Interfacial Tension in Microemulsions along a Path in the Middle Phase Region up to the Tricritical Point

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LETTER
Interfacial Tension in Microemulsions along a Path in the Middle Phase Region up to the Tricritical Point

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Measurements of low interfacial tension, σ, in microemulsions were performed using the spinning drop tensiometer technique. The thermodynamic path followed, was in the middle phase region between critical end points loci, up to the neighbourhood of the tricritical point. When approaching this point, σ values grow, which may be indicative of a discontinuity. Experimental results are discussed.

KEY WORDS: Molecular interactions. Microstructure.

INTRODUCTION

It is well-known that it is more difficult to make a correct theoretical prediction about the interfacial tension in amphiphilic systems than in other liquid system (such as liquid metals i.e.).[1,2] There are several reasons to account for this: the complex nature of molecular interactions, the difficulty in modelling the microstructure and the great number of different chemical components; hence the existence of the phenomenological, the thermodynamic and the statistico-mechanical approaches, which are aimed at tackling this problem.[3,4,5,6,7]

Yet, these approaches are not always concordant with one another and the quantitative corroboration with experimental data is neither easy nor straightforward.[8] Nevertheless, when we study a system from the point of view of its critical behaviour, the analysis becomes independent from its specific physico-chemical nature as, under these conditions, the system shows some universality. This fact is reflected in the possibility of describing the phenomenon under scaling laws.

In microemulsions we can observe the appearance of the so-called critical end points and tricritical points.[8,9] Suppose, we have a liquid system with three phases, namely α, β and γ, where β is the middle phase. If α and β are in a critical point of their own phase equilibrium with the γ phase, the system is in a state which is called an $\alpha\beta$ critical end point, $\alpha\beta$ (c.e.p.). A symmetrical definition is used for the case when β and γ are in a critical point of their own equilibrium, $\beta\gamma$ (c.e.p.). When the two lines $\alpha\beta$, $\beta\gamma$ (c.e.p.) in the phase diagram intersect, the system is in a tricritical point, which physically means that three phases become simultaneously identical. The three phase

state is bounded by the loci of $\alpha\beta$ (c.e.p.) and $\rho\gamma$ (c.e.p.) and one can arrive at the tricritical point by following different thermodynamical paths across this region. For scientific and technological reasons, we are interested in studying the so-called "optimum" microemulsions, say, these systems in which the oil-microemulsion interfacial tension (σ_{M-O}) is the same as the water-microemulsion interfacial tension (σ_{M-W}). The goal of this work, is the study of the behaviour of σ along the particular thermodynamical way determined by "optimum" microemulsions, up to the tricritical points. Our field thermodynamic variable, according to Griffiths[10] should be the chemical potential (μ) because we have changed the surfactant and cosurfactant concentrations and other variables—pressure, temperature and hydrocarbon and brine concentration—have been held constant.

EXPERIMENTAL PROCEDURES AND RESULTS

Microemulsions were prepared using dodecane, brine triethalonamine sulphonate dodecylbencene (surfactant) and normal amyl alcohol. The hydrocarbon/brine ratio was held equal to unity for all microemulsions in order to lower the number of independent components. Firstly, liquid samples were mechanically shaken for 24–48 hours, and then by means of an ultrasonic device. They were immediately plunged into a thermostatic bath.

The stabilisation period depends on each microemulsion but varied it between 7 to 14 days. Afterwards, the composition and volume of each phase was established. In Figure 1 we have represented the kind of phase equilibrium which was obtained for different concentrations. It can be observed how the three phase region is limited by the loci of $\alpha\beta$ (c.e.p.) and $\beta\gamma$ (c.e.p.) which intersect at the tricritical point. The interfacial tensions were determined through the spinning drop tensiometer technique (Texas University 500 Model). The experimental conditions make it possible to apply the formula.[11]

$$\sigma = (\Delta\rho)\omega^2 r^3/4$$

where $\Delta\rho$ = difference in density between the two phases
         ω = angular frequency (radians/second)
         r = radius of the cylindrical droplet

Special care was taken to measure the interfacial tension of the "optimum" microemulsions (σ_{M-O_p}). We consider that the error in the ultra-low tension region was less than 10%. Our estimation is based on previous studies[12] and on the reproducibility we observed in our own experiments.

As a matter of fact, Jost *et al.*[13] have compared this technique with the pendant drop and light scattering techniques, the results being obtained by using three different methods in agreement with each other. In Figure 2 σ_{M-W}, σ_{M-O} are represented as a function of the alcohol concentration, at constant surfactant concentration. In Figure 3 σ_{M-O_p} is shown as a function of the surfactant and cosurfactant concentration.
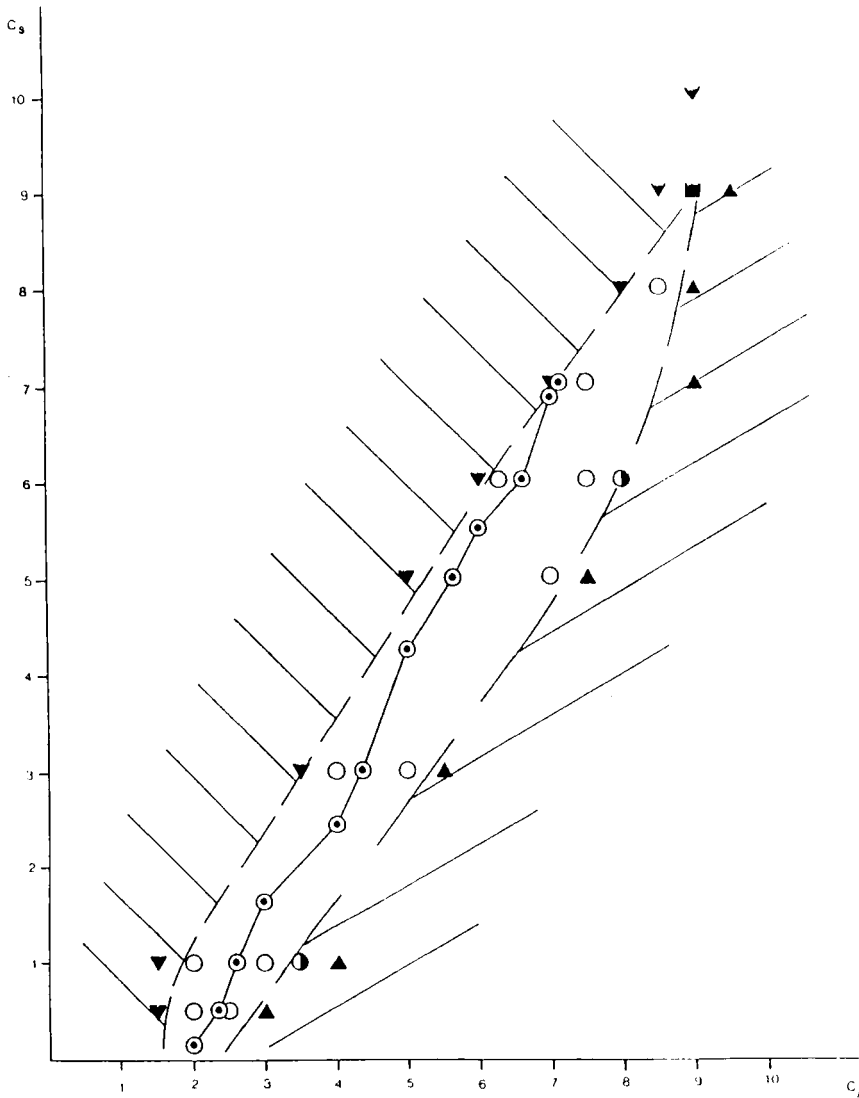
Figure 1 Phase equilibrium diagram C_s = surfactant concentration; C_A = cosurfactant concentration; ▼ microemulsion in equilibrium with oil phase; ▲ = microemulsions in equilibrium with brine; ○ = Middle microemulsion; ☉ = Optimum microemulsion; ◑ = Critical end points; ■ = Tricritical point.

DISCUSSION

As we have seen above, when we reach the tricritical point, σ_{M-O_p} grows, in the case we choose the thermodynamic path which corresponds to the optimum microemulsions. Now, due to the fact that interfacial tension can not diverge, and must vanish in the single phase, we are in the presence of a finite but dicontinuous transition. This is
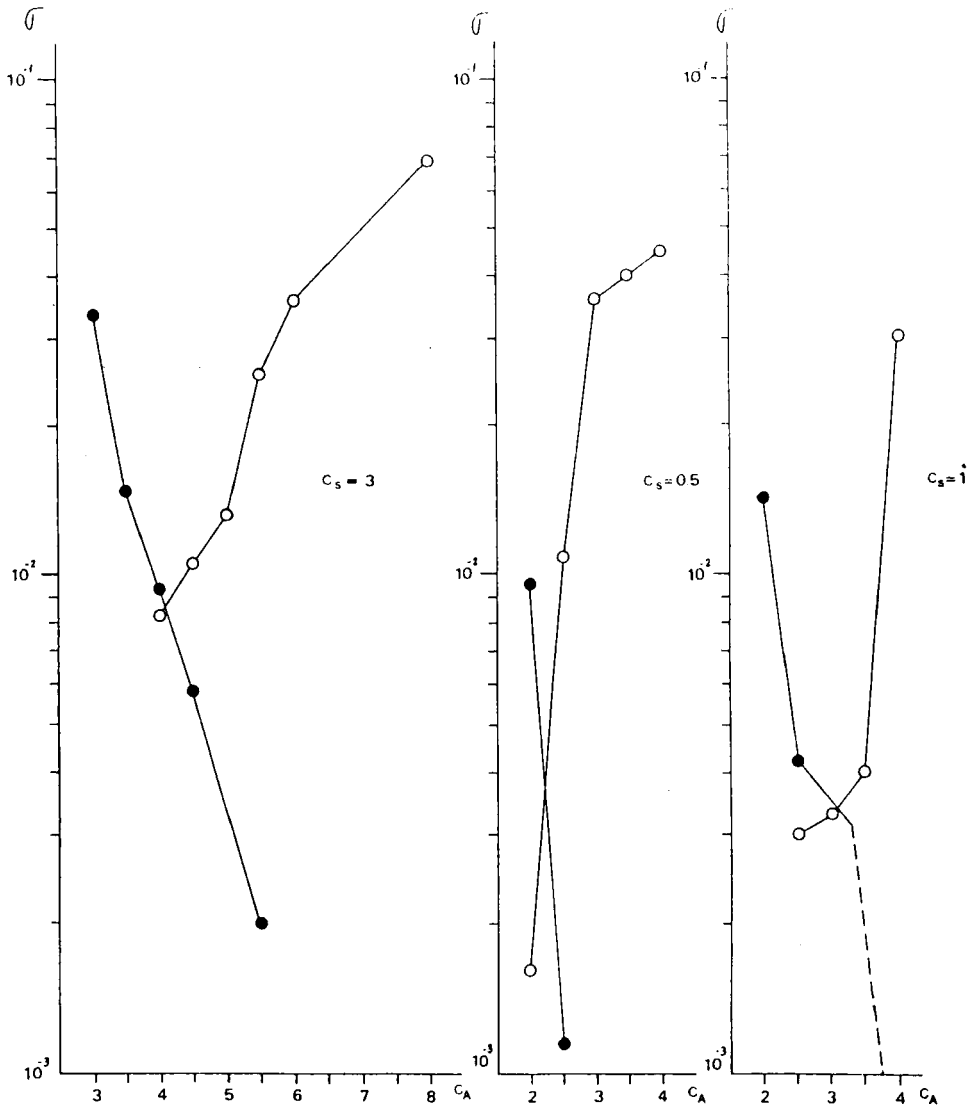
Figure 2 Interfacial tension as a function of cosurfactant concentration (C_s = surfactant concentration) (σ_{M-O}, σ_{M-W}).

qualitatively similar to what is predicted by the mean field theory about the constant volume heat capacity for liquid-vapor transition in a one-component fluid.[14]

Nevertheless, to carry out an analysis similar to the one made in the critical phenomena theory, we are faced with several problems. As it is well-known the scaling theories propose simple laws of the type
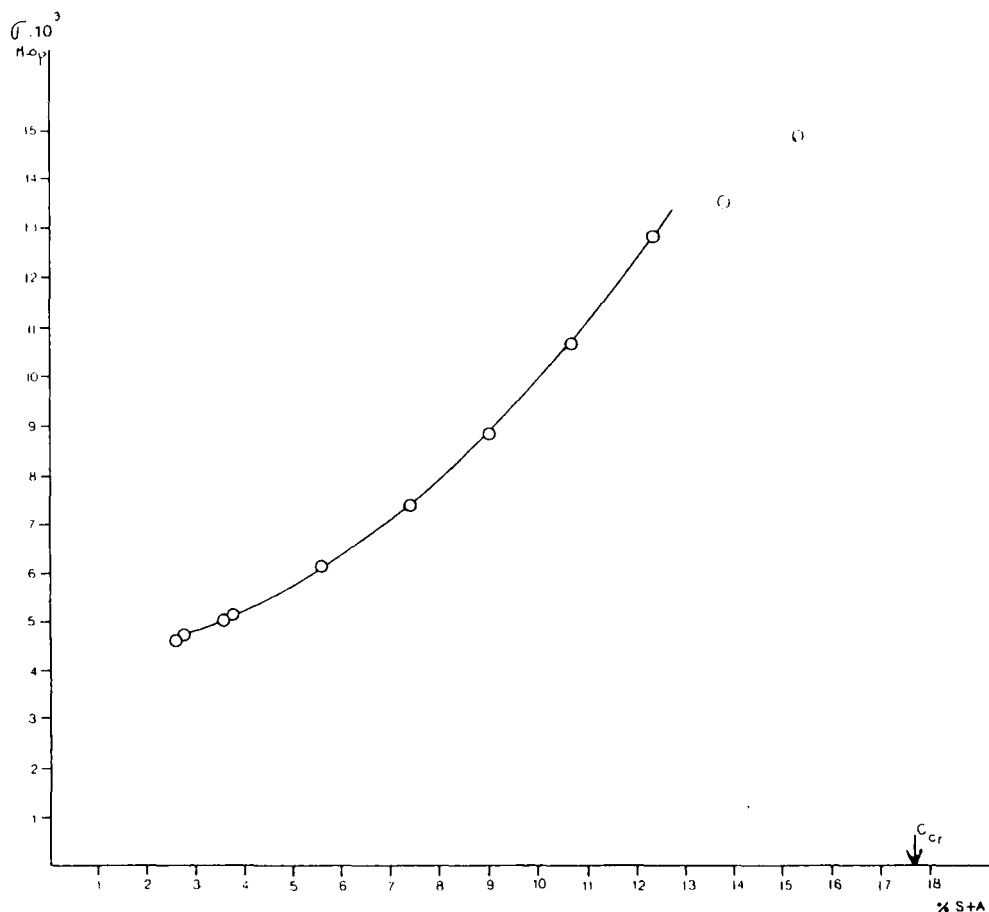
$$\sigma = \sigma_0 \varepsilon^x$$

Figure 3 Interfacial tension as a function of active substance $(C_s + C_A)$. (σ_{M-O_p}).

where σ_o is a scale factor, ε the distance to the critical point in the phase diagram and x is the critical exponent, whose value can provide physical information concerning this problem, since it can be compared to the aforesaid values from the different models.

In our case it is the variation in the chemical composition—keeping the pressure and the temperature constant—that results in the appearance of a single phase.

The order natural parameter to describe the process would be the chemical potential, but it is difficult to determine experimentally this thermodynamic magnitude.

Following Fleming[15] another order parameter would be the difference between the concentration of active substance (surfactant + cosurfactant) of each microemulsion (C) and the concentration of the single critical phase (C_{cr}). In Figure 4 we have represented a log-log plot of the interfacial tension as a function of the difference $|C - C_{cr}|$. The exponent value is -0.33 (correlation $= 0.98$). Nearly the same result is
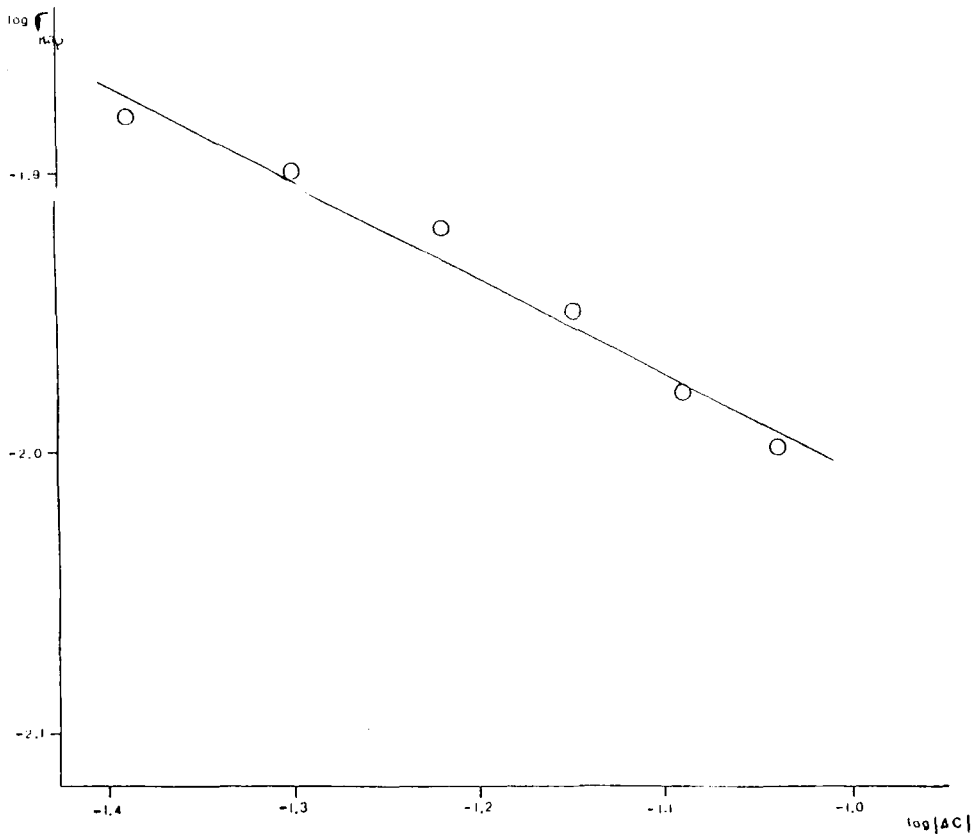
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Figure 4 Log–log plot of interfacial tension as a function of concentration difference $|C - C_{cr}|$; C = active substance concentration in each microemulsion; C_{cr} = active substance concentration in the single critical phase. (σ_{M-O_p}).

obtained using the difference between the densities $|\rho - \rho_{cr}|$ (exponent value $= -0.34$ with a correlation of 0.99).

Lastly, the σ_{M-O_p} behaviour, can be related to De Gennes model[16], in which the space is divided into adjacent cubes of length edge ζ filled at random either with hydrocarbon or with water. In this model the following formula is proposed

$$\xi = 6\phi_0\phi_w/C_s\Sigma$$

ϕ_w = water volume fraction;
C_s = number of surfactant molecules per unit volume;
Σ = area covered by a surfactant molecule

On increasing the radius of the particles $\Sigma \rightarrow \Sigma^*$ (saturated state) which has a constant value. On the other hand the following relation has been proposed.

$$\sigma \sim k_B.T/\xi^2$$

Table 1

$\sigma_{M-O_p}(dynes\ cm^{-1})$	$\phi_0\phi_w/C_s$
5×10^{-3}	1252.78
6.4×10^{-3}	784.94
6.7×10^{-3}	451.16
8.5×10^{-3}	420.45
9.7×10^{-3}	352.2
1.2×10^{-2}	333.7

Consequently, on increasing σ_{M-O_p}, ξ must decrease as well as the product $\phi_0\phi_w$ (as long as Σ is kept constant). In Table 1 it is shown that this hypothesis is experimentally verified.

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