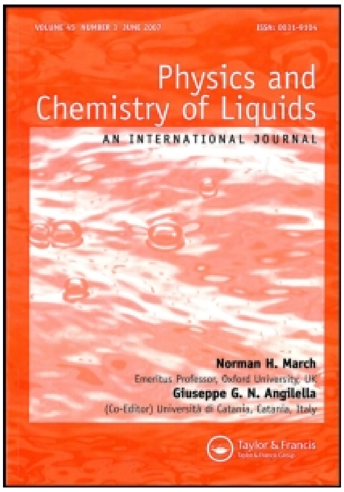

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Correlation of Experimental Phase Equilibria in a 5-Component Microemulsion System with a Phenomenological Model

P. B. Balbuena[a]; B. Ginzberg[b]; D. Kurlat[b]
[a] INTEC, Universidad Nacional del Litoral, Santa Fe, Argentina [b] Facultad de Ingenieria, Universidad de Buenos Aires, Buenos Aires, Argentina

To cite this Article Balbuena, P. B. , Ginzberg, B. and Kurlat, D.(1992) 'Correlation of Experimental Phase Equilibria in a 5-Component Microemulsion System with a Phenomenological Model', Physics and Chemistry of Liquids, 24: 3, 193 — 198
To link to this Article: DOI: 10.1080/00319109208027269
URL: http://dx.doi.org/10.1080/00319109208027269

Phys. Chem. Liq., 1992, Vol. 24, pp. 193–198
Reprints available directly from the publisher
Photocopying permitted by license only

LETTER

Correlation of Experimental Phase Equilibria in a 5-Component Microemulsion System with a Phenomenological Model

P. B. BALBUENA

INTEC, Universidad Nacional del Litoral, Güemes 3450, (3000) Santa Fe, Argentina

B. GINZBERG and D. KURLAT

Facultad de Ingenieria, Universidad de Buenos Aires, Paseo Colón 850, (1063), Buenos Aires, Argentina

(Received 15 August 1991)

The objective of this work is to determine the utility of a simple phenomenological model in correlating and predicting phase equilibria and interfacial tensions in complex systems, such as the ones involved in the enhanced oil recovery processes.

The model we have chosen is the one proposed by Widom[1] to describe microemulsions. The space is divided into cubes of edge-length ξ, and each cube filled at random, with oil or water, with the surfactant confined to the interface that separates oil-filled from water-filled cells.

The length ξ acts as a variational parameter, so the free energy is minimized with respect to it. There is a cutoff value a for this variable, which is set as the radius of a single molecule, a few Å.

Assuming that there is a fraction ϕ of cells oil-filled and $(1 - \phi)$ water-filled and that the surfactant film is composed of molecules with number density ρ, the model free energy density[1] is written as:

$$F(\phi, \rho, \xi) = \begin{cases} [\phi \ln \phi + (1 - \phi) \ln(1 - \phi)]\, kT/\xi^3 + 6\sigma_0 \phi(1 - \phi)/\xi & \\ \quad + \rho kT \ln[\xi \rho a^2/\phi(1 - \phi)] + D\rho[1 - \Lambda(2\phi - 1)\xi]/2\xi^2, & (\xi > a) \\ \infty, \quad (\xi < a) & \end{cases}$$

where σ_0 is the oil-water interaccion energy per unit area of contact oil and water filled cells; D and Λ are two parameters in the curvature free energy of the surfactant film. The parameter D determines the magnitude of the curvature free energy while Λ is the Bancroft parameter which determines a favored radius of curvature.

The free energy density is composed of five terms, the first three correspond to the regular solution model for the binary mixture oil-water. The remaining terms respond to the presence of the surfactant treated as if it were a two dimensional ideal gas. Hence one of these terms involves the film pressure. The last one takes into account the free energy curvature of the film, that is described as the sum of two contributions proportional to the first and second powers of the mean curvature.

It has been shown[1,2] that the model is able to describe phase equilibria for Winsor[3] I, II and III cases. This is accomplished by varying the three dimensionless model parameters: $p = j\sigma_0 a^2/kT$, with j the coordination number (6 for a cubic array), $q = D/a^2kT$ and $\lambda = \Lambda a$.

In this letter we present some experimental results on phase equilibria for a pentanary system: brine, surfactant, cosufarctant and oil. We compare these results with the ones obtained with the model, and discuss analogies between the model parameters and the system variables.

The system we are considering is composed by water, NaCl, dodecane, triethanolamine dodecylbencensulphonate and *n*-amyl alcohol.

The experimental phase equilibria for this system was determined by fixing the pressure, the salt concentration and the oil-water ratio. Details of the experimental procedure are given in a previous work[4].

In the above conditions, the system can be represented in bidimensional plot: % surfactant vs % (surfactant + cosurfactant).

Figure 1(a) shows this diagram for $T = 20°C$. Following a line of constant surfactant we can see the transition from a 2-phase zone to the 3-phase and again to the 2-phase zone. Thus two lines of phase transition points are well defined. Figure 1(b) shows calculated lines for the model, in a diagram q, the rigidity parameter, vs λ.

Experimental volume fractions of water in a lower phase microemulsion that coexists with an oil phase at a phase transition point are plotted vs temperature in Figure 2(a). Each curve is parametric in the surfactant density. On the other hand, Figure 2(b) shows the calculated values for the volume fractions of water as function of p, with q as a parameter.

Here we want to make an analysis from the two sets of figures. As remarked by Widom[1], by tuning the Bancroft parameter, the system moves from the two-phase region with a lower phase microemulsion (oil in water) into the three phase region and later on into a different 2-phase region where the microemulsion (water in oil) is the upper phase.

In the real system we are considering, and in the conditions stated above, this role is being played by the cosurfactant. However, as it can be seen by comparing Figures 1(a) and 1(b), the experimental 3-phase envelope is not symmetric as the one displayed by the model. Thus, it seems that both parameters λ and q are represented by some combination of the variables S and A. It is important to note that the inverse of the film rigidity parameter, q, is being compared with the amount of surfactant in the system, this analogy is again shown in Figure 2. Besides, the oil-water interaction parameter, p, is related to the temperature. An estimation of this parameter value has been done[1] by associating it to the oil-water solubility, which is given approximately by e^{-p}. For very unmiscible systems, like oil and water, the solubility

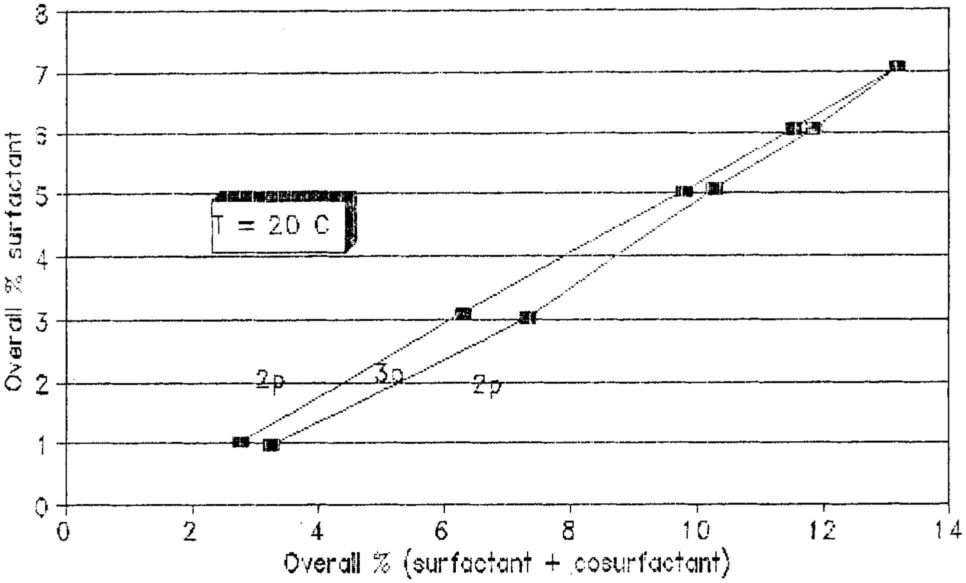

Figure 1a

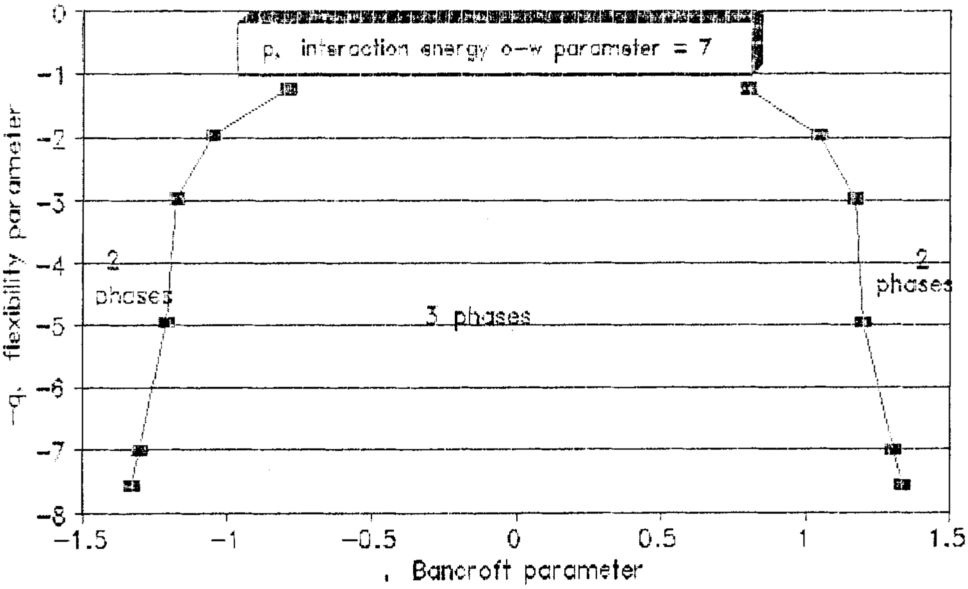

Figure 1b

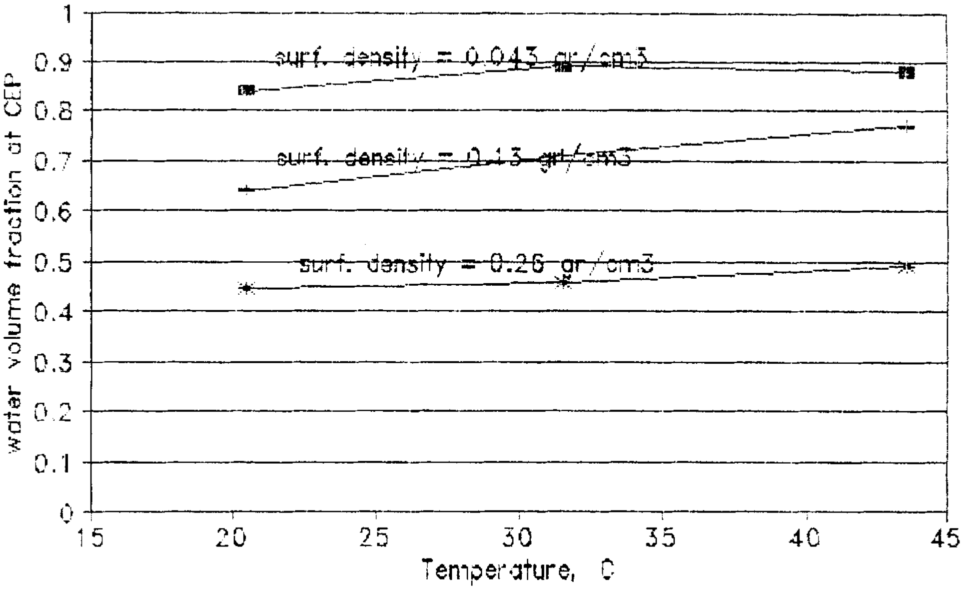

Figure 2a

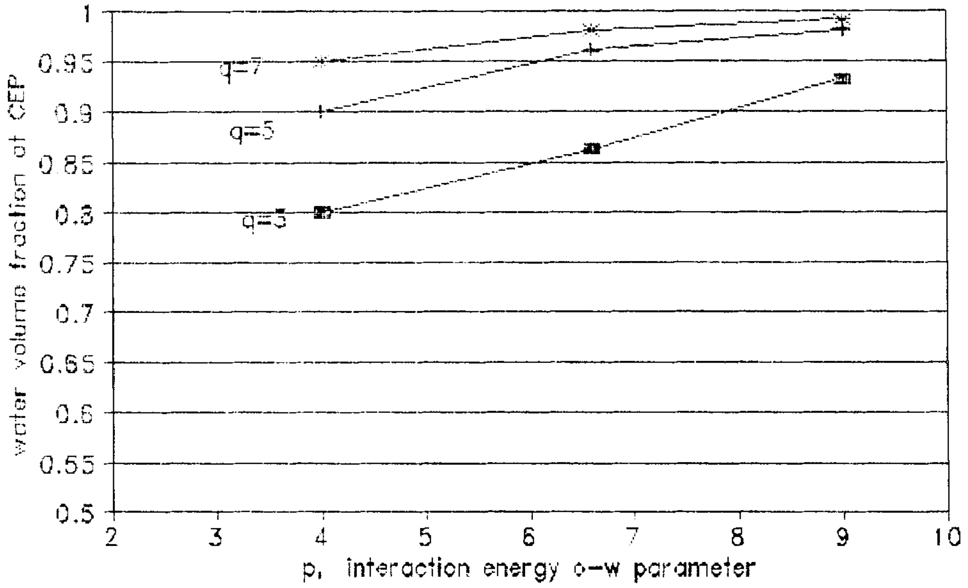

Figure 2b

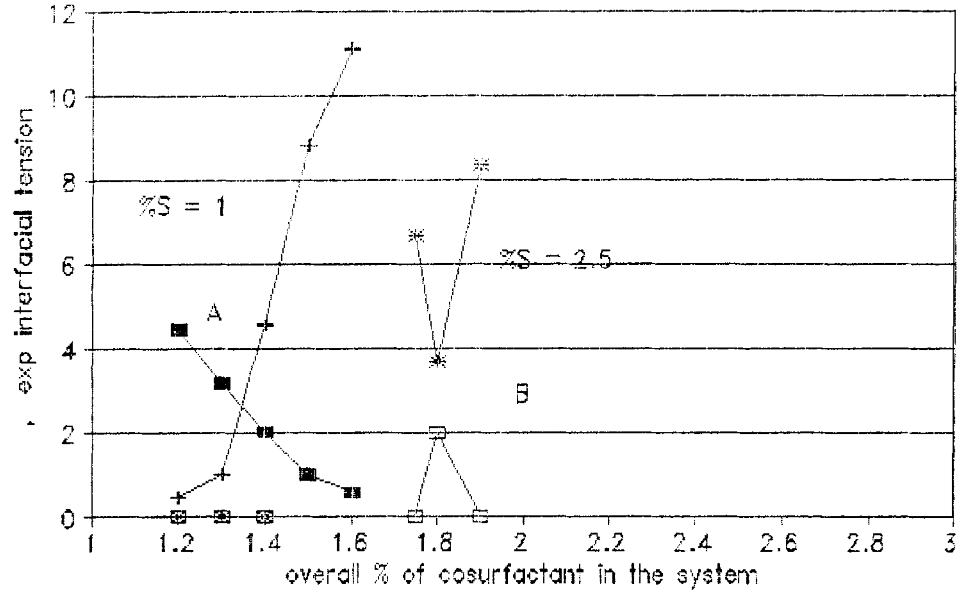

Figure 3a

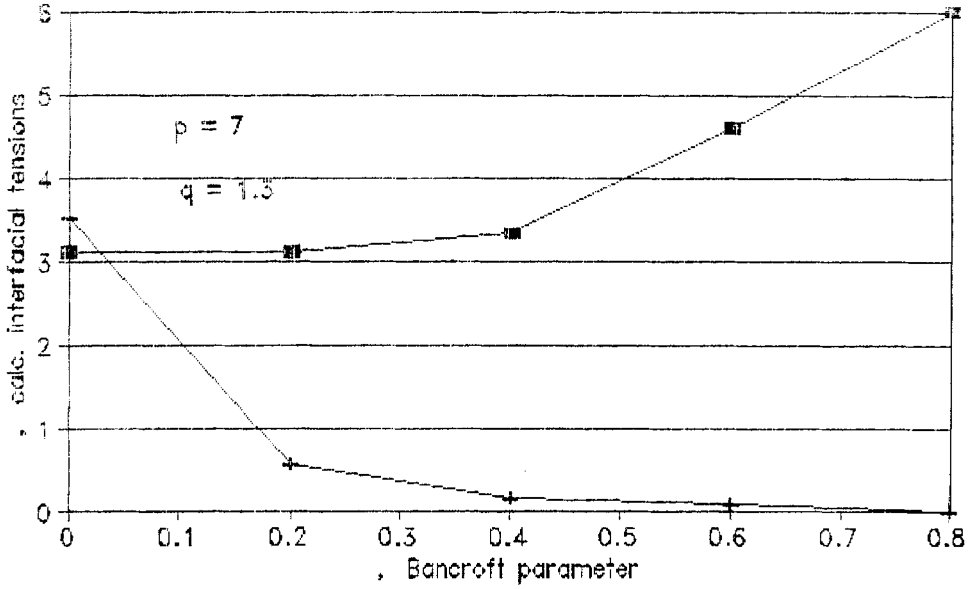

Figure 3b

decreases with temperature, and this would imply that increasing T, p also increases, as follows from Figure 2.

The values of the interfacial tensions for the model have been computed with the approximations given by Borzi *et al*[5]. Thus, we have calculated the composition profiles and tensions of the interfaces from mean field theory in the square-gradient approximation.

From curve A, it follows that the interfacial tension between microemulsion and water increases from the value at the phase transition point between these two phases, up to a maximum value at the other, between microemulsion and oil. The opposite behavior is given for the interface between microemulsion and oil.

By increasing the overall amount of surfactant in the system, a different behavior is observed. Curve B shows two different branches, the upper corresponding to σ_{mw} and the lower one to σ_{mo}.

Figure 3(b) shows the calculated $\sigma_{\alpha\beta}$ and $\sigma_{\beta\gamma}$ interfacial tensions, where the subindex β holds for the microemulsion phase. Notice that the plot is done for positive values of λ. This means that the three phase triangle changes as λ departs from 0, until it is transformed in a binodal line, at the CEP. In this plot, the $\alpha\beta$ interface is the one that becomes critical. Quantitatively, the real system behavior for these particular conditions is reproduced by the model.

The point we want to emphasize here is that some of the main features of the behavior of this complex system can be interpreted through the parameters of this simple phenomenological model.

The analogies and differences that are found from the behavior of the real system and that from the model can help to improve it.

More extensive calculations and measurements of interfacial tensions should be done in order to draw other conclusions about this point.

References

1. Widom, B. *J. Chem. Phys.*, **81**, 2 (1984).
2. Balbuena, P., Borzi, C. and Widom, B. *Physica*, **138A**, 55–75 (1986).
3. Winsor, P. A. *Chemical Reviews*, **68**, 1 (1968).
4. Kurlat, D., Ginzberg, B. and Condori, B. presented to the 8th Symposium on Surfactants in Solution, 1990.
5. Borzi, C., Lipowsky, R. and Widom, B. *J. Chem. Soc. Faraday Trans.*, *2*, **82**, 1739–1752 (1986).
6. Rowlinson, J. S. and Widom, B. *Molecular Theory of Capilarity*, (Clarendon Press, Oxford, 1982), Chapter 8.