

Modeling of microemulsion phase diagrams from excess Gibbs energy models

Fernando García-Sánchez*, Gaudencio Elosa-Jiménez, Alejandrina Salas-Padrón,
Otilio Hernández-Garduza, David Ápam-Martínez

Grupo de Simulación Molecular, Instituto Mexicano del Petróleo, Eje Central Lázaro Cárdenas 152, 07730 México, D.F., Mexico

Received 21 March 2000; received in revised form 11 October 2000; accepted 16 October 2000

Abstract

Projects on tertiary oil recovery by means of microemulsions have been mainly concerned with, first, the ability of a microemulsion to dissolve oil and water simultaneously and, second, the attainment of very low interfacial tensions. Therefore, the design and analysis of chemical flooding processes for enhanced oil recovery must be based on calculations of phase equilibria for these systems, which are composed of water (brine), oil, surfactant and co-surfactant (usually an alcohol). Consequently, the understanding of phase behavior of these systems is of fundamental importance to the development of any surfactant-based chemical flooding process.

The purpose of this work was to give a thermodynamic analytical representation of the phase diagram of microemulsion systems similar to those used in enhanced oil recovery. The algorithms presented for the calculation of multiphase liquid equilibria and the methods for the estimation of the excess Gibbs energy model interaction parameters were successfully tested for the representation of experimental multiphase liquid equilibrium data of an oil–brine–surfactant–alcohol model system. In addition, to represent effectively the phase diagram of this system, an empirical expression was introduced into the selected excess Gibbs energy model to account for the specific role of the surfactant in these complex systems. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Microemulsion; Phase equilibria; Tertiary oil recovery; Excess Gibbs energy models

1. Introduction

Phase behavior of microemulsion systems is one of the major factors that determine the displacement efficiency of a surfactant flood [1,2]. Therefore, the knowledge of phase behavior is important for the design of surfactant-flooding processes as well as for the interpretation of core-flooding experiments in the laboratory and the development of physical models for the prediction of phase behavior or for use in surfactant flooding simulators. In addition, physical quantities affecting oil displacement, such as the interfacial tensions and viscosity, are related to phase behavior.

Microemulsions are obtained from the mixtures of oil, water (brine), and a surfactant (an amphiphile molecule). In most cases, the addition of a co-surfactant (alcohol) is required to ensure the stability of the microemulsion. For a given overall composition, one can obtain: an oil-in-water microemulsion in equilibrium with an excess oil phase (Winsor I), a water-in-oil microemulsion in equilibrium with

an excess water-phase (Winsor II), and a microemulsion in equilibrium with both water and oil excess phases (Winsor III). Middle-phase microemulsions are often favorable for a surfactant-flooding process [3]. Hence, it is fundamental in surfactant flooding to maintain a middle microemulsion phase as long as possible during the process.

Winsor I microemulsions consist of spherical micelles of surfactant and co-surfactant dispersed in water, and filled with oil. Reciprocally, Winsor II microemulsions consist of micelles dispersed in oil, and filled with water. Winsor III microemulsions are generally pictured as bicontinuous media where oil and water domains are separated by aggregated surfactant.

For a given chemical system, any of these phase behaviors will generally be observed when salt or alcohol compositions are varied. Influence of pressure and temperature on phase behavior of these systems has a similar effect [4–9]. Thus, a correct knowledge and modeling of this phase behavior is essential for engineering purposes. However, this is a very difficult topic, since the number and nature of the equilibrium phases are very sensitive to the overall composition, temperature, and pressure.

* Corresponding author. Tel.: +52-5-333-8432; fax: +52-333-6239.
E-mail address: fgarcias@imp.mx (F. García-Sánchez).

Rossen et al. [10] and Kilpatrick et al. [11] have shown that this complex behavior could be modeled as a conventional liquid–liquid equilibrium by using a simple expression of the excess Gibbs energy derived from the Flory theory, but these authors did not compare their simulations with experimental data. Negahban et al. [12] modeled quantitatively the phase equilibrium of some simple ternary systems exhibiting a phase behavior of the same type using the UNIQUAC activity coefficient model. However, it has been recognized that one of the most challenges in computing phase equilibria for these complex systems is to ensure the stability, i.e. that the Gibbs energy of the system reaches its global minimum.

In order to circumvent this problem, we have applied in the present work a developed regression technique to represent the phase behavior of microemulsion systems similar to those used in enhanced oil recovery.

2. Solution approach

At given temperature and pressure, the variance of a system of N components exhibiting p phases in equilibrium, is $N-p$. It is therefore possible to set $N-p$ mole fractions in one phase and solve the equilibrium equations for the other compositions. Such methods are often used for calculating simple phase equilibria but they cannot be used when the number of calculated equilibrium phases (which depends strongly on parameter values) is unknown.

Many methods are also based on the solution of the equilibrium equations written as the equality of the chemical potentials for each component between the different phases. It must be emphasized that the equality of chemical potentials is simply a necessary condition of equilibrium and that it can lead to solutions which are not the global minimum of the Gibbs energy (i.e. local minima, maxima or saddle points).

In our case, the data include the global composition of the system, which is known accurately. Consequently, we prefer to calculate the phase equilibrium compositions from the global composition by minimizing the Gibbs energy under the constraint of mass balance. Initially, the system is assumed to be monophasic. A stability test allows checking if this solution is stable or not. If not, it provides an estimation of the composition of an additional phase to take into account for the equilibrium calculation. The number of phases is then increased by one, and equilibrium is converged by minimizing the Gibbs energy. This procedure is continued until a stable solution is found.

2.1. Stability test

As mentioned above, a severe problem associated with phase equilibrium calculations of a multicomponent system at specified temperature and pressure is that the number of phases is not known in advance. The conventional approach is to fix arbitrarily this number and to calculate the

phase equilibrium compositions. However, this may lead to convergence failure with numerical methods not reliable or may require a substantial amount of calculations only to arrive at a trivial solution in cases where the number of phases is too high. This problem is of particular importance when it is integrated, for instance, to the simulation of reservoirs in enhanced oil recovery.

Gibbs first addressed the problem of determining whether a homogeneous multicomponent mixture can be divided spontaneously and irreversibly into two or more different phases, in 1876 and it has been the object of several publications. The stability criteria, from the thermodynamic point of view, are well known and they have been already discussed in the literature (see [13,14]). These criteria, based on the local convexity of the Gibbs energy are, to date, of limited application for some binary or ternary mixtures. Van Dongen et al. [15] presented a rigorous extension to multicomponent mixtures; however, there is still disagreement in the development of practical applications [16]. This is mainly due to the following two reasons. Firstly, the test is only locally applicable, hence it is a qualitative one; therefore, it does not allow to provide the compositions of a new phase if an instability is detected. Secondly, this approach does not allow, for a given phase, to distinguish the stable zone from the metastable one; the function of the Gibbs energy being convex for both zones.

To overcome this problem, several authors have developed alternative approaches for thermodynamic stability analysis that enables to predict the number and type of phases in equilibrium as well as to obtain the accurate initial estimates for phase equilibrium calculations.

In this work, the stability analysis of a homogeneous system of composition $\mathbf{x}^{(\varphi)}$, based on the minimization of the distance separating the Gibbs energy from the tangent plane at $\mathbf{x}^{(\varphi)}$, has been considered. This stability criterion was initially presented as a theorem by Baker et al. [17] and it has given place to numerical applications by Michelsen [18] and by Nghiem and Heidemann [19], among others.

Baker et al. [17] demonstrated that the necessary and sufficient condition for a system to be stable, at a specified temperature and pressure, is that the tangent plane to the Gibbs energy surface at composition $\mathbf{x}^{(\varphi)}$ should at no other point intersect the Gibbs energy surface. The resulting corollary would express that at a given composition, a system is unstable if the tangent plane to the Gibbs energy surface at that point intersects the Gibbs energy surface at some other point in the overall composition range. These authors indicate that mathematically the solution of the phase equilibria problem can be obtained by finding a tangent plane to the Gibbs energy surface at two or more points which leads to the least value of the Gibbs energy. Such points of tangency correspond to the compositions of the predicted equilibrium phases being required by the material balance restrictions, so that the global composition of the system lies within the region bounded by these points. Since the slope of the tangent plane corresponds to the chemical potentials of the

components, this tangent plane criterion is equivalent to that requiring equality of chemical potentials. That is, preservation of the material balance and a state of lowest possible Gibbs energy as the conditions for equilibrium at the specified temperature and pressure.

Michelsen [18] suggested a numerically efficient method for solving the stability analysis based on the tangent plane criterion which does not require estimates of the number of phases at equilibrium and that provides compositions of the new phases for unstable systems as a preliminary step in flash calculations. This test has its foundation on the fact that if a decrease in Gibbs energy cannot be achieved when a homogeneous mixture is divided into two phases (formed by removing an infinitesimal amount of the original mixture), then the mixture is stable. In terms of activity coefficients, γ_i , this criterion for stability can be written as

$$F(\mathbf{x}) = \sum_{i=1}^N x_i [\ln x_i + \ln \gamma_i(\mathbf{x}) - h_i] \geq 0 \quad \forall \mathbf{x} \quad (1)$$

where

$$h_i = \ln x_i^{(\varphi)} + \ln \gamma_i(\mathbf{x}^{(\varphi)}) \quad i = 1, \dots, N \quad (2)$$

Eq. (1) requires that the tangent plane at no point lies above the Gibbs energy surface and this is achieved when $F(\mathbf{x})$ is positive in all its minima. Consequently, a minimum of $F(\mathbf{x})$ should be considered in the interior of the permissible region:

$$\sum_{i=1}^N x_i = 1 \quad \forall \mathbf{x} \geq 0 \quad (3)$$

Since to test condition (1) for all trial compositions is not physically possible, Michelsen [18] asserts that it is sufficient to test the stability at all stationary points of $F(\mathbf{x})$ since this function is not negative at all stationary points. That is, points where the derivatives of $F(\mathbf{x})$ with respect to all independent variables are equal to zero. Hence, by solving the following equation describing the stationary point:

$$\ln \xi_i + \ln \gamma_i(\mathbf{x}) - h_i = 0 \quad i = 1, \dots, N \quad (4)$$

the stability is verified providing that at all stationary points $F(\mathbf{x}) \geq 0$, corresponding to $\sum_{i=1}^N \xi_i \leq 1$. Conversely, a phase is considered unstable if stationary points where $F(\mathbf{x}) < 0$ or $\sum_{i=1}^N \xi_i > 1$ can be located. In Eq. (4), the independent variables ξ_i can be interpreted as mole number with corresponding mole fractions, $x_i = \xi_i / \sum_{j=1}^N \xi_j$ ($i = 1, \dots, N$).

An equivalent stability criterion to that given by Eq. (5) but based on variables ξ_i was also formulated by Michelsen [18] as

$$F^*(\xi) = 1 + \sum_{i=1}^N \xi_i [\ln \xi_i + \ln \gamma_i(\mathbf{x}) - h_i - 1] \geq 0 \quad (5)$$

where no constraints on ξ_i except that $\xi_i > 0$ ($i = 1, \dots, N$) are required, so that the stationary points of $F^*(\xi)$ correspond to those of function $F(\mathbf{x})$. Moreover, since $F^*(\xi)$ is negative in all points where $F(\mathbf{x})$ is negative, then a negative value of $F^*(\xi)$ indicates an instability of the system.

Thus, solving for Eqs. (4) and (5) and obtaining $\sum_{i=1}^N \xi_i$, are all the necessary calculations required to determine the stability of the system of composition $\mathbf{x}^{(\varphi)}$ at constant temperature and pressure. The methods proposed by Michelsen [18] for solving the stationary points, Eq. (8), are direct substitution and accelerated direct substitution. Acceleration methods such as the general dominant eigenvalue method [20] or Broyden's method [21] are recommended while a minimization method applied to the stability function, Eq. (5), is also suggested.

Here, the quasi-Newton BFGS minimization method (see [22]) has been applied to Eq. (5) to determine the stability of a given system of composition $\mathbf{x}^{(\varphi)}$ at specified temperature and pressure. Since the function $F^*(\xi)$ allows usually multiple points, which can be minima, maxima or saddle points, then the adoption of such a method for solving $F^*(\xi)$, under the constraints $\xi_i > 0$, will prove to be effective in so far as it leads to the search of local minima of $F^*(\xi)$; the sign of $F^*(\xi)$ in these minima enables to conclude with regard to the stability of the system.

The iterative procedure used by the quasi-Newton BFGS method can be written as

$$\mathbf{s}^{(k)} = -\mathbf{H}^{(k)} \mathbf{q}^{(k)} \quad (6)$$

$$\boldsymbol{\alpha}^{(k+1)} = \boldsymbol{\alpha}^{(k)} + \lambda \mathbf{s}^{(k)} \quad (7)$$

where \mathbf{q} is the gradient of $F^*(\xi)$ considered as a function of the iteration variables, $\alpha_i = 2\sqrt{\xi_i}$, and is given by

$$\mathbf{q} = \sqrt{\xi_i} [\ln \xi_i + \ln \gamma_i(\mathbf{x}) - h_i] \quad i = 1, \dots, N \quad (8)$$

whereas the Hessian matrix is

$$\mathbf{A} = \mathbf{B} + \frac{1}{2} \delta_{ij} [\ln \xi_i + \ln \gamma_i(\mathbf{x}) - h_i] \quad i, j = 1, \dots, N \quad (9)$$

where

$$\mathbf{B} = \delta_{ij} + \sqrt{\xi_i \xi_j} \left(\frac{\partial \ln \gamma_i(\mathbf{x})}{\partial \xi_j} \right) \quad i, j = 1, \dots, N \quad (10)$$

δ_{ij} denoting the Kronecker symbol which is unity if $i = j$ and equal to zero otherwise.

In a stationary point, the gradient is null and the Hessian matrix \mathbf{A} equals to matrix \mathbf{B} , which is very close to the identity matrix. Also, it can be seen that the trivial solution $\xi = \mathbf{x}^{(\varphi)}$ corresponding to a stationary point, is a local minimum of $F^*(\xi)$ if and only if \mathbf{B} is positive definite in that point. The approximant \mathbf{H} to the inverse Hessian matrix of $F^*(\xi)$, \mathbf{A}^{-1} , can be initialized by any symmetric positive definite matrix such as the identity matrix and it is corrected or

updated by the double-rank BFGS formula:

$$H^{(k+1)} = H^{(k)} + \left(1 + \frac{\gamma^{(k)T} H^{(k)} \gamma^{(k)}}{\delta^{(k)T} \gamma^{(k)}} \right) \frac{\delta^{(k)} \delta^{(k)T}}{\delta^{(k)T} \gamma^{(k)}} - \left(\frac{\delta^{(k)} \gamma^{(k)T} H^{(k)} + H^{(k)} \gamma^{(k)} \delta^{(k)T}}{\delta^{(k)T} \gamma^{(k)}} \right) \quad (11)$$

with

$$\delta^{(k)} = \alpha^{(k+1)} - \alpha^{(k)} \quad (12)$$

$$\gamma^{(k)} = q^{(k+1)} - q^{(k)} \quad (13)$$

during the subsequent iterations. In addition, this method requires a line search algorithm to compute the step length λ . This is done by using a rigorous method such as the proposed by Fletcher [22]. The purpose of the line search being to ensure a satisfactory decrease of the function $F^*(\xi)$, then the following requirements have been set to achieve this aim:

$$F^*(\xi)^{(k)} - F^*(\xi)^{(k+1)} \geq -\rho \lambda q^{(k)T} s^{(k)} \quad (14)$$

$$q^{(k+1)T} s^{(k)} \geq \sigma q^{(k)T} s^{(k)} \quad (15)$$

Since test given by Eq. (15) does not reduce to an exact line search in the limit $\sigma \rightarrow 0$, then the following test

$$|q^{(k+1)T} s^{(k)}| \leq -\sigma q^{(k)T} s^{(k)} \quad (16)$$

is recommended to obtain an exact line search in this limit.

In general, the line search algorithm to compute the step length λ is started with a weak line search ($\sigma = 0.9$) and finished with a fairly accurate line search ($\sigma = 0.1$); the parameter ρ being fixed equal to 0.01. Restricted, quadratic interpolations or cubic extrapolations and interpolations depending on the test of Eqs. (14)–(16), are used to reach an acceptable value of λ .

Fig. 1 shows the overall structure of the one-dimensional line search algorithm used in this work. Fletcher [22] has shown that this algorithm takes into account the effect of round-off errors and turns out into an exact line search when σ tends to zero.

In so far as the approximant H remains positive definite, the property of descent on $F^*(\xi)$ is effective and the convergence is always toward a local minimum. However, it does not guarantee the convergence to a negative one immediately after having found any kind of minimum; the only arbitrary part in this method being the initialization of variables ξ_j . This method has a superlinear rate of convergence at the

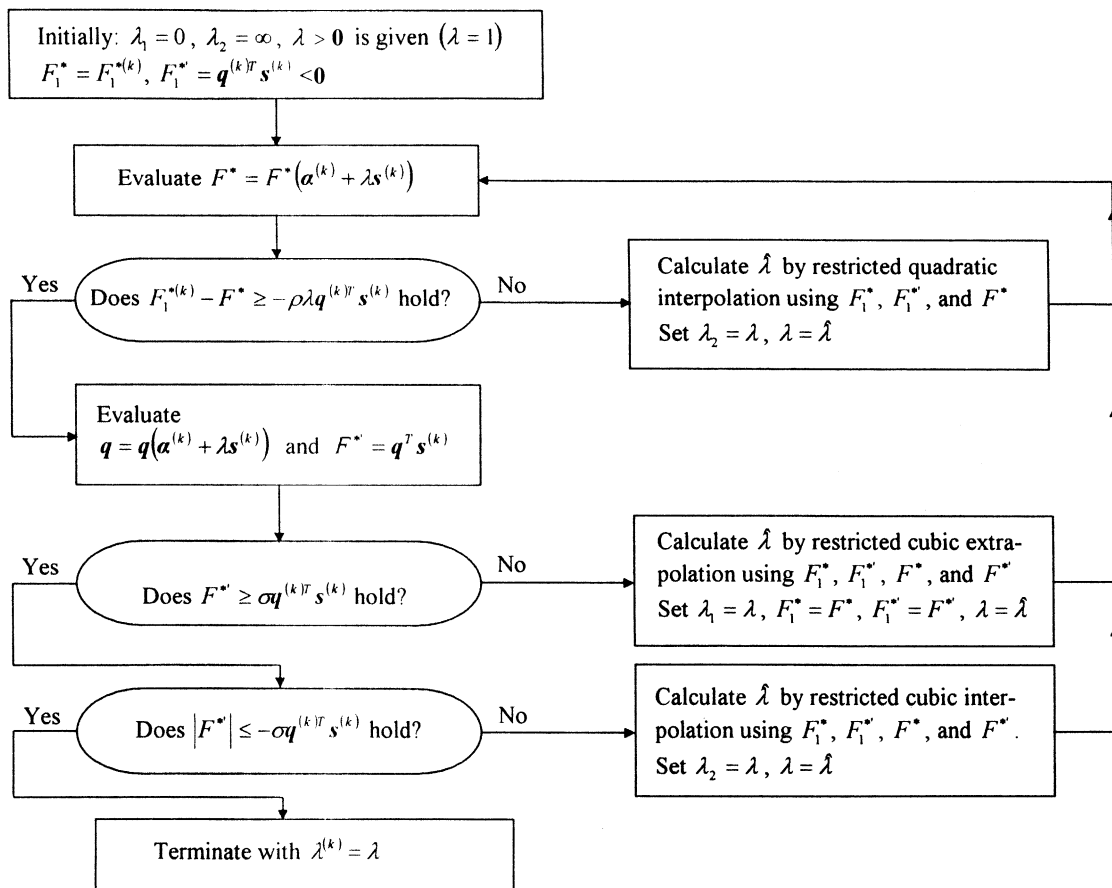


Fig. 1. Overall structure of the one-dimensional line search algorithm.

end of calculations and the converged approximant to the inverse of the Hessian matrix is very close to the real one.

When the stability of a system is studied in relation to multiphase liquid equilibria, several minima of the function $F^*(\xi)$ may coexist so that different initializations should be used to reach them. Here, the search is initialized from almost pure phases (N different initializations) and from an equimolar mixture. The initializations corresponding to pure trial phases have the advantage that liquid immiscibility in highly non-ideal systems is promptly detected and component activity coefficients are evaluated cheaply. Nonetheless, it is certain that for a large number of cases, one of these initial guesses involves an approach toward the trivial solution, i.e. $\xi = x^{(\varphi)}$. These calculations can be avoided if after each iteration the convergence variable

$$r = \frac{2F^*(\xi)}{\sum_{i=1}^N ((\xi_i - x_i^{(\varphi)})/\alpha_i)(\partial F^*(\xi)/\partial \alpha_i)} \quad (17)$$

is evaluated. Thus, the value of r will approach the unity as ξ approaches the trivial solution, so the search is abandoned when

$$|r - 1| < 0.2 \text{ and } F^*(\xi) < 10^{-3} \quad (18)$$

while the criterion of convergence used for the non-trivial solution was

$$\|g\|_2^2 = \sum_{i=1}^N \left(\frac{\partial F^*(\xi)}{\partial \alpha_i} \right)^2 < 10^{-7} \quad (19)$$

When the stability of a single-phase system is tested, all different initializations are explored until finding two negative minima (if they exist) of the function $F^*(\xi)$. Therefore, two minima at least exist if the system is locally unstable; the compositions corresponding to these minima are used to initialize the two-phase equilibrium calculation. On the contrary, if $F^*(\xi)$ admits only a minimum, then the system is metastable and the composition which corresponds to this minimum together with the overall composition are used to initialize the equilibrium calculation. A system with several phases in equilibrium is always metastable (the equilibrium having been already calculated); hence, we search only an instability and the phase equilibrium calculation is initialized from the new composition and from the compositions of the initial phases in equilibrium.

2.2. Phase equilibrium calculations

The problems that are commonly found when we solving a set of equations describing the equilibrium between multiple phases, are translated by a multitude of solutions without physical significance because of the lack of convergence with certain numerical methods or due to the absence of a good initialization.

The number of p phases in equilibrium being unknown in advance, then two different approaches have been developed for solving the problem. The first one consists of assuming

a maximum number of phases that can be deduced from the phase rule, then removing that one which does appear during phase equilibrium calculations. This approach is not economical in terms of the number of calculations that it is necessary to carry out, and may fail to find a solution or may lead to erroneous solutions. The second approach allows solving the problem at p phases when instability is detected with the solution at $p - 1$ phases. This approach, more frequently used, only is effective if it is accompanied of a rigorous stability test for multiphase systems and of an appropriate numerical method of calculation.

Arguably, one of the most useful methods to calculate phase equilibria reported in the literature is based on the minimization of the total Gibbs energy. This method offers scope for solving phase equilibrium at p phases immediately after stability at $p - 1$ phases is carried out. Basically, the formulation of the problem can be stated as the search for the global minimum of the molar Gibbs energy of the system, G , at specified temperature, T , and pressure, P ,

$$\text{Min}_{n_i^{(\varphi)}} G = \sum_{\varphi=1}^p \sum_{i=1}^N n_i^{(\varphi)} \mu_i^{(\varphi)} \quad (20)$$

under the material balance constraints

$$\sum_{\varphi=1}^p n_i^{(\varphi)} = z_i \quad i = 1, \dots, N \quad (21)$$

and the inequality constraints

$$n_i^{(\varphi)} \geq 0 \quad i = 1, \dots, N; \varphi = 1, \dots, p \quad (22)$$

where z_i is the mole fraction of component i in the system and $n_i^{(\varphi)}$ is the mole number of component i in phase p per mole of feed. If the chemical potentials $\mu_i^{(\varphi)}$ ($i = 1, \dots, N; \varphi = 1, \dots, p$) are expressed in terms of activity coefficients and assuming the composition $n_i^{(p)}$ of the phase p as dependent of the variables $n_i^{(\varphi)}$ ($i = 1, \dots, N; \varphi = 1, \dots, p$), then the problem reduces to the following constrained minimization

$$\text{Min}_{n_i^{(\varphi)}} \Delta g = \sum_{\varphi=1}^p \sum_{i=1}^N n_i^{(\varphi)} \ln(x_i^{(\varphi)} \gamma_i^{(\varphi)}) \quad (23)$$

with the inequality constraints given by Eq. (22) and

$$\sum_{\varphi=1}^{p-1} n_i^{(\varphi)} \leq z_i \quad i = 1, \dots, N \quad (24)$$

where the variables $n_i^{(p)}$, $x_i^{(p)}$, and $\gamma_i^{(p)}(T, P, \mathbf{x}^{(p)})$ are considered functions of $n_i^{(\varphi)}$ ($i = 1, \dots, N; \varphi = 1, \dots, p - 1$); the inequalities (22) and (24) defining a convex domain of the variables $n_i^{(\varphi)}$ in $R^{N(p-1)}$.

The gradient g and the Hessian matrix G of Δg , can then be evaluated from

$$g = \ln \left(\frac{x_i^{(\varphi)} \gamma_i^{(\varphi)}}{x_i^{(p)} \gamma_i^{(p)}} \right) \quad i = 1, \dots, N; \varphi = 1, \dots, p - 1 \quad (25)$$

and

$$\mathbf{G} = \left[\begin{array}{c} \delta_{\varphi\phi} \left(\frac{\delta_{ij}}{n_i^{(\varphi)}} - \frac{1}{N^{(\varphi)}} + \frac{\partial \ln \gamma_i^{(\varphi)}}{\partial n_j^{(\varphi)}} \right) \\ + \left(\frac{\delta_{ij}}{n_i^{(p)}} - \frac{1}{N^{(p)}} + \frac{\partial \ln \gamma_i^{(p)}}{\partial n_j^{(p)}} \right) \end{array} \right] \quad (26)$$

$i, j = 1, \dots, N; \varphi, \phi = 1, \dots, p-1$

If the equilibrium ratios of each component i between phase φ and the reference phase p (which is generated from a stability test)

$$K_i^{(\varphi)} = \frac{x_i^{(\varphi)}}{x_i^{(p)}} \quad i = 1, \dots, N; \quad \varphi = 1, \dots, p-1 \quad (27)$$

are introduced, we can then express the Hessian matrix \mathbf{G} as the summation of two symmetrical matrices \mathbf{A} and \mathbf{Q} of order $N(p-1)$, defined as

$$\mathbf{A} = \begin{pmatrix} \mathbf{A}^{(1)} & & & \\ & \mathbf{A}^{(2)} & & \\ & & \ddots & \\ & & & \mathbf{A}^{(p-1)} \end{pmatrix} \quad (28)$$

and

$$\mathbf{Q} = \begin{pmatrix} \mathbf{Q}^{(1)} & \mathbf{R} & \dots & \mathbf{R} \\ \mathbf{R} & \mathbf{Q}^{(2)} & & \vdots \\ \vdots & & \ddots & \mathbf{R} \\ \mathbf{R} & \dots & \mathbf{R} & \mathbf{Q}^{(p-1)} \end{pmatrix} \quad (29)$$

where $\mathbf{A}^{(\varphi)}$, $\mathbf{Q}^{(\varphi)}$, and \mathbf{R} are all symmetrical matrices of order N such that for $\varphi = 1, \dots, p-1$ we have

$$\mathbf{A}^{(\varphi)} = \left(\frac{\partial \ln K_i^{(\varphi)}}{\partial n_j^{(\varphi)}} \right) = \left[\delta_{ij} \left(\frac{1}{n_i^{(\varphi)}} + \frac{1}{n_i^{(p)}} \right) - \frac{1}{N^{(\varphi)}} - \frac{1}{N^{(p)}} \right] \quad (30)$$

$i, j = 1, \dots, N$

$$\mathbf{Q}^{(\varphi)} = \left(\frac{\partial \ln \gamma_i^{(\varphi)}}{\partial n_j^{(\varphi)}} \right) + \left(\frac{\partial \ln \gamma_i^{(p)}}{\partial n_j^{(p)}} \right) \quad i, j = 1, \dots, N \quad (31)$$

$$\mathbf{R} = \left[\frac{\delta_{ij}}{n_i^{(p)}} - \frac{1}{N^{(p)}} + \left(\frac{\partial \ln \gamma_i^{(p)}}{\partial n_j^{(p)}} \right) \right] \quad i, j = 1, \dots, N \quad (32)$$

Ammar [23] has shown that matrices $\mathbf{A}^{(\varphi)}$ ($\varphi = 1, \dots, p-1$) are all positive definite inside the same domain of

coexistence involving the p phases. Hence, matrix \mathbf{A} and its inverse \mathbf{A}^{-1} can easily be evaluated from matrices $\mathbf{A}^{(\varphi)}$ and $\mathbf{A}^{(\varphi)-1}$ which are evaluated analytically.

In this work, the following scheme based on the minimization of the total Gibbs energy and using $\ln \mathbf{K}^{(\varphi)}$ ($\varphi = 1, \dots, p-1$) as variables, at specified temperature and pressure, has been adopted for solving the multiphase liquid equilibria for multicomponent systems:

1. Initialize the equilibrium ratios $\ln \mathbf{K}^{(\varphi)}$ ($\varphi = 1, \dots, p-1$) from a stability test.
2. Solve the set of non-linear equations by Newton–Raphson iteration:

$$\sum_{i=1}^N \frac{z_i (K_i^{(\varphi)} - 1)}{J_i} = 0 \quad \varphi = 1, \dots, p-1 \quad (33)$$

with

$$J_i = 1 + \sum_{\varphi=1}^{p-1} N^{(\varphi)} (K_i^{(\varphi)} - 1) \quad i = 1, \dots, N \quad (34)$$

to compute the phase fractions $N^{(\varphi)}$

$$N^{(\varphi)} = \sum_{i=1}^N n_i^{(\varphi)} \quad \varphi = 1, \dots, p-1 \quad (35)$$

3. Calculate the mole fractions $\mathbf{x}^{(\varphi)}$ of the different phases from

$$x_i^{(p)} = \frac{z_i}{J_i} \quad i = 1, \dots, N \quad (36)$$

$$x_i^{(\varphi)} = K_i^{(\varphi)} x_i^{(p)} \quad i = 1, \dots, N; \varphi = 1, \dots, p-1 \quad (37)$$

4. Calculate Δg , \mathbf{g} , and perform the convergence test

$$\|\mathbf{g}^{(k)}\|_2^2 = \sum_{\varphi=1}^{p-1} \sum_{i=1}^N \left[\ln \left(\frac{x_i^{(\varphi)} \gamma_i^{(\varphi)}}{x_i^{(p)} \gamma_i^{(p)}} \right) \right]^2 < 10^{-10} \quad (38)$$

5. Define new values of $\ln \mathbf{K}^{(\varphi)}$ and return to step (2).

The whole process is then repeated until convergence is achieved. It has been identified [24] that Eq. (23) can efficiently be solved from an unconstrained minimization algorithm by keeping the variables $n_i^{(\varphi)}$ ($i = 1, \dots, N; \varphi = 1, \dots, p-1$) inside the convex constraint domain given by Eqs. (22) and (24) during the search for the solution. Nevertheless, mainly for multiphase systems, some algorithms can lead to a violation of these constraints at the earliest iterations when the initialization is far from the solution even if the latter was obtained from a stability test. That is, the projection of the variables $n_i^{(\varphi)}$ on the constraints domain cannot be numerically justified with some algorithms and results in a singularity of matrix \mathbf{A} and, consequently, in an erratic behavior of the subsequent iterations.

In order to overcome these difficulties, we have adopted a hybrid approach to minimize the total Gibbs energy of the

system starting with the steepest–descent method in conjunction with a robust initialization supplied from the stability test to ensure a certain progress from initializations, and ending with the quasi-Newton method which ensure the property of strict descent of the Gibbs energy surface; the converged solutions from both methods representing local minima of the Gibbs energy.

The iterative scheme presented above is common for these two methods and only the form to update the values of $\ln \mathbf{K}^{(\varphi)}$ in step (5) of the scheme will differ from one method to another.

2.3. Steepest–descent method

This method is a gradient-type one and it is an extension of the successive substitution algorithm incorporating a line search to estimate the step length λ , and can be expressed as

$$\mathbf{s}^{(k)} = -\mathbf{A}^{(k)-1} \mathbf{g}^{(k)} \quad (39)$$

$$\mathbf{p}^{(k)} = \mathbf{A}^{(k)} \mathbf{s}^{(k)} = -\mathbf{g}^{(k)} \quad (40)$$

$$\ln \mathbf{K}^{(k+1)} = \ln \mathbf{K}^{(k)} + \lambda \mathbf{p}^{(k)} \quad (41)$$

2.4. Quasi-Newton BFGS method

This method has a superlinear convergence at the end of calculations and although is slower to reach the solution than with the Newton method (with quadratic convergence rate), it has the advantage of generating a matrix very close to the inverse Hessian matrix \mathbf{G}^{-1} so that this method has the same feature as the Newton method under the circumstances where the initiation procedure is performed near of converged points. The BFGS step can be written as

$$\mathbf{s}^{(k)} = -\mathbf{H}^{(k)-1} \mathbf{g}^{(k)} \quad (42)$$

$$\mathbf{p}^{(k)} = \mathbf{A}^{(k)} \mathbf{s}^{(k)} \quad (43)$$

$$\ln \mathbf{K}^{(k+1)} = \ln \mathbf{K}^{(k)} + \lambda \mathbf{p}^{(k)} \quad (44)$$

where the approximant \mathbf{H} to the inverse of the Hessian matrix is set equal to \mathbf{A}^{-1} at the end of the steepest–descent method and it is updated by the BFGS formula

$$\delta^{(k)} = \ln \mathbf{K}^{(k+1)} - \ln \mathbf{K}^{(k)} \quad (45)$$

$$\boldsymbol{\gamma}^{(k)} = \mathbf{g}^{(k+1)} - \mathbf{g}^{(k)} \quad (46)$$

and Eq. (11) during the subsequent iterations. All matrices \mathbf{H} are positive definite since matrix \mathbf{A}^{-1} is positive definite; hence, the descent property is ensured and convergence is always to local minima.

The common feature of these methods is that both require a partial line search algorithm to compute the step length

λ , which is done by imposing the following requirements upon λ

$$\Delta g^{(k)} - \Delta g^{(k+1)} \geq -\rho \lambda \mathbf{g}^{(k)T} \mathbf{s}^{(k)} \quad (47)$$

$$\mathbf{g}^{(k+1)T} \mathbf{s}^{(k)} \geq \sigma \mathbf{g}^{(k)T} \mathbf{s}^{(k)} \quad (48)$$

and

$$|\mathbf{g}^{(k+1)T} \mathbf{s}^{(k)}| \leq -\sigma \mathbf{g}^{(k)T} \mathbf{s}^{(k)} \quad (49)$$

in order to ensure a satisfactory decrease of Δg , and restricted, quadratic interpolations or cubic extrapolations and interpolations are used to find λ .

In addition, it is worth noting that one of the most important steps of our algorithm is the switch from the steepest–descent method to the quasi-Newton BFGS one, since it should lead to a decrease in execution time during the calculations; otherwise, the switch is not necessary. Therefore, based on extensive testing of phase equilibrium calculations, it is suggested that the passage to the quasi-Newton BFGS method takes place after at least five iterations and when the gradient norm is lower than $10^{-3} RT$. Nonetheless, in certain situations corresponding to an ill conditioning of the Hessian matrix, it may be necessary to get back temporarily (2–3 iterations) to the steepest–descent method.

3. Data regression

In order to use an excess Gibbs energy model for liquid–liquid equilibrium calculations, it is essential to obtain the required adjustable model parameters from regression of experimental data which, in turn, can be used for interpolation of the data or extrapolations in regions beyond where measurements have been made. Therefore, with a given set of model parameters, it is possible to calculate the number of phases in equilibrium and their compositions from the global composition of the system. However, if the minimization of Δg is started from any set of parameters, the phase equilibrium calculation could, for instance, lead to a homogeneous system in which the distance to the experimental system will be independent of the parameter values inside a certain domain. Consequently, it is necessary to initialize these parameters with reasonable values. Toward this end, the following procedures are given to estimate the model parameters from liquid–liquid equilibrium data:

1. Minimization of the sum of squared differences between activity logarithms of each component in each phase

$$F_a = \sum_{j=1}^{N_{\text{eq}}} \sum_{i=1}^N w_{ij} [(\ln a_{ij}^{\text{I}} - \ln a_{ij}^{\text{II}})^2 + (\ln a_{ij}^{\text{I}} - \ln a_{ij}^{\text{III}})^2] + Q \sum_{m=1}^{N_{\text{par}}} p_m^2 \quad (50)$$

where w_{ij} is the weighting factor associated to the component i of tie line (or tie triangle) j and $a_{ij}^I = x_{ij}^I \gamma_{ij}^I$ is the activity of component i of tie line (or tie triangle) j in phase I ; x_{ij}^I being the corresponding experimental mole fraction and γ_{ij}^I the activity coefficient, which is calculated from an excess Gibbs energy model depending on x_{ij}^I and the model parameters p_m ($m = 1, \dots, N_{\text{par}}$). Eq. (50) has been written for three equilibrium phases but for systems with two equilibrium phases, it reduces to contents of the first bracketed term.

2. Minimization of the sum of squared differences between experimental and calculated mole fractions

$$F_x = \sum_{k=1}^{N_{\text{eq}}} \sum_{j=1}^{N_{\text{ph}}} \sum_{i=1}^N w_{ijk} (x_{ijk}^{\text{expl}} - x_{ijk}^{\text{calc}})^2 + Q \sum_{m=1}^{N_{\text{par}}} p_m^2 \quad (51)$$

where w_{ijk} , x_{ijk}^{expl} , and x_{ijk}^{calc} represent, respectively, the weighting factor, the experimental mole fraction, and the calculated mole fraction of component i in phase j corresponding to the tie line (or tie triangle) k .

The second term of the right-hand side of Eqs. (50) and (51), i.e. the “penalty” term, is added to the objective functions F_a and F_x to ensure that we can get relatively small parameters without increasing the minimum of these functions, so that the risk of multiple solutions is avoided. This term has also the advantage that the minimum of F_a and F_x becomes sharper promoting thus the convergence, and it is activated only if one or more of the model parameters are greater than a specified value. In this work, we have chosen the value of constant Q in such a way that the quantity $Q(500)^2$ is approximately one per cent of the value of the objective function (F_a or F_x). This approach has been systematically used to estimate the interaction parameters of the selected excess Gibbs energy model. In addition, we have also replaced the experimental uncertainties (which in general are not available) by weighting factors that can be used to force the thermodynamic model to represent with more accuracy certain concentrations. Here, unless otherwise stated, all these factors were fixed equal to unity.

Although the activity objective function F_a has been frequently used in the literature, it suffers from the disadvantage that it only contains the differences between computed activities. Hence, minimization of this function does not necessarily lead to small differences between experimental and calculated mole fractions, which is desired in practice. Notwithstanding, to obtain an initial guess of the model parameters, it is often advantageous to use function F_a since it can be evaluated explicitly. Parameters obtained in this fashion provide a sufficiently good initial estimate to enable fairly easy convergence in subsequent iterations based on F_x .

Conversely, minimization of objective function F_x is more complicated and time consuming [25–27]. It involves the computation of mole fractions x_{ijk}^{calc} for a given set of parameters from which will arise a new set of parameters.

Computation is continued until the value of F_x is smaller than a prescribed tolerance.

In Eq. (51), the experimental and calculated phases corresponding to each point of overall composition are coupled by order of decreasing proximity. However, it is possible that during minimization of function F_x , there exists a mismatch in the number of calculated and experimental phases, e.g. when there are two experimental phases but three calculated ones. In this case, the calculated phase that is the farthest from experimental phases will not be taken into account in the objective function. In fact, it is expected that this last phase will only appear in a very small amount as soon as the other calculated phases are close to the experimental ones since both the calculated and experimental systems correspond to the same overall composition. In this regard, based on the representation of a wide variety of binary, ternary, and quaternary systems, this approach always matched correctly the number of calculated and experimental phases for all systems studied.

Here, the estimation of the interaction parameters of the selected excess Gibbs energy model was carried out in a two-step procedure, which involves the minimization of functions F_a and F_x by using the simplex [28] and the Marquardt [29] optimization methods.

4. Microemulsion phase diagram representation

Although the system of interest contains electrolytes (the surfactant and sodium chloride), we use a simple non-electrolyte expression of the excess Gibbs energy. In fact, we have no quantitative information on the partitioning of salt between water and microemulsion phases. We shall therefore consider the brine as a unique pseudo-component (which is not fully justified in the case of Winsor I or III equilibria). We have also considered oil and surfactant as pseudo-components. There is experimental evidence that this assumption is correct. The system is then reduced to four components: surfactant, alcohol, brine, and oil.

4.1. Experimental data

Data determined at 25°C by Minssieux et al. [30] at the French Petroleum Institute are used in this work. These data cover the complete phase diagram for a model system made up from:

- Witco TRS 10–80. This is a commercial ionic surfactant (a sodium alkylbenzene sulfonate) of average molecular weight equal to 420.
- *n*-Butanol as co-surfactant.
- Brine (8 g/l of sodium chloride).
- Esso “Pétrole D” (a dearomatized fraction in C₁₂–C₁₄).

This system is a very complex one because: (a) it uses an industrial surfactant that is not anymore a pure component;

(b) oil is also a mixture (an oil fraction); and (c) the system contains salt no analyzed.

As the overall salinity of the mixtures was not varied along the experimental study, it is assumed that the brine (water + salt) behaves as a pseudocomponent. This hypothesis is not fully justified by the experimental results themselves; one notes that the vertices of the microemulsion trinodal triangles do not describe a curve according to the analysis of variance, but distribute them on a surface [31,32]. We can expect therefore some difficulties for the correlation of the experimental data of type Winsor III. Nevertheless, the experimental data are abundant and cover a large domain of the phase diagram (Winsors I, II and III).

Samples of known overall composition were allowed to reach the phase equilibrium at 25°C. Once the equilibrium is reached (i.e. the constancy in the time of phase volumes is verified), compositions of the different phases in equilibrium were then analyzed for surfactant, alcohol, water, and oil. Partitioning of salt between phases were not measured.

The experimental phase diagram can be visualized in a tetrahedron trirectangle whose vertices are brine, alcohol, oil and surfactant, respectively (see Fig. 2). The quaternary diagram defining the system used (to determine the

multiphase domains and to analyze the systems in equilibrium), has been explored systematically by cutting up the tetrahedron in different vertical planes corresponding to mixtures of constant water-to-oil ratios (WOR). In every plane WOR, sets of mixtures at constant content in surfactant (S_n on Fig. 3) and at increasing content in alcohol were prepared.

The strategy adopted for the exploration of the phase diagram is schematized on Fig. 3. In this figure, it is shown the trajectories followed inside the tetrahedron by the global compositions of the mixtures situated in a determined WOR plane. The maximum contents in surfactant and in alcohol were limited to 20% in mass fraction.

By considering the ternary diagrams gotten in two faces of the tetrahedron shown in Fig. 2, one observes the following features:

- The ternary diagram brine–oil–surfactant (see Fig. 4) is of type Winsor I, which indicates that in the absence of alcohol, the surfactant has more affinity for the brine than for oil.
- The ternary diagram brine–oil–alcohol (see Fig. 5) shows an inversion of partition of the alcohol between the phases water and oil, when the content in alcohol of the

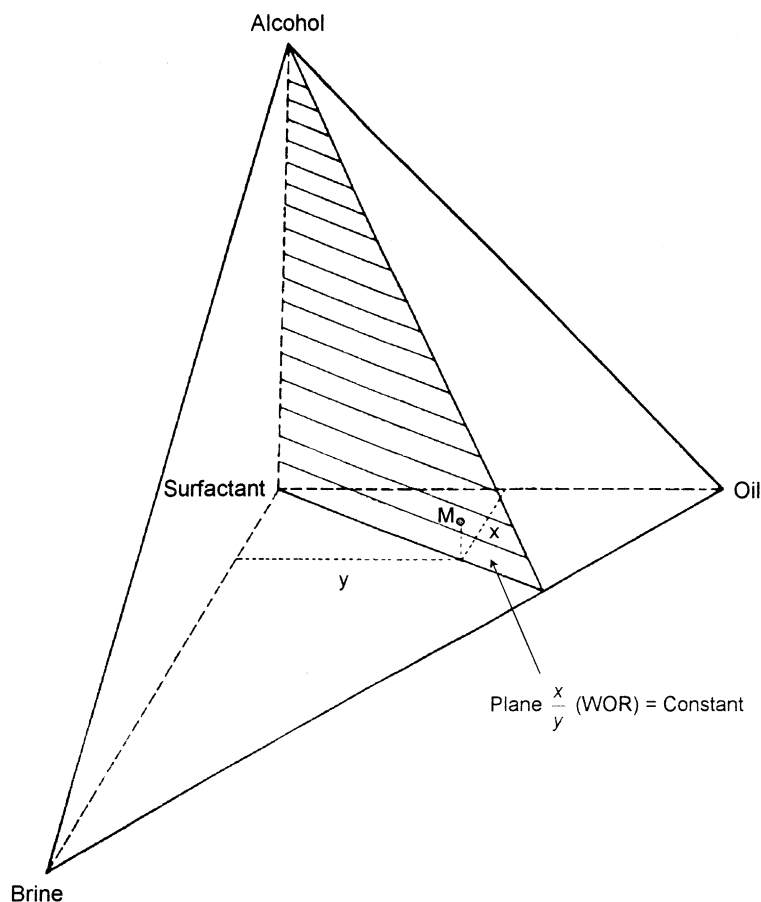


Fig. 2. Quaternary representation of the model system: brine (8 g/l NaCl)–oil (a dearomatized fraction in C_{12} – C_{14})–alcohol (*n*-butanol)–surfactant (Witco TRS 10–80) at 25°C.

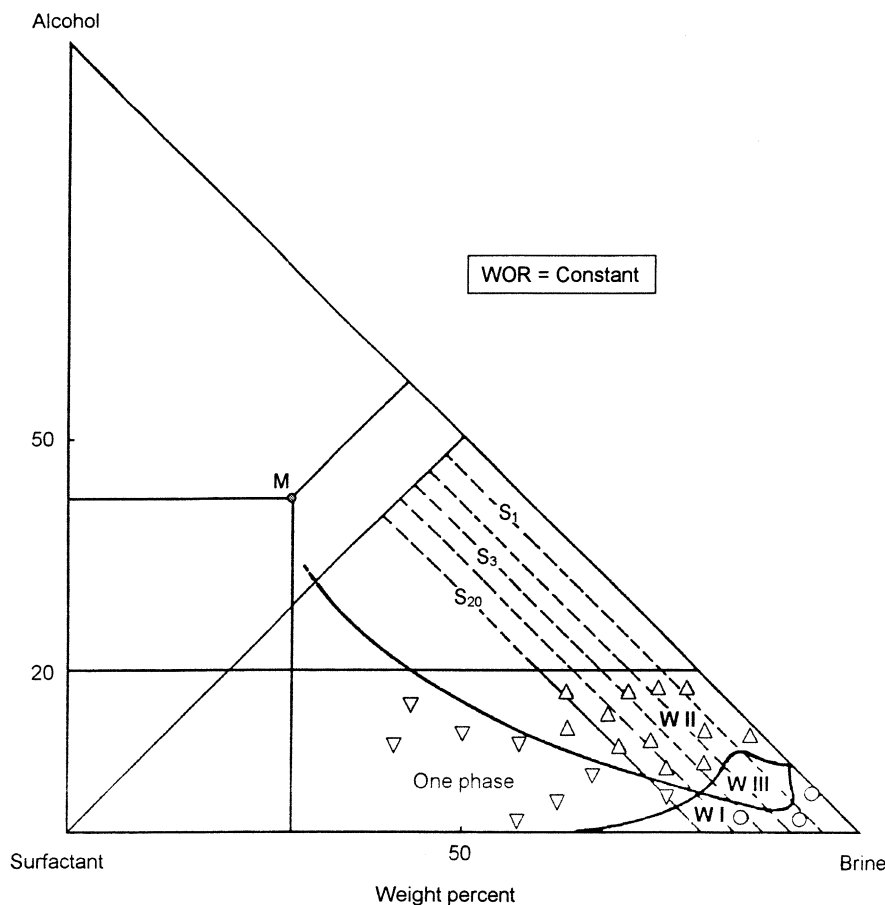


Fig. 3. Plane of a vertical cut of the model system tetrahedron corresponding to mixtures where the water-to-oil ratio is constant.

mixtures increases. It is interesting to note on this face, the horizontal tie line corresponding to mixtures containing about 5% in mass fraction of alcohol, which produces a coefficient of partition of the alcohol equal to one.

On the other hand, Fig. 6 presents the planes $WOR = 1$ and $WOR = 3$. An examination of this figure shows the following features:

- A single-phase zone that links up to the line of demixing of the ternary brine-surfactant-oil.
- A three-phase region, very extended in the direction water-oil, that links up to the tie line of the ternary water-oil-alcohol.
- Above the three-phase domain (i.e. the zone with higher content in alcohol), a region of type Winsor II is developed where the upper micellar phases are the richest in alcohol and in surfactant.

It can also be noted in Fig. 6, the existence of an intersection point where converge the four domains (Winsors I, II, III, and a single-phase zone). This point of confluence represents the highest mutual solubility of water and oil in the presence of a minimum amount of surfactant and alcohol.

Several hundreds of equilibrium points were measured: for water-oil ratios ranging from 0.08 to 20, and for various

compositions in surfactant and alcohol. However, only the experimental data for a water-oil ratio equal to one were used in our calculations.

4.2. Thermodynamic model

In spite of its importance in tertiary oil recovery, the thermodynamic study of microemulsion phase diagrams remains still little developed. Beyond the survey of the variance according to the number of components and phases [31–33], it is essential in tertiary oil recovery to represent these phase diagrams by means of an correlation or a molecular model that allows the calculation of compositions in coexistence for a mixture of given composition and fixed temperature. This model must be analytical, based on methods of the classical thermodynamics, and should contain adjustable parameters from experimental data. Once the model parameters are determined, it should be possible to extrapolate them, as a function of the composition and temperature, in regions beyond where experimental data are not available.

As mentioned above, the studied systems in tertiary oil recovery contain at least four components: water, oil, surfactant and co-surfactant (alcohol), to which one adds, in order to represent the reality of an oil reservoir, at least a salt such

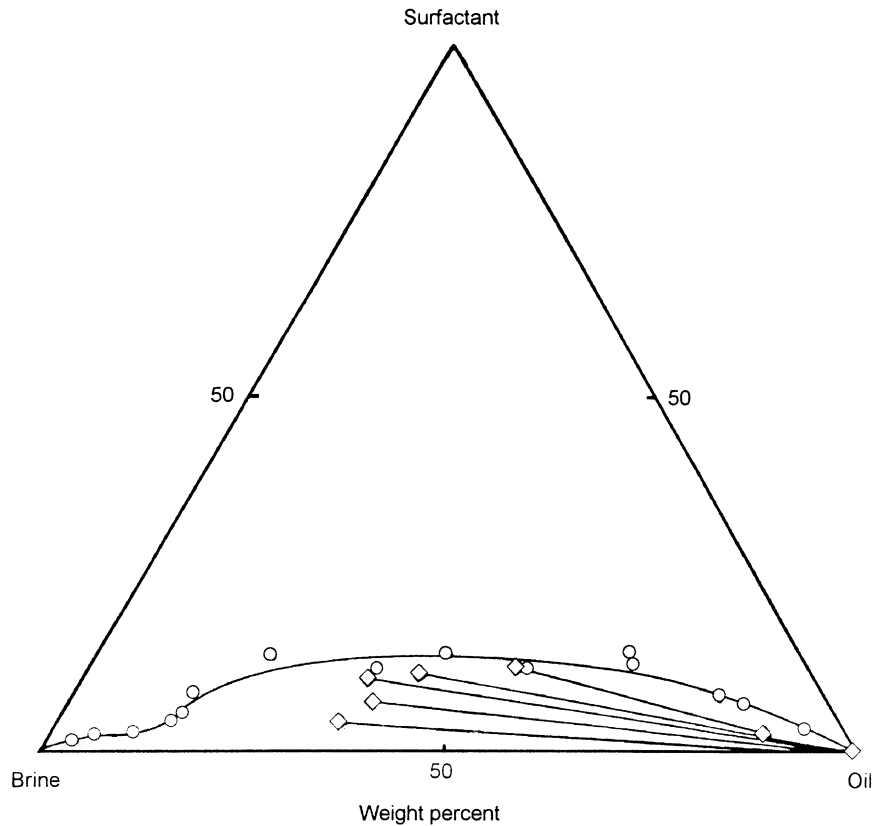


Fig. 4. Experimental liquid-liquid equilibria diagram of the system brine-oil-surfactant at 25°C [42]. The circles are the experimental results obtained by turbidity titration, which are connected by a full line. The squares are the experimental end points of the tie lines (solid lines).

as sodium chloride. It is therefore a system of five components (containing ions) that it is necessary to modeling. In fact, oil and surfactant are often complex mixtures, which can be considered as “true pseudocomponents” in the sense that all other components of oil or surfactant distribute in the same way between phases.

The approach that we have chosen for modeling the phase equilibria of microemulsion systems, consists in using expressions of the excess Gibbs energy commonly used in chemical engineering and whose flexibility has been recognized. Therefore, we do not take explicitly into account the formation of micelles (see [34–39]).

Calculated phase equilibrium compositions will be matched to experimental compositions by adjusting the model parameters without making more hypotheses on the structure of the solution. Besides, we make no simplifying hypothesis on the distribution of the other components into the phases in equilibrium.

The usual thermodynamic models are separated between models of electrolytes and non-electrolytes. In fact, the main difference between these two classes of models is due to the presence of an electrostatic interaction term (i.e. the Debye-Hückel term) in electrolyte models. This term has an important influence on the behavior at infinite dilution of the ionic species as the phases found in enhanced oil

recovery are either nonionic (oil phase in Winsor I) or highly concentrated in ionic species, and where we do not have any information on the partition of salt between the phases, it appears valid to use models of nonelectrolytes. One considers the brine (water + salt) as a pseudocomponent. This last approximation is imposed by the insufficient experimental information, and permits therefore only an inaccurate representation of the phase equilibrium data.

Toward this end, we have chosen the extended UNIQUAC equation of Nagata [40] for our calculations. The expression of the excess Gibbs energy for this equation is

$$g^E = g^{E,\text{comb}} + g^{E,\text{res}} \quad (52)$$

where $g^{E,\text{comb}}$ is the combinatorial term which takes into account the differences of size between molecules:

$$\frac{g^{E,\text{comb}}}{RT} = \sum_{i=1}^N x_i \ln \left(\frac{\phi_i}{x_i} \right) - \frac{z}{2} \sum_{i=1}^N q_i x_i \ln \left(\frac{\phi_i}{\theta_i} \right) \quad (53)$$

and $g^{E,\text{res}}$ is the residual term which takes into account the interactions between molecules and the shape of a term of local compositions:

$$\frac{g^{E,\text{res}}}{RT} = - \sum_{i=1}^N q_i^* x_i \ln S_i \quad (54)$$

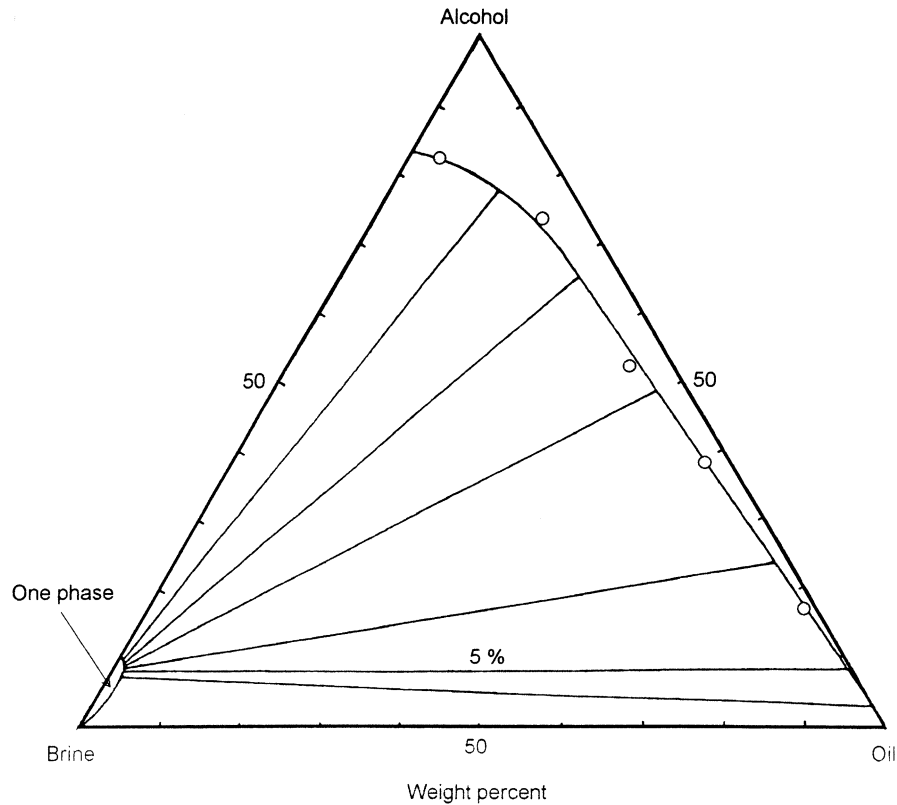


Fig. 5. Experimental liquid-liquid equilibria diagram of the system brine-oil-alcohol at 25°C [42]. The circles are the experimental results obtained by turbidity titration, which are connected by a full line. The solid lines are the experimental tie lines. Note the inversion of partition of the alcohol between the brine and oil phases as the content in alcohol of the mixture increases.

with

$$\theta_i = \frac{x_i q_i}{\sum_{j=1}^N x_j q_j} \quad (55)$$

$$\varphi_i = \frac{x_i r_i}{\sum_{i=1}^N x_j r_j} \quad (56)$$

and

$$S_i = \sum_{j=1}^N \theta_j \tau_{ji} \quad (57)$$

where Z is the lattice coordination number equal to 10, and r_i , q_i and q_i^* parameters, are molecular and structural properties of component i , which depend on the size and external area of the molecules.

We find in the combinatorial term, the expression of Flory-Huggins, which is also used in the model of Kilpatrick et al. [11] and that of Trouilly [41]. This term is “predictive” in the sense that it can be calculated from the structures of the molecules present in the solution. We used the parameters of the UNIFAC group given by Gmehling et al. [42] to determine the parameters of volume and surface of the pure components.

On the other hand, the expression of the residual term has largely shown its superiority over the model based on the

regular solution theory in the correlation of phase equilibria of simple systems. Parameters τ_{ij} are, in principle, related to the differences of energies between molecules according to the following expression

$$\tau_{ij} = \exp\left(-\frac{a_{ij}}{T}\right) \quad (58)$$

These are the binary parameters (and sometimes the pure-component parameter q_i^*) that we will adjust to fit the experimental data, in the sense that they can rather translate the nature attractive or repulsive of the interactions between molecules i and j .

Parameters r_i and q_i are obtained from group contributions while parameter q_i^* can be estimated as $q_i^* = q_i^{0.2}$. This correlation was used for oil, while for water and n -butanol we used values recommended by Nagata [40]. For surfactant, this parameter was fitted to the experimental data.

In order to represent the strong increase of the mutual solubilities of oil and water in presence of surfactant, we also introduce an effect of surfactant concentration on the binary parameter water-oil. This allows us to have different values for the interaction parameters of oil with water depending on the surfactant concentration [43]:

$$\tau_{w-o} = \tau_{w-o}^{(1)} + (\tau_{w-o}^{(0)} - \tau_{w-o}^{(1)}) \exp(-\sigma_{w-o-s}^2 x_s) \quad (59)$$

and similarly for the oil-water interaction. In this

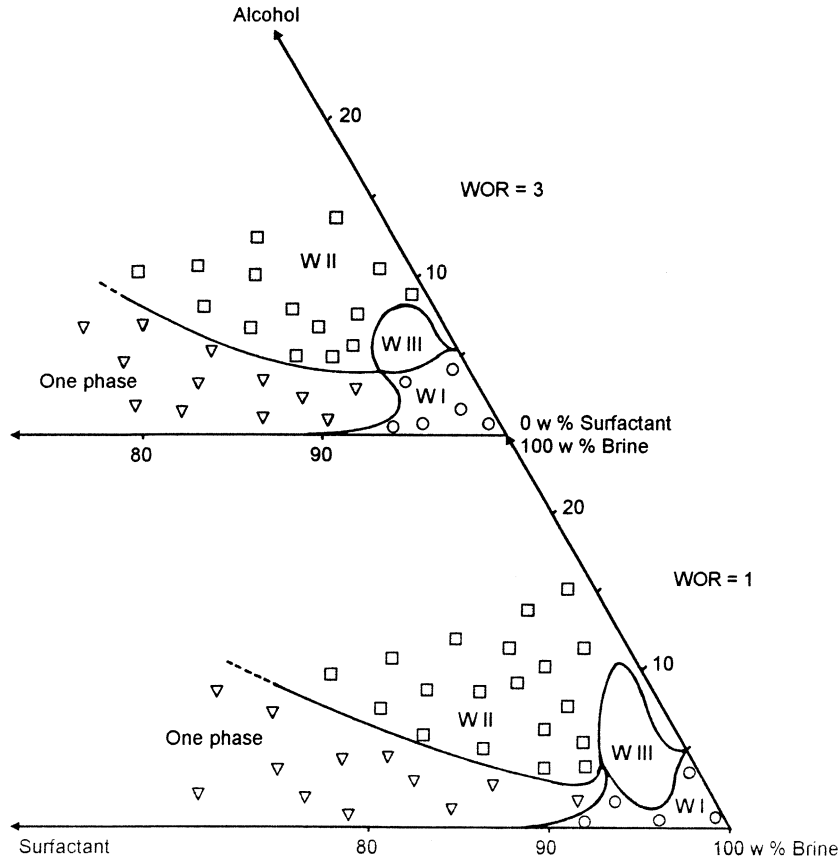


Fig. 6. Ternary diagrams showing vertical cuts of the tetrahedron representing the model system (brine–oil–alcohol–surfactant) in two different WOR planes [42]. The triangles, circles, and squares are the experimental global composition points of the homogeneous, Winsor I, and Winsor II regions, respectively. The solid lines are the experimental boundaries, which separate the domains Winsors I, II, III, and a single-phase zone.

expression, parameter $\tau_{ij}^{(0)}$ represents the value of the interaction coefficient water–oil in the absence of surfactant and this coefficient tends to $\tau_{ij}^{(1)}$ in presence of a high content of surfactant; the ternary parameter σ_{w-o-s} being equivalent to the “screen” parameter used by Kilpatrick et al. [11] and by Trouilly [41]. The generalized expression of Eq. (59) can be written as

$$\tau_{ij} = \tau_{ij}^{(1)} + (\tau_{ij}^{(0)} - \tau_{ij}^{(1)}) \exp\left(-\sum_{k=1}^N \sigma_{ijk}^2 x_k\right) \quad (60)$$

in such a way that there are four parameters per binary: $\tau_{ij}^{(0)}$, $\tau_{ji}^{(0)}$, $\tau_{ij}^{(1)}$ and $\tau_{ji}^{(1)}$, plus $2(N - 2)$ ternary parameters representing the influence of the other components of the mixture over this binary (i.e. parameters σ_{ijk} and σ_{jik} for $k = 1, \dots, N$ and $k \neq i, j$). The activity coefficient expression of component i derived from Eq. (52) is then

$$\ln \gamma_i = \ln \gamma_i^{\text{comb}} + \ln \gamma_i^{\text{res}} \quad (61)$$

where

$$\ln \gamma_i^{\text{comb}} = 1 - \left(\frac{\phi_i}{x_i}\right) + \ln\left(\frac{\phi_i}{x_i}\right) - \frac{z}{2} q_i \left[1 - \left(\frac{\phi_i}{\theta_i}\right) + \ln\left(\frac{\phi_i}{\theta_i}\right)\right] \quad (62)$$

and

$$\ln \gamma_i^{\text{res}} = -q_i^* \ln S_i + q_i \sum_{j=1}^N \frac{q_j^*}{q_j} x_j \left(1 - \frac{\tau_{ij}}{S_j}\right) - \sum_{j=1}^N \sum_{l=1}^N \left[\frac{q_j^* x_j \theta_j (\tau_{lj}^{(0)} - \tau_{lj}^{(1)}) (\sigma_{lji} - \sum_{k=1}^N \sigma_{ljk}^2 x_k)}{S_j \exp\left(\sum_{k=1}^N \sigma_{ljk}^2 x_k\right)} \right] \quad (63)$$

4.3. The ternary system brine–alcohol–oil

We first tried to represent the ternary system brine–alcohol–oil. In fact, it is the only face of the tetrahedron for which enough experimental data are available. In particular, these data characterize the partition of the alcohol between phases as shown in Fig. 7.

As mentioned early, a characteristic of this ternary system is the change of orientation of the tie lines around a global mass fraction in alcohol of 5%. It is essential to represent this behavior well since it determines the passage of systems of type Winsor I to Winsor II in the absence (or at weak concentrations) of surfactant.

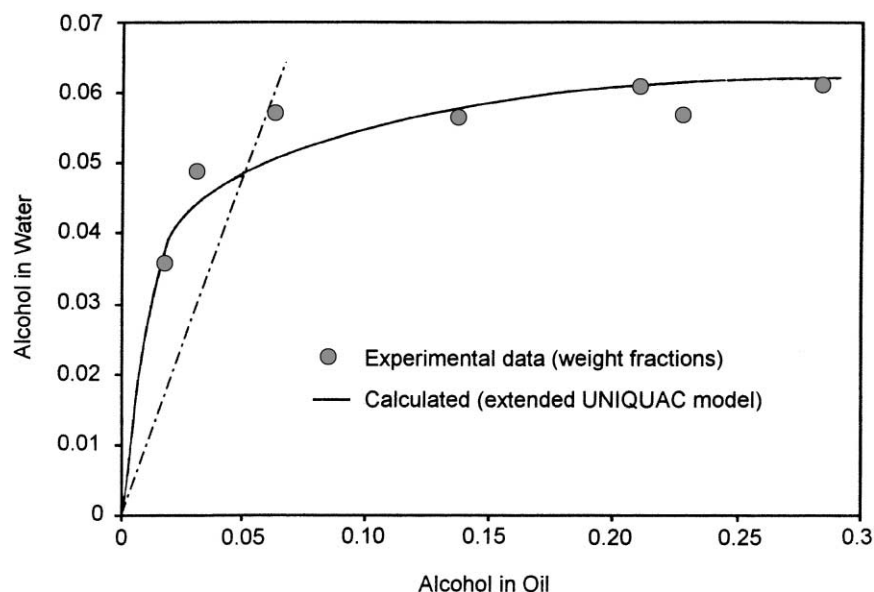


Fig. 7. Representation of the alcohol partitioning between oil and brine phases. The circles are the experimental data used for the estimation of the extended UNIQUAC [40] model parameters. The solid line is the calculated two-phase equilibria for the system brine–oil–alcohol at 25°C. The dashed-dotted line shows the occurrence of inversion of partition of the alcohol (about 5 mass%) between the brine and oil phases.

Fig. 7 shows the representation of the coefficient of partition of the alcohol between water and oil. The curve representing the mass fraction of alcohol in water according to its mass fraction in oil cut effectively the bisector to the neighborhood of a concentration of 5%. The estimated binary parameters τ_{w-o} and τ_{o-w} , lead to a strong immiscibility water–oil in the absence of any amphiphile. The success of this representation is a proof of the efficiency of the UNIQUAC expression.

4.4. The quaternary system brine–alcohol–oil–surfactant

The representation of the experimental data containing surfactant is naturally more difficult, and the adjustment of parameters is very long of the fact of the calculation complexity. We are therefore constraint to treat sets of data while adjusting subsets of parameters in order to approach very gradually to the optimal parameters on the whole of points. Besides, the convergence of the adjustment process is attributed mainly to the parameter initialization.

The follow-up strategy was to preserve the parameters water–oil, water–alcohol and alcohol–oil estimated from the representation of the ternary water–alcohol–oil, and to only adjust the other parameters (surfactant with the other components). In fact, it can be noted that the UNIQUAC expression of Nagata [40] did not allow taking into account simultaneously the strong solubilization of water in oil (Winsor II) in presence of surfactant and alcohol, and of the immiscibility of these two components in the absence of surfactant. Since parameters representing the mutual solubilities water–oil are essentially τ_{w-o} and τ_{o-w} , we have

chosen to consider them dependent of the surfactant content according to Eq. (59), so that solely the water–oil–surfactant σ_{w-o-s} and oil–water–surfactant σ_{o-w-s} ternary parameters were estimated during the regression of the data. This allows us to have different values for the interaction parameters of oil with water depending on the surfactant concentration.

It is important to point out that we do not try to give a precise molecular significance to these ternary parameters. We try simply to get an expression of the excess Gibbs energy having enough flexibility to represent the phase behavior of complex mixtures such as micellar systems. The ternary parameters are only an artifice that permits to treat the formation of micelles like a physical contribution to the Gibbs energy of the system rather than a chemical contribution.

Parameters $\tau^{(0)}$ relative to the pair water–oil have been already determined from ternary data water–alcohol–oil, and they assure to represent well the immiscibility water–oil in the absence of surfactant. The new expression of the excess Gibbs energy allows then to introduce parameters $\tau_{w-o}^{(1)}$ and $\tau_{o-w}^{(1)}$ as well as the ternary parameters water–oil–surfactant and oil–water–surfactant. In order to get a unique set of parameters regardless is the type of micellar system, we should handle simultaneously the phase equilibria of type Winsors I, II and III.

The whole set of parameters we obtained is listed in Table 1. Parameters τ_{ij} are expressed in terms of the differences in interaction energies a_{ij} according to Eq. (58).

The results of the fit are shown in Fig. 8. In this figure, we have reported the experimental domains (Winsors I, II, III, and a single-phase zone) for the water–oil ratio equal to one. The axes represent the global weight fractions of alcohol and surfactant. This diagram shows clearly the transition Winsor

Table 1

Estimated parameters of the modified UNIQUAC model for the system surfactant: (1): alcohol; (2): brine; (3): oil (4) at 25°C

Component	r_i	q_i	q_i^*	
Pure component parameters				
Surfactant (Witco TRS 10–80)	9.5370 ^a	7.4858 ^a	1.3575 ^a	
Alcohol (<i>n</i> -butanol)	3.4500	3.0500	0.8800	
Brine (8 g/l NaCl)	0.9200	1.4000	0.9600	
Oil (a C ₁₂ –C ₁₄ fraction)	9.2206	7.6360	1.5017	
i, j	$a_{ij}^{(0)}$	$a_{ji}^{(0)}$	$a_{ij}^{(1)}$	$a_{ji}^{(1)}$
Binary parameters				
1, 2	–1919.5	–399.5	0.0	0.0
1, 3	–817.75	–2813.7	0.0	0.0
1, 4	–292.69	2259.5	0.0	0.0
2, 3	2556.4	370.97	0.0	0.0
2, 4	523.18	1321.9	0.0	0.0
3, 4	781.67	3080.5	–968.13	1189.2
i, j, k	σ_{ijk}	σ_{jik}		
Ternary parameters				
3, 4, 1	3.6986	11.061		

^a Estimated during data regression.

I → Winsor III → Winsor II when alcohol is added to the system.

We can see in this figure that the model correctly represents the qualitative phase behavior of most points (e.g. the experimental Winsor II domain), with the exception of the borderline between the Winsor I and Winsor III domains. It is shown thus that the proposed extremely simple model permits to represent adequately the different types of micellar

systems according to the global composition of the mixture. In addition, data of the micellar phase of type Winsor II are represented quantitatively (see Fig. 9).

On the contrary, the representation of the micellar phase compositions Winsors I and III remains poor. In particular, the calculated concentrations of oil in the aqueous phase of a system of type Winsor I are very lower than observed data. With regard to systems of type Winsor III, the importance of

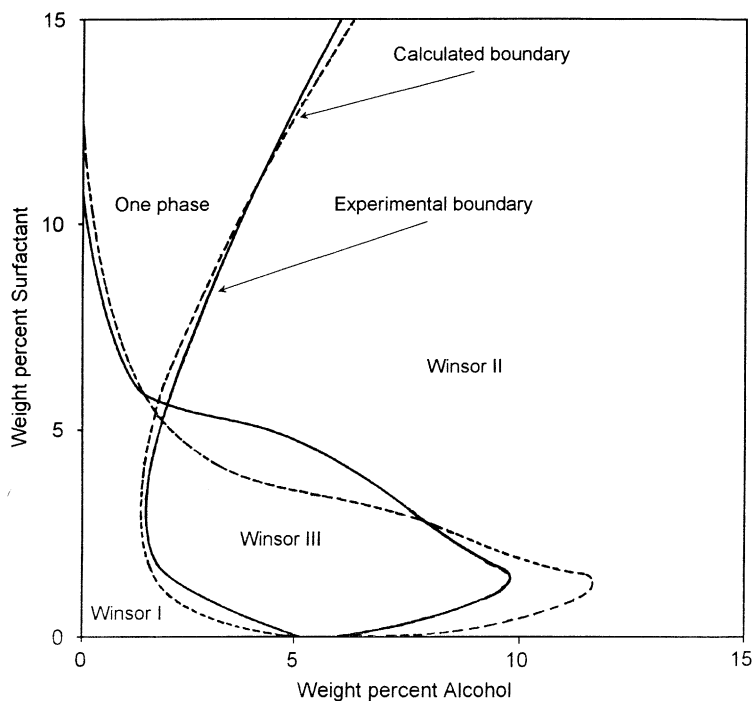


Fig. 8. Experimental and calculated phase equilibrium domains of the model system at 25°C for a water-to-oil ratio equal to one. The solid line is the experimental boundary and the dashed line is the calculated one with the proposed equation.

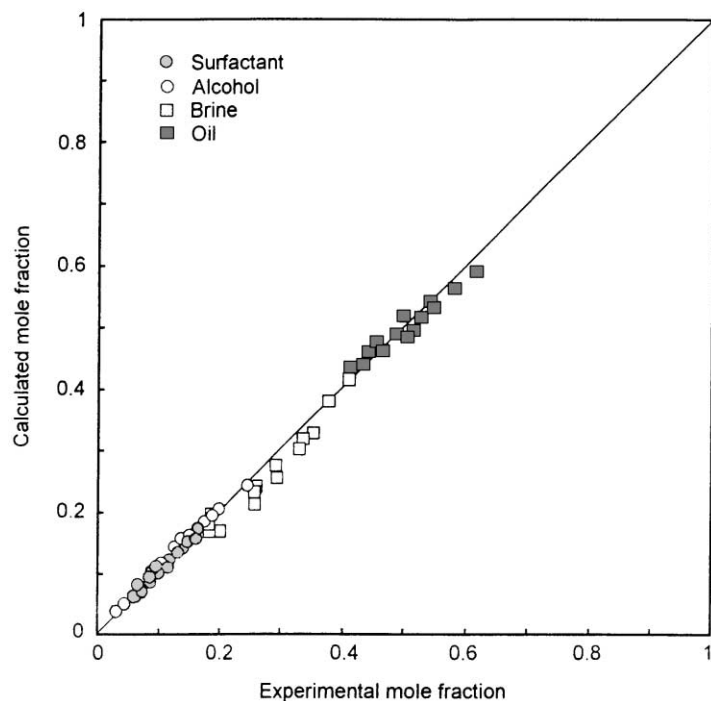


Fig. 9. Comparisons between experimental and calculated mole fractions at 25°C of the phase micellar of type Winsor II, for a water-to-oil ratio equal to one.

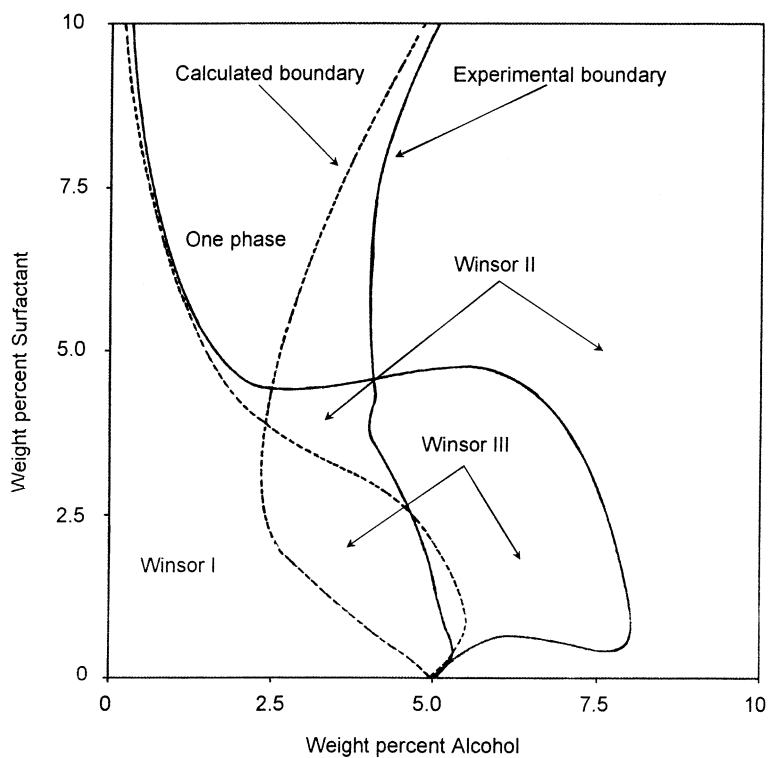


Fig. 10. Experimental and calculated phase equilibrium domains of the model system at 25°C for a water-to-oil ratio equal to three. The solid line is the experimental boundary and the dashed line is the calculated one with the proposed equation.

the salt partition between the aqueous phase and the micellar phase makes difficult to get a quantitative representation from a pseudo-quaternary representation of the problem. It is therefore little surprising to observe large residues on the composition of the micellar phase. Nevertheless, this argument may be not sufficient to explain the bad representation of the data of type Winsor I.

Finally, we tried to predict in a plane alcohol–surfactant the different phase domains for a water-to-oil ratio equal to 3, from parameters adjusted with data of the water-to-oil ratio equal to 1, while using data of global composition of the first one. Fig. 10 shows both the experimental and calculated domains. It can be observed from this figure that it is possible to predict the existing four domains on this plane (i.e. Winsors I, II, III, and a single-phase zone) in spite of a representation quantitatively insufficient.

5. Conclusions

The purpose of this work for representing micellar systems by means of chemical engineering tools has been well justified even though it was necessary to adapt the usual thermodynamic models to the nature of these systems. Thus, during this study we presented a thermodynamic model able to represent, at least qualitatively, the phase behavior of quaternary microemulsion systems.

This model is in fact a modification of the extended UNIQUAC expression of Nagata [40]. It allows, while using parameters of ternary interaction, to take into account the strong solubilization of water in oil in presence of surfactant and alcohol, as well as of the immiscibility of these two components in the absence of surfactant. In particular, the ternary parameter water–oil–surfactant plays here a similar role to the screen parameter used by Kilpatrick et al. [11] and by Trouilly [41] in their calculations. Nonetheless, it should be pointed out that this model does not consider the type of existing structure in these micellar systems.

For the Winsor II microemulsions, the model correctly represents the phase behavior for most experimental points; i.e. the compositions of these phases is quantitatively represented in most of the cases. For the Winsor I or III microemulsions, however, the oil content is always strongly underestimated by the model, which reveals a lack of flexibility of our equation or perhaps due to oversimplification in the definition of pseudocomponents.

Besides, in order to represent data of type Winsor III quantitatively it will be necessary to achieve complementary experimental determinations to have access to the partition of salt between phases water and microemulsion and, consequently, a complement of modeling to introduce the effect of salt explicitly. Also, an investigation of the influence of pressure and temperature on the phase behavior of microemulsion systems is recommended to elucidate oil reservoir conditions. This will allow minimizing the

consumption of surfactant and at the same time maximizing the recovery of residual oil in surfactant flooding processes.

Thus, it can be concluded that simple equations for the excess Gibbs energy are able to represent the qualitative phase behavior of microemulsions. However, a precise quantitative representation of the whole phase diagram will still require much additional work.

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