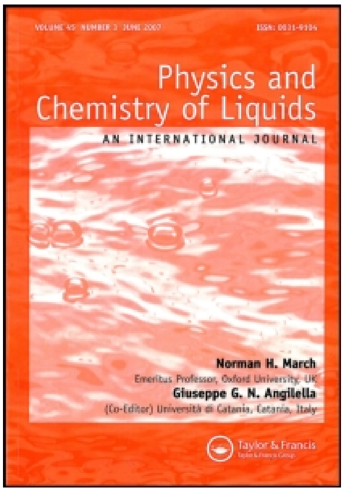

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DETERMINATION OF A TRICRITICAL POINT IN A PENTANARY MICROEMULSION

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Multicomponent fluid mixtures are particularly suitable for the search of tricritical points. We have studied a pentanary microemulsion, dodecane, ionic amphiphile, alcohol and brine, following a method originally proposed by Kahlweit. This way, it is possible to determine (at constant pressure) the composition and temperature at which these kind of critical points exist. Opalescence appears at approximately 5°C from this critical point.

KEY WORDS: Microemulsions, phase diagrams, critical points.

INTRODUCTION

The possibility of finding critical points in a thermodynamic phase diagram, where three or more phases become identical, has been a challenging problem in the study of phase transition phenomena.[1]

As it has been remarked by different authors,[2,3,4] multicomponent fluid mixtures are particularly suitable systems to search tricritical points. F. Zernicke[5] has used the phase rule to establish thermodynamic conditions which must be followed in order to obtain high order critical points ($n > 2$). At a critical point, the requirement that two phases become identical, introduces an additional constraint and reduces the number of degrees of freedom by one. Hence, for a critical point of order n, $n - 1$ additional conditions must be added according to Gibbs phase rule $F = C + 2 - P - (n - 1) = C + 3 - P - n$. So, in a three phase pentanary system and for $n = 3$, $F = 2$, one can expect a tricritical line to exist (at constant pressure). We must point out that, though determinations of this point in different systems have been reported since 1962,[6,7,8] there is not much data of this kind on 5-component microemulsions.[9]

METHOD

We have followed the experimental method which was originally proposed by Kahlweit[10] to determine tricritical points. Basically, this method consists in arbitrarily fixing the pressure, the water/oil and surfactant/cosurfactant ratios while

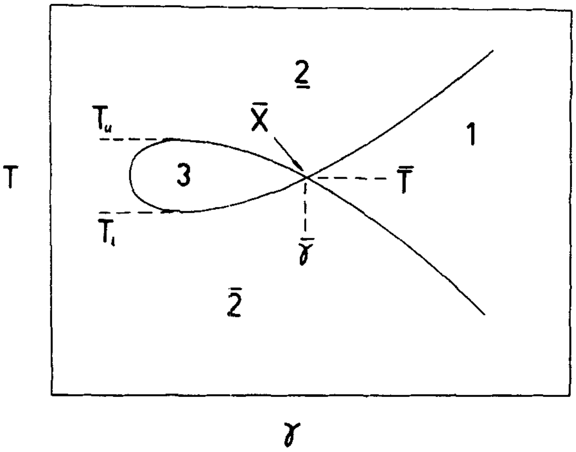


Figure 1 "Loop" schematic representation.

changing the salinity of each sample. The water/oil ratio is fitted at the end of the experience while the surfactant/cosurfactant ratio is held constant.

Compositions are redefined as: $\alpha = B/A + B + E$, the mass fraction of the oil in the mixture of oil and brine, $\gamma = C + D/A + B + C + D + E$, mass fraction of alcohol and ionic amphiphile in the mixture of all five components, $\delta = D/C + D$, mass fraction of the ionic in the mixture of alcohol and ionic amphiphile, $\varepsilon = E/A + E$, mass fraction of the salt in the brine, where A (water), B (oil), C (cosurfactant), D (surfactant), E (electrolyte).

The three phase zone is determined in the diagram of temperature, T, versus γ at constant salinity (Figure 1).

Experimentally, at a high γ one finds the sequence $\underline{2}$–1–$\bar{2}$, at a lower γ $\underline{2}$–3–$\bar{2}$ and at a very low γ two phases that are $\underline{2}$–$\bar{2}$. Let us note as $\bar{X}$ the point at which the three phase zone and the single one touch each other. In the T–γ plane, the $\bar{X}$ coordinates are denoted as $\bar{T}$, $\bar{\gamma}$.

We point out that the microemulsion middle phase appears at T_l and disappears at T_u ($T_l > T_u$). Following Kahlweit,[11,12] these two critical end points have the coordinates $T_l, \gamma_l, \alpha, \varepsilon, \delta$ and $T_u, \gamma_u, \alpha, \varepsilon, \delta$.

Now at a certain thermodynamic condition, the three phase surface, which is bounded by a loop (a "fish" according to Kahlweit's denomination) characteristic of this kind of diagram, becomes of minimum area until it disappears.

Because the tricritical point is considered to be at the intersection of two critical end point lines,[2] the progressive shrinkage of the three phase zone up to a unique phase point is indicative that the vicinity of the tcp has been reached.

The tricritical points belong to the $\bar{X}$ set. By changing ε and finally α, one can find the required critical point.[9]

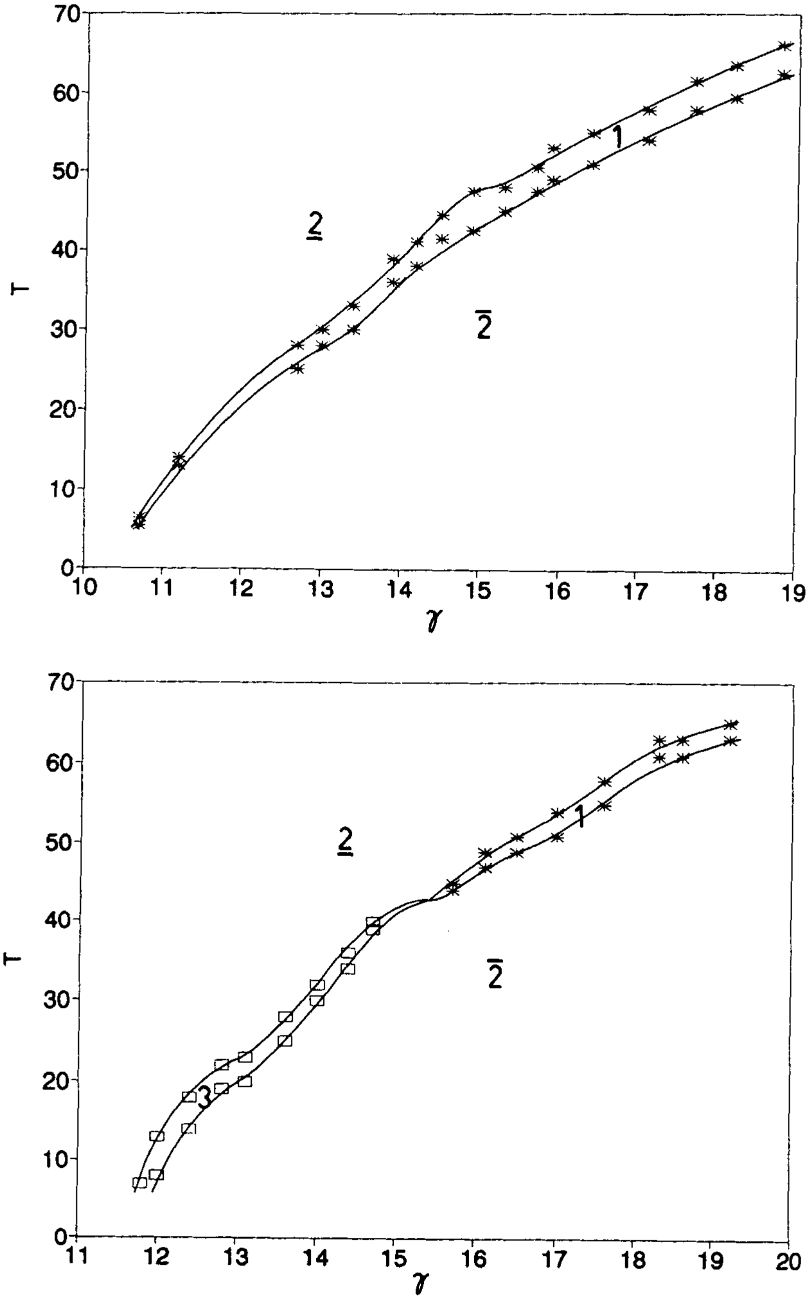
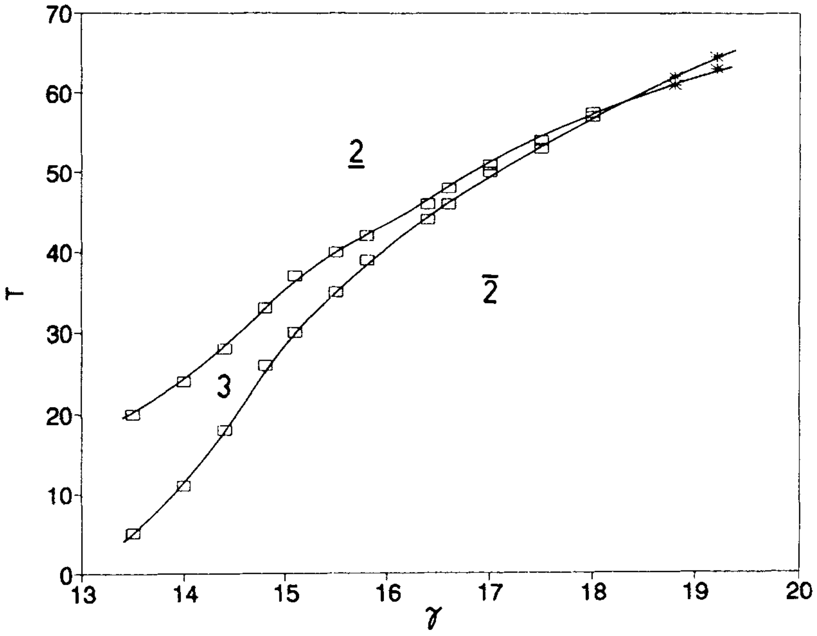


Figure 2 Equilibrium diagrams of temperature (T) versus γ (ε = 1%wt; α = 0.5 wt). 2a—D = 3%(wt), $\bar{2}$: upper microemulsion, $\underline{2}$: lower microemulsion, 3: middle microemulsion, 1: single phase. 2b—D = 4%(wt), $\bar{2}$: upper microemulsion, $\underline{2}$: lower microemulsion, 3: middle microemulsion, 1: single phase. 2c—D = 5%(wt), $\bar{2}$: upper microemulsion, $\underline{2}$: lower microemulsion, 3: middle microemulsion. 2d—D = 6%(wt), $\bar{2}$: upper microemulsion, $\underline{2}$: lower microemulsion, 3: middle microemulsion.



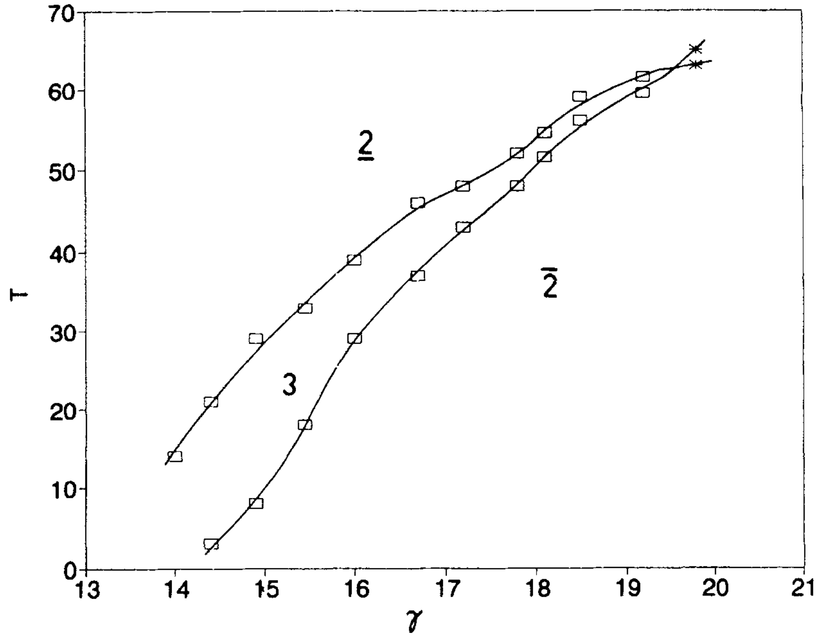


Figure 2 (*Continued*)

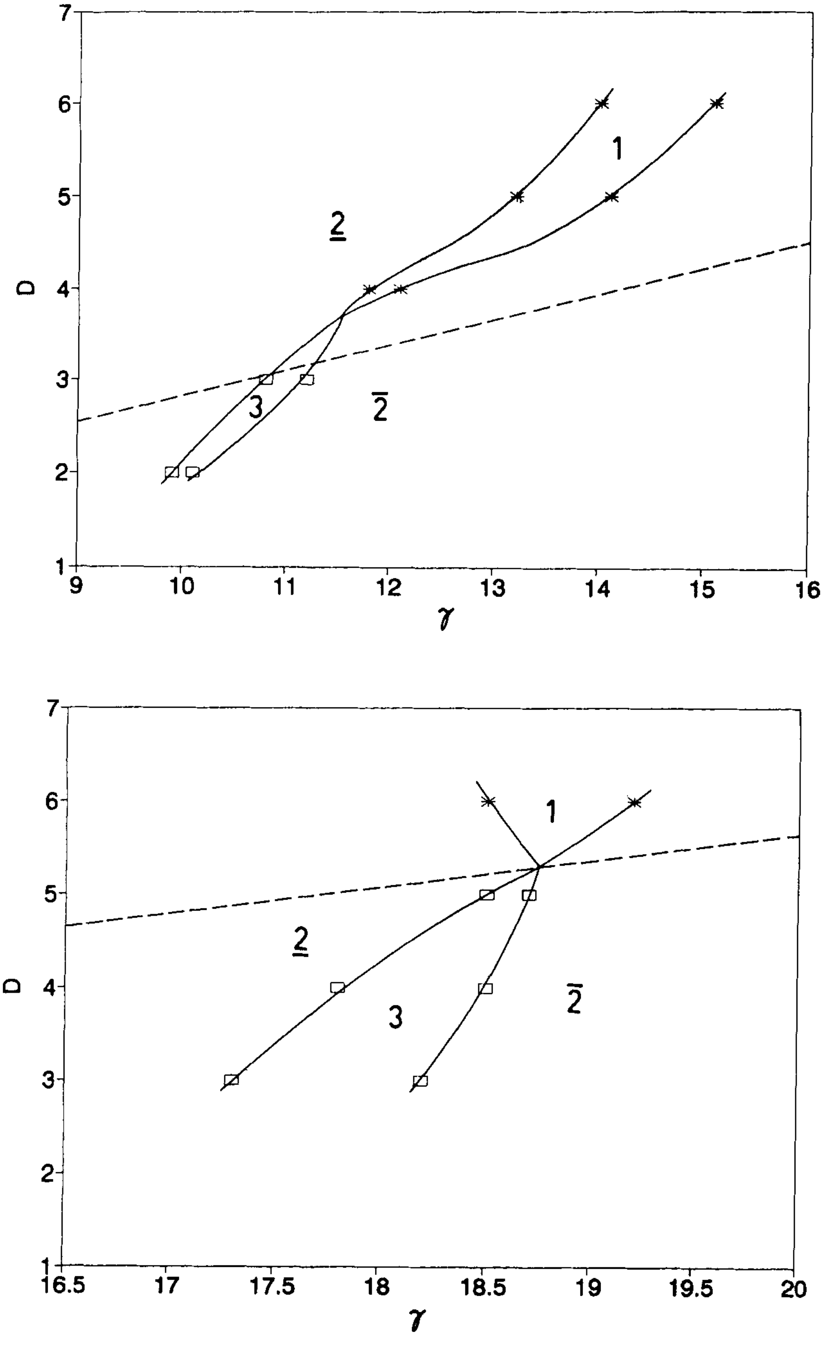


Figure 3 Equilibrium diagrams of surfactant concentration (D) versus γ. ($\varepsilon = 1\%$wt; $\alpha = 0.5$ wt). $\bar{2}$: upper microemulsion, $\underline{2}$: lower microemulsion, 3: middle microemulsion, 1: single phase. 3a—T = 10°C; 3b—T = 60°C.

EXPERIMENTAL

We have used the following compounds: $DDBSO_3$ trietanolamine, dodecane, normal amyl alcohol and brine (IK). The liquid samples were placed in screwed, graduated and teflon sealed tubes. The thermostatic stabilization accuracy was of ±0.1°C. We have proceeded by successive steps. First, we shall choose an approximate α value (0.495), because by a previous coarse analysis we knew that the three phase zone is in the proximity of this concentration. Obviously, the exact α value was adjusted at the end of the experimental running.

Next, we shall choose a δ value which must be near to the critical zone in order to modify the brine concentration (experimentally this is a better procedure because salt concentration can be adjusted with greater accuracy).

Equilibrium diagrams temperature vs γ (cosurfactant + surfactant concentration) were performed for $D = 3$, 4, 5 and 6 %wt at constant brine concentration (Figures 2a, 2b, 2c, 2d). So, we are in condition to represent isothermal diagrams D vs γ (Figures 3a, 3b).

In Figure 4 it is shown a three-dimensional display of T, D and γ variables.

It is easily seen, that isothermal diagrams which have been represented in Figure 3, are obtained by intersection of single and three phase bodies (Figure 2) with constant temperature planes ($T = 10°C$ and $60°C$).

Now, each straight line which passes through the origin (Figure 3) has a slope value that represents the corresponding δ. Therefore, the zone of three phase equilibria as a function of temperature is plotted in temperature vs γ for each δ. The δ value which corresponds to the least surface bounded by the loop (since it is the

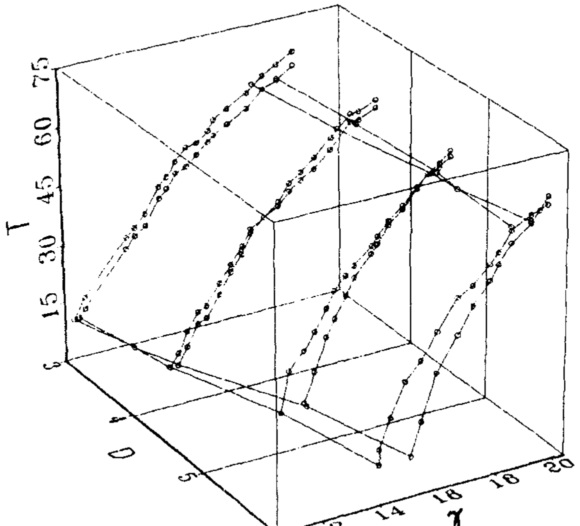
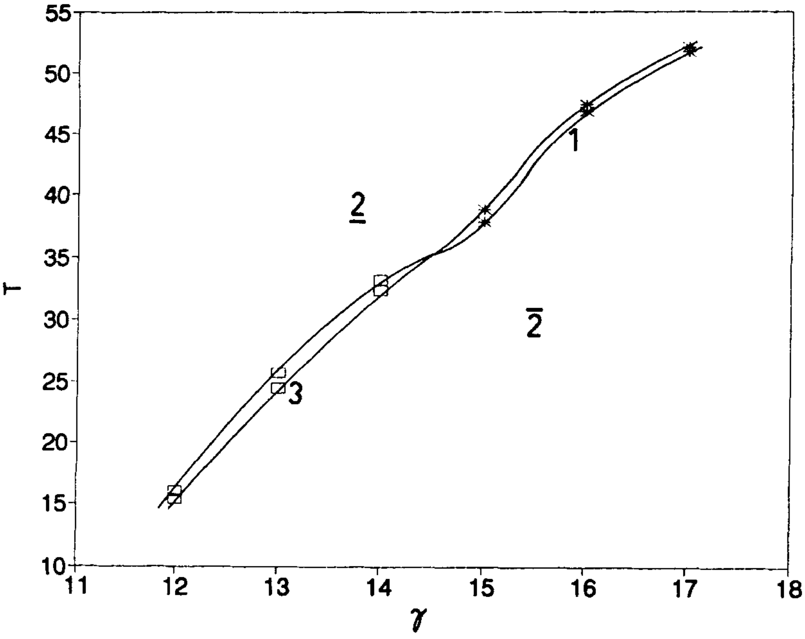


Figure 4 Equilibrium diagrams in T–D–γ space. For discussion see text.



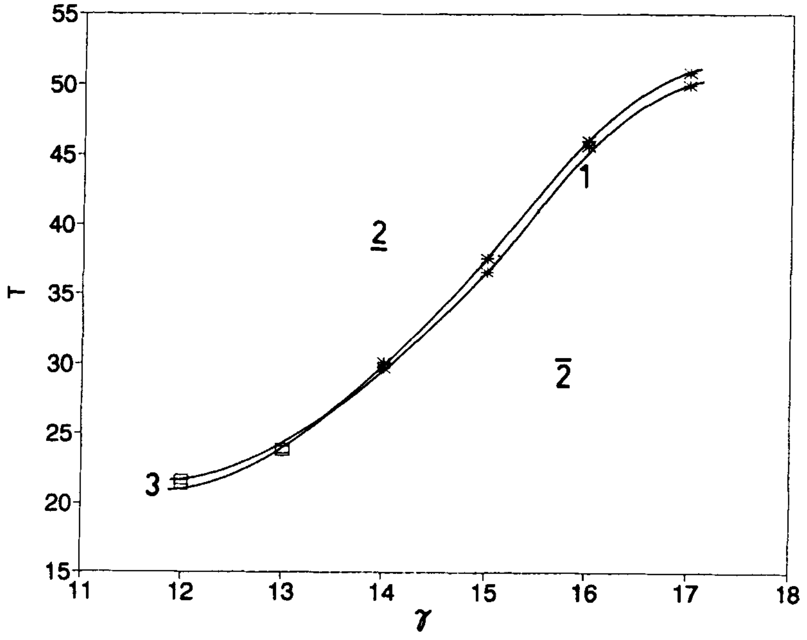


Figure 5 Equilibrium diagrams of temperature versus γ. ($\delta = 0.28$). $\bar{2}$: upper microemulsion, $\underline{2}$: lower microemulsion, 3: middle microemulsion, 1: single phase. 5a—$\varepsilon = 0.98\%$(wt); 5b—$\varepsilon = 0.96\%$(wt).

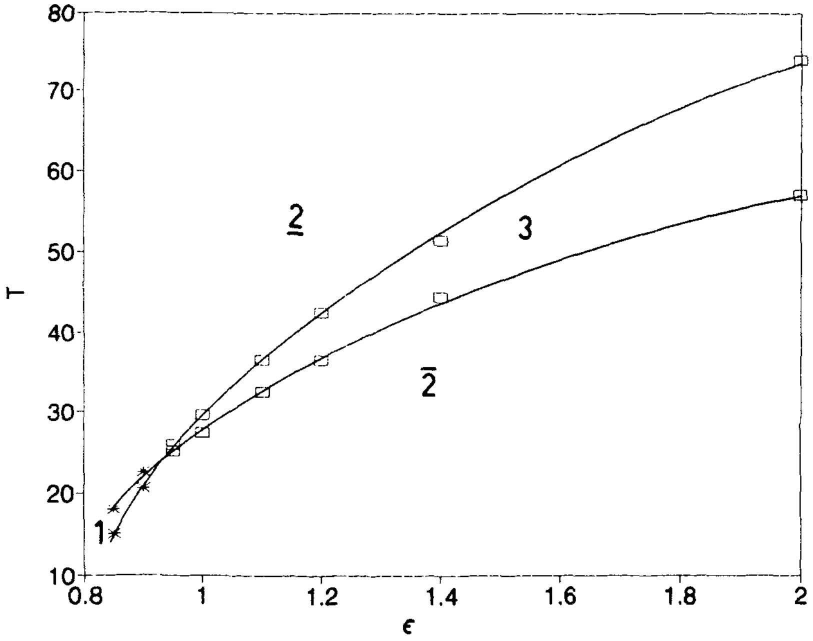


Figure 6 Equilibrium diagram of temperature versus ε. ($\gamma = 13$ %wt; $\alpha = 0.495$ wt; $\varepsilon = 0.24$ %wt). $\overline{2}$: upper microemulsion, $\underline{2}$: lower microemulsion, 3: middle microemulsion, 1: single phase.

nearest to the tricritical line) must be selected again. In our case $\delta = 0.28$. For this δ value, T is plotted as a function of γ (Figure 5) for different ε. The ε value is diminished until the three phase zone is reduced to its minimum surface. If we should continue to decrease ε, the three phase zone would disappear and both single and two phase zones would only be observed (Figure 6).

In Figure 6, the cusp-shaped three phase body with the apex lying near the tricritical point coordinates is shown. The upper line represents the transition temperatures between w/o and middle microemulsions, whereas the lower line is indicative of the middle to o/w transition zones. Previously, the α value had been fitted.

From our experimental values it can be estimated that the tricritical point is in the neighborhood of the following composition

$$T = 26°\mathrm{C};\ X_A = 43.51\%;\ X_B = 43.07\%;\ X_c = 9.36\%;$$

$$X_D = 3.64\%;\ X_D = 0.42\%\ \text{(Figure 6)}.$$

We can conclude that Kahlweit's method is self consistent. As it has been pointed out[3,13] it is not possible, by mere visual inspection, to assert that different phases become simultaneously identical. Furthermore, near the estimated experimental values, upper and lower phase volumes are so little that it is very difficult to follow the movements of the meniscuses.

On the other hand, liquid samples become opalescent at or more 5°C from the tricritical point.[14]

References

1. Ch. M. Knoblerand and R. L. Scott in *Phase Transitions and Critical Phenomena*; Chapter 2, Vol. 9, Academic Press, New York; C. Domb, J. L. Lebowitz, Eds. (1984).
2. B. Widom, *J. Phys. Chem.*, **77**, (18), 2196 (1973).
3. R. Griffiths and B. Widom, *Phys. Rev.*, **A8**, 2173 (1973).
4. M. Kaufman and R. B. Griffiths, *J. Chem. Phys.* **76** (3) (1982).
5. J. Zernike, *Recl. Trav. Chim. Pays-Bas*, **68**, 585 (1949).
6. I. R. Krichevskii, *et al.*, *Russ. J. Phys. Chem.*, **46**, 1411 (1972).
7. I. R. Krichevskii, G. D. Efremova, R. O. Pryanokova and A. V. Serebryakova, *Russ. J. Phys. Chem.*, **37**, 1046 (1963).
8. G. S. Radyshevskaya, N. I. Nikurashina and R. V. Mertslin, *J. Gen. Chem. USSR*, **32**, 673 (1962).
9. M. Kahlweit and R. Strey, *J. Phys. Chem.*, **90** (21) (1986).
10. M. Kahlweit, R. Strey *et al.*, *Langmuir*, **5** (2), 305 (1989).
11. M. Kahlweit, R. Strey *et al. J. Chem. Phys.* **95** (4), 2842 (1991).
12. M. Kahlweit and R. Strey, *J. Phys. Chem.*, **92** (6), 1557 (1988).
13. D. Langevin, *Mol. Cryst. Liq. Cryst.*, **138**, 259 (1986).
14. H. Kunieda and K. Shinoda, *J. Coll. Int. Sci.*, **75**, 601 (1980).