critical point. By decreasing the value of α_{wn} from 1.0 to 0.8 and by decreasing the value of m_w/m_n from 0.1 to 0.05, the binary amphiphile–water miscibility gap decreases in extent from 57% to 39%. The resulting series of ternary phase diagrams as β_o increases from 0 to 25 is shown in Figure 13. The agreement with the experimental phase diagrams in Figure 9 is quite good and could no doubt be made better by statistical regression of the parameters of the model. We made no attempt to do so.

Summary

In summary, two distinct patterns of three-phase equilibria are observed in ternary mixtures of ethoxylated alcohols, *n*-alkanes, and water. These patterns are sensitive to amphiphile size, relative sizes of hydrophilic and lipophilic moieties of the amphiphile, *n*-alkane chain length, and temperature. In one pattern, the third phase arises from within and collapses into the same ternary oil–water miscibility gap. In the other pattern, the third phase arises from fusion of two different two-phase regions. Both patterns can be modeled by a modified Flory–Huggins equation of state. The modification accounts directly for the attenuation, or “screening”, of oil–water enthalpic repulsion of amphiphile. In the second pattern of three-phase emergence, two screening terms are necessary.

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Registry No. C_4E_1 , 111-76-2; C_4E_2 , 112-34-5; C_6E_2 , 112-59-4; C_8E_3 , 19327-38-9; $C_{10}E_4$, 5703-94-6; hexane, 110-54-3; octane, 111-65-9; nonane, 111-84-2; decane, 124-18-5; dodecane, 112-40-3; tetradecane, 629-59-4; pentadecane, 629-62-9; hexadecane, 544-76-3; undecane, 1120-21-4.