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Phase Behavior of Oil + Water + Nonionic Surfactant Systems for Various Oil-to-Water Ratios and the Representation by a Landau-Type Model**E. S. J. Rudolph, M. A. Caçao Pedroso, Th. W. de Loos,* and J. de Swaan Arons***Delft University of Technology, Faculty of Chemical Engineering and Materials Science, Laboratory of Applied Thermodynamics and Phase Equilibria, Julianalaan 136, 2628 BL Delft, The Netherlands**Received: July 23, 1996; In Final Form: December 11, 1996*[⊗]

The phase behavior of oil + water + nonionic surfactant systems under the influence of the temperature is usually only measured at an oil-to-water ratio of 1:1 ($\alpha = 0.5$). In this work, experimental phase equilibrium data at atmospheric pressure are presented for the systems nonane + water + 2-butoxyethanol at oil-to-water ratios of $\alpha = 0.126, 0.354, 0.568, 0.747$, and 0.918 , decane + water + 2-butoxyethanol at oil-to-water ratios of $\alpha = 0.134$ and 0.923 , and nonane + water + 2-(2-butoxyethoxy)ethanol at an oil-to-water ratio of $\alpha = 0.114$. A Landau-type approach, which was developed by Kleinert,^{1,2} is further extended and used to fit the data at an oil-to-water ratio of $\alpha = 0.568$ for the system nonane + water + 2-butoxyethanol, at $\alpha = 0.134$ for the system decane + water + 2-butoxyethanol, and at $\alpha = 0.114$ for the system nonane + water + 2-(2-butoxyethoxy)ethanol. The fitted parameters are used for the prediction of the phase behavior at other oil-to-water ratios. The predictions by the modified model are in good agreement with the experimental data.

Introduction

Mixtures of oil, water, and surfactant are widely applied in chemical, pharmaceutical, and oil industry. Experimentally the phase behavior of oil + water + nonionic surfactant systems is thoroughly investigated.^{3–9} Experiments proved that not only the structure of the surfactant and the oil but also parameters like temperature and pressure influence the phase behavior of these systems.

The impact of the oil-to-water ratio α in oil + water + nonionic surfactant systems on the phase behavior and especially on the occurrence of the three-phase region is not as thoroughly investigated as the temperature or the pressure influence.³ Such investigations on the impact of the oil-to-water ratio, e.g., for the system decane + water + C₈E₃,³ were performed to study the homogeneous channel of the one-phase region between the two two-phase regions. Usually data at an oil-to-water ratio of 1:1 are used for the characterization of the efficiency of a surfactant with the assumption that oil + water + nonionic surfactant systems form balanced microemulsions. The quite different phase behavior of the binary subsystems water + surfactant and oil + surfactant and also experimental data^{4,9} at $\alpha = 0.5$ lead to the assumption that not for all oil + water + nonionic surfactant systems can a balanced microemulsion be expected. Experiments at different oil-to-water ratios have to be performed to prove this.

Kahlweit⁴ gives an explanation of the phase behavior of oil + water + nonionic surfactant systems based on the proximity of a tricritical point. Departing from the tricritical point by changing the temperature, the pressure, or the nature of the oil or the surfactant, the observed phase behavior can be understood. Griffiths^{10,11} proposed to describe such systems by a Landau free energy. This idea was further developed and applied to some water + phenylalkane + nonionic surfactant systems by

Kleinert.^{1,2} His regressions well represent the experimental data for equal amounts of oil and water. Predictions at other oil-to-water ratios have not been performed.

In this work, the influence of the oil-to-water ratio and the temperature on the phase behavior of oil + water + nonionic surfactant systems was systematically investigated. The oil-chain length and the hydrophilicity of the surfactant are varied to gain an insight into the influence of these properties on the liquid phase behavior at oil-to-water ratios different from 1:1. The experimental data are represented using a modified version of the approach of Kleinert.^{1,2} Further, phase behavior for oil-to-water ratios different from the one used for the fit was predicted. For the fit an oil-to-water ratio of $\alpha = 0.568$ (oil-to-water weight fraction ratio $\alpha_w = 0.5$) for the system nonane + water + 2-butoxyethanol (C₄E₁), of $\alpha = 0.134$ ($\alpha_w = 0.1$) for the system decane + water + 2-butoxyethanol, and of $\alpha = 0.114$ ($\alpha_w = 0.1$) for the system nonane + water + 2-(2-butoxyethoxy)ethanol (C₄E₂) were used. The predictions were made for $\alpha = 0.126, 0.354, 0.747$, and 0.918 ($\alpha_w = 0.1, 0.3, 0.7$, and 0.9 , respectively) for the system nonane + water + C₄E₁ and for $\alpha = 0.923$ ($\alpha_w = 0.9$) for the system decane + water + C₄E₁.

Theory

Commonly, the phase behavior of oil + water + surfactant systems at constant oil-to-water ratios is expressed in quasi-binary temperature–composition diagrams. At a constant oil-to-water ratio the phase boundaries between the three-phase and the two two-phase regions and between the one- and the two-phase regions have the shape of a “fish”.^{3,4} The point where one finds a direct transition from the three-phase to the one-phase region is the so-called X-point. It is usually used to describe the efficiency of a surfactant to solubilize the same amounts of water and oil.

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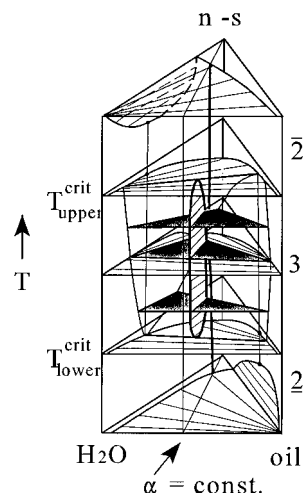


Figure 1. Schematic temperature–composition phase prism at constant pressure for an oil + water + nonionic surfactant system.

The macroscopical phase behavior of oil + water + nonionic surfactant systems in dependence on the temperature at various oil-to-water ratios can be depicted in temperature–composition phase prisms at constant pressure (Figure 1). The occurrence of the different phases found in the quasi-binary phase diagram at constant oil-to-water ratio α can easily be explained by Figure 1. For low temperatures the coexistence of an almost pure oil phase with a phase consisting of almost all the water, most of the surfactant, and some oil can be observed (Winsor I or 1). With increasing temperature the nonionic surfactant becomes more hydrophobic and tends to dissolve in the oil phase. For high temperatures an almost pure excess water phase coexists with a phase that is rich in oil and surfactant (Winsor II, 2). For the systems investigated here the phase sequence is not the direct transition from a Winsor I to a Winsor II region with increasing temperature but is intercepted by the occurrence of a three-phase coexistence. At the lower critical temperature $T_{\text{lower}}^{\text{crit}}$, a third liquid phase appears (Winsor III, 3). This microemulsion middle phase coexists with two excess phases, which are almost pure water and almost pure oil, respectively. An increase of the temperature results in an increasing hydrophobicity of the surfactant, so that within the three-phase region the middle phase contains more oil and less water. At the upper critical temperature $T_{\text{upper}}^{\text{crit}}$, the third phase vanishes, and one finds a 2 system.

In the literature¹² it is stated that a balanced microemulsion is depicted by a “fish” at equal amounts of oil and water that has a zero tilt. This means that the ternary phase diagram would be symmetrical with respect to the oil-to-water ratio line of 1:1. The surfactant concentrations in either excess phase would be identical. Considering the experimental results of Kahlweit⁴ and Sassen,⁸ one sees that a balanced microemulsion is not found for all systems at atmospheric pressure. This is indicated by a clear inclination of the “fish” for a constant oil-to-water ratio of 1:1. The occurrence of a balanced microemulsion is based on the different types of phase behavior of the binary subsystems. Therefore, a balanced microemulsion can be induced by variation of the pressure and the temperature.

Kahlweit and Strey⁴ pointed out that the three-phase equilibria of oil + water + nonionic surfactant systems evolve from a tricritical point by changing field variables such as the temperature or the pressure or by changing other properties such as the nature of the oil or the surfactant. The upper and the lower critical temperatures, describing the borders of the three-phase region, are identical at the tricritical point. If one moves away from the tricritical point in the direction of the three-phase

coexistence by changing at least one of the field variables, e.g. the pressure, the distance between the upper and the lower critical temperatures is increasing.

Griffiths^{10,11} proposed to describe these systems with a Landau-type model, which is based on the expansion of the free energy in a power series of an order parameter x . The order parameter x describes the distance from the critical point in terms of one of its variables, e.g. the temperature, as in the classical theory of Landau. For the description of tricritical points an expansion to at least the sixth order is needed.

$$f_{\text{pot}} = a_1x + a_2x^2 + a_3x^3 - 3/2x^4 + x^6 \quad (1)$$

The parameters a_i are functions of the order parameter x at the minima of the free energy f_{pot} . By the freedom of rescaling, the term $a_4x^4 + a_6x^6$ can be written as $-(3/2)x^4 + x^6$. The parameter a_3 can then be expressed in terms of one of the field variables, so it is identical to $\tau/2$.^{1,2}

The free energy is factorized in terms of its k roots ($x_m \pm i\bar{x}_m$) by¹¹

$$f_{\text{pot}} = \prod_m [(x - x_m)^2 + \bar{x}_m^2] - \prod_m (x_m^2 + \bar{x}_m^2) \quad (2)$$

The parameter m takes the values 1, 2, and 3. Due to the constraint that $a_5 = 0$, the sum of the values of x at the minima of the free energy must be equal to zero. With the evaluated values of a_3 to a_6 , eq 2 allows the computation of the parameters a_1 and a_2 as functions of the order parameter x .

In the case of three coexisting phases the three roots of eq 2 are real; in the case of two phases coexisting only two of the solutions are real and one is complex. The regions of two-phase equilibria can be visualized as surfaces, which intersect in a curve representing three coexisting phases. This curve can be parametrized as a function of one of the field variables, e.g. the reduced temperature τ .^{1,2}

$$4x^3 - 3x + \tau = 0 \quad (3)$$

The order parameter x is related to the volume fractions of oil and water by $\alpha = \alpha^0 + ax$ with $\alpha = \Phi_{\text{oil}}/(\Phi_{\text{oil}} + \Phi_{\text{water}})$. Φ_i is the volume fraction of component i . The surfactant concentration is assumed to have a quadratic dependence on the order parameter $\Phi_{\text{surfactant}} = \Phi_{\text{surfactant}}^0 + b[x^2 - \alpha_2(\alpha_2 - 9/16) - \alpha_1(\alpha_1 + \tau/4)]$. The parameter a depends on the tilt of the “fish”, the parameter b on the length of the “fish”. The reduced temperature is defined using the upper and the lower critical temperature so that $\tau = 1$ and -1 , respectively. The parameters α_1 and α_2 are obtained from experimental points describing the phase transitions from the one-phase to the two two-phase regions. At the transitions from the three-phase region to the two-phase regions the parameters a_1 and a_2 are equal to $-\tau/4$ and $9/16$, respectively. For a more detailed description see Griffiths^{10,11} and Kleinert.^{1,2}

The variables denoted by superscript 0 describe the values of crucial points. It is assumed that for oil + water + nonionic surfactant systems these are found for equal amounts of water and oil, where the order parameter x is equal to zero. This implies the occurrence of the so-called balanced microemulsion.

As already pointed out above, not all oil + water + nonionic surfactant systems show a balanced microemulsion at atmospheric pressure. This means that the ternary phase diagram at atmospheric pressure is not symmetrical with respect to the line representing an oil-to-water ratio of 1:1. Since the occurring phase behavior is explained in terms of the vicinity of the tricritical point, this proves that the given systems do not show

symmetrical phase behavior close to their tricritical point. The original Landau theory with its great simplicity is developed to describe systems that show a symmetrical phase behavior close to their tricritical point.¹¹ To be able to describe the phase behavior of the given systems, the original Landau theory had to be extended. This can be done by either developing a more complicated form of the free energy or a different dependence of the order parameter x on the concentrations. We decided to follow the latter idea. The X-point surfactant concentrations in dependence on the oil-to-water ratio α describe a parabola. The shape of the parabola of the computed X-point surfactant concentrations depends on the definition of the order parameter x . In order to match the experimental evolution of the X-point surfactant concentrations, the original definition of the order parameter x in dependence on the oil-to-water ratio α was modified. The parabola described by the original definition of the order parameter x resulting from X-point surfactant concentrations in dependence on α showed a too rigid relation. The relation of the order parameter x to the volume fraction α of the oil in the water given by $\alpha = \alpha^0 + a(z^2 + z + 1)x$, where $z = |(\alpha - \alpha^0)|$, gives better results. It should be noted that the actual value of α^0 is not automatically 0.5, describing an oil-to-water ratio of 1:1, but that it is the value of α for which the X-point surfactant concentration reaches its maximum.

Experiments

The experiments at atmospheric pressure were carried out in simple test tubes that were submerged in a temperature-controlled water bath. Using this experimental setup, the phase transition temperatures at a constant overall composition were visually determined.

The samples were prepared on a weight basis using the following composition variables:

$$\alpha_W = w_{\text{oil}} / (w_{\text{oil}} + w_{\text{water}})$$

$$\gamma_S = w_{\text{surfactant}} / (w_{\text{oil}} + w_{\text{water}} + w_{\text{surfactant}})$$

where w_i is the weighed amount of component i .

The water used was double distilled with a conductivity of less than 10^{-6} S cm⁻¹. The used nonionic surfactants were 2-butoxyethanol (C₄E₁) and 2-(2-butoxyethoxy)ethanol (C₄E₂). Both were products of Merck-Schuchardt with purities of at least 99 and 98 wt %, respectively. The oils were *n*-nonane and *n*-decane. The *n*-nonane was provided by Janssen Chimica, the *n*-decane by Aldrich. The stated purities were at least 99 wt %. The surfactant was stored over a 3 Å molecular sieve before use. The other chemicals were used without further purification.

Results

The phase behavior of the systems nonane + water + 2-butoxyethanol (C₄E₁), decane + water + 2-butoxyethanol, and nonane + water + 2-(2-butoxyethoxy)ethanol (C₄E₂) was investigated at various oil-to-water ratios as a function of temperature. The results are presented in Figures 2–5. The weight fractions were transformed into volume fractions using the molar volume of the components at 298 K and assuming a zero volume of mixing. The transformation results in “fishes” with less inclination, which allows the use of the original Landau approach with only small extensions. For all systems we found that varying the oil-to-water ratio results in a change of the inclination of the “fishes”. The extension of the three-phase region especially at high and low oil-to-water ratios with respect to the surfactant concentration is quite large. This supports the

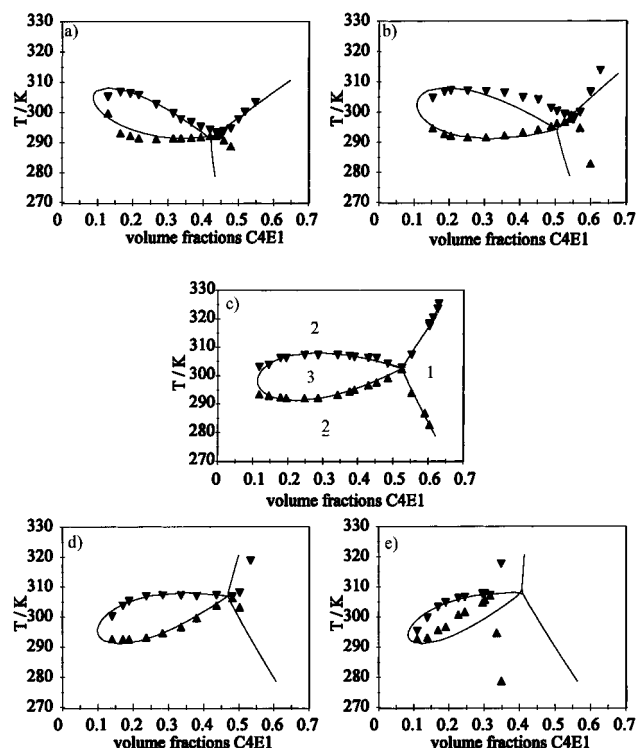


Figure 2. *n*-Nonane + water + 2-butoxyethanol (C₄E₁) system. (▲, ▼) Experimental points; (—) fit for $\alpha = 0.568$ (c), extrapolation for all other α (a, b, d, e). (a) $\alpha = 0.126$, (b) $\alpha = 0.354$, (c) $\alpha = 0.568$, (d) $\alpha = 0.747$, (e) $\alpha = 0.918$. (c) Fit: $a = 0.568$, $\Phi_s^0 = 0.532$, $b = -0.556$, $\alpha_1 = 0.066$, $\alpha_2 = 0.167$. (a, b, d, e) Extrapolations from the “fish” at $\alpha = 0.568$ using the parameters given above.

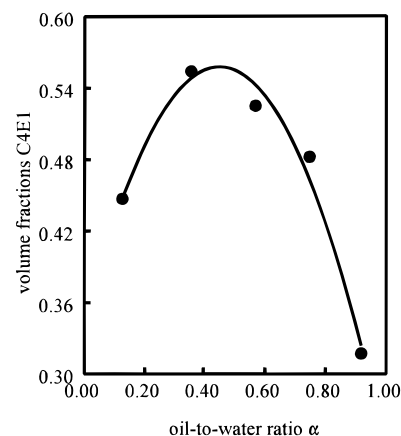


Figure 3. X-point surfactant concentrations Φ_s^X in dependence on the oil-to-water ratio α . The line is drawn to guide the eye.

often made assumption that in the case of a three-phase equilibrium the coexisting excess phases almost only contain water and surfactant or oil and surfactant. The experimental data also show that the excess water phase contains less oil than the excess oil phase water.

The system nonane + water + 2-butoxyethanol was examined meticulously. Experiments were carried out for $\alpha = 0.126$, 0.354, 0.568, 0.747, and 0.918. The results are shown in Figure 2. One can see that with increasing value of α the inclination of the “fish” changes. The X-point temperatures of the “fish” shift from lower temperatures toward higher temperatures, and the X-point surfactant concentrations describe a parabola with its maximum at $\alpha \neq 0.5$ (Figure 3). The picture gives the impression that the maximum should be found for an oil-to-water ratio lower than 0.5. For a low oil-to-water ratio as for example for $\alpha = 0.126$ the surfactant concentration at the X-point is found around 0.45, for $\alpha = 0.568$ it is found around

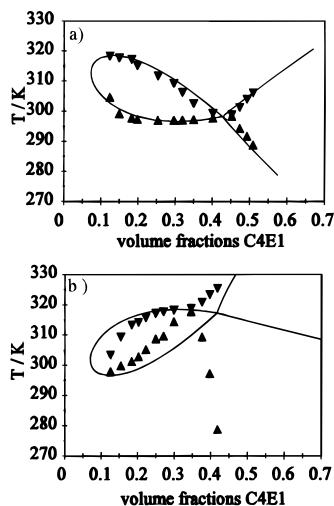


Figure 4. *n*-Decane + water + 2-butoxyethanol (C_4E_1) system. (\blacktriangle , \blacktriangledown) Experimental points; (—) fit for $\alpha = 0.134$ (a), extrapolation for $\alpha = 0.923$ (b). (a) $\alpha = 0.134$. Fit: $a = 0.7$, $\Phi_s^0 = 0.467$, $b = -0.529$, $\alpha_1 = -0.335$, $\alpha_2 = 0.648$. (b) $\alpha = 0.923$.

0.56, and finally for a high oil-to-water ratios as for example $\alpha = 0.918$ it is found around 0.32. For $\alpha = 0.126$ (Figure 2a) the “fish” tilts “upward”. For $\alpha = 0.568$ (Figure 2c) one observes a “fish” with only a slight “downward” tilt. Further increase of α results in a “fish” clearly pointing “downward”.

For the fit of the modified Landau-type theory to the experimental data the “fish” for $\alpha = 0.568$ is used. The upper critical temperature is found at 308 K, the lower critical temperature at 291 K. The obtained parameters are $a = 0.553$, $b = -0.556$, $\alpha_1 = 0.066$, $\alpha_2 = 0.167$, and $\Phi_{\text{surfactant}}^0 = 0.532$.

Using these parameters the “fishes” at the other oil-to-water ratios could be predicted (Figure 2a,b and d,e). The actually fitted “fish” is in very good agreement with the experimental data. The predicted “fishes” show some deviation from the experimental points. The change of the “fish” shape and the inclination of the “fish” with varying oil-to-water ratio are nicely reproduced. The X-point temperatures of the “fishes” are well described, while the X-point surfactant concentrations are deviating, especially in the cases of $\alpha = 0.918$ and $\alpha = 0.354$. For the “fish” at $\alpha = 0.354$ the change of the inclination is overpredicted, meaning that the X-point temperature is predicted too low. This results also in a less extended three-phase region with respect to the surfactant concentration. The “fish” at $\alpha = 0.126$ is represented better. Still the predicted values of the temperature and surfactant concentration at the X-point are too low. However the deviations are small. The “fishes” for oil-to-water ratios that are bigger than the oil-to-water ratio at which the fit was performed ($\alpha > 0.568$) show the opposite behavior. The predicted “fish” at $\alpha = 0.918$ is more extended than the experiments show. The X-point temperature is represented well. The “fish” at $\alpha = 0.747$ is predicted very well. The phase transitions from the one-phase to the two two-phase regions are not as well predicted as the phase transitions to the three-phase region. One can see that for the oil-to-water ratios of $\alpha < 0.568$ only the phase transitions from 1 to $\bar{2}$ are described rather nicely, while the transitions from 1 to $\underline{2}$ are poorly described. For the oil-to-water ratios of $\alpha > 0.568$ it seems that the transitions for temperatures lower than the X-point temperature of the “fish” at the given oil-to-water ratio are represented better.

To check the influence of the oil-chain length for high and low oil-to-water ratios, further experiments were carried out for the system decane + water + 2-butoxyethanol at $\alpha = 0.134$ and 0.923. In Figure 4 the experimental and fitted results are

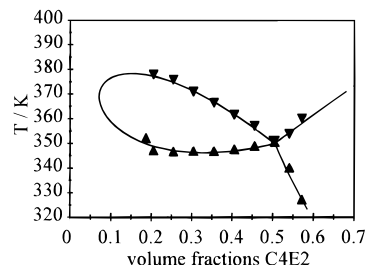


Figure 5. *n*-Nonane + water + 2-(2-butoxyethoxy)ethanol (C_4E_2) system. (\blacktriangle , \blacktriangledown) Experimental points; (—) fit. $\alpha = 0.114$. Fit: $a = 0.887$, $\Phi_s^0 = 0.552$, $b = -0.630$, $\alpha_1 = 0$, $\alpha_2 = 0.325$.

depicted. One sees that, compared to the “fishes” using nonane as an oil, the “fishes” are more tilted. The three-phase region widens and shifts toward higher temperatures, while the surfactant concentration range slightly increases with increasing oil-chain length. The upper critical temperature is 318.5 K; the lower critical temperature is 296.5 K.

In this system we adjusted the model to the “fish” of $\alpha = 0.134$. The “fish” at the oil-to-water ratio of $\alpha = 0.923$ is predicted. The adjusted parameters are $a = 0.746$, $b = -0.529$, $\alpha_1 = -0.335$, $\alpha_2 = 0.648$, and $\Phi_{\text{surfactant}}^0 = 0.485$. The fit reproduces all phase transitions very well. The predicted “fish” at $\alpha = 0.923$ matches the experimental data qualitatively. As for the system nonane + water + C_4E_1 the predicted “fish” is more extended with respect to the surfactant concentration than the one found experimentally. The predicted X-point temperature agrees well with the experiments. The high-temperature phase transitions from the one-phase region to the two-phase region are reasonably represented, while those transitions for temperatures lower than the X-point temperature of the given “fish” are not in agreement with the experimental findings.

In Figure 5 the phase behavior of the system nonane + water + 2-(2-butoxyethoxy)ethanol for $\alpha = 0.114$ is shown. With increasing hydrophilicity of the surfactant (C_4E_1 to C_4E_2) the three-phase region shifts toward higher temperatures. The upper critical temperature of the system containing C_4E_2 is found at 378.4 K, the lower critical temperature at 346.1 K. Again the inclination of the “fish” of the system containing C_4E_2 is more pronounced than that of the system containing C_4E_1 .

The fit for the system nonane + water + C_4E_2 gives the following values of the adjusted parameters $a = 0.114$, $b = -0.63$, $\alpha_1 = 0$, $\alpha_2 = 0.325$, and $\Phi_{\text{surfactant}}^0 = 0.556$. The fit agrees very well with the experimental data for all phase transitions.

Discussion

The influences of the oil-chain length and the surfactant nature are in agreement with earlier investigations on oil + water + surfactant systems for equal amounts of oil and water^{3,4} at atmospheric pressure. Also with increasing oil-chain length and increasing hydrophilicity of the surfactant (C_4E_1 to C_4E_2) the three-phase region widens and shifts toward higher temperatures. The experiments show that the oil-to-water ratio has a strong impact not only on the one-phase channel but also on the shape of the three-phase region of oil + water + nonionic surfactant systems.

The clear inclination of the “fishes” at constant oil-to-water ratios shows that the surfactant becomes more hydrophobic with increasing temperature. The same amounts of surfactant are solubilized in the water and in the excess oil phase when the X-point temperature coincides with the mean of the upper and lower critical temperature of the given system. Only if the X-point temperature fulfills this condition at an oil-to-water ratio

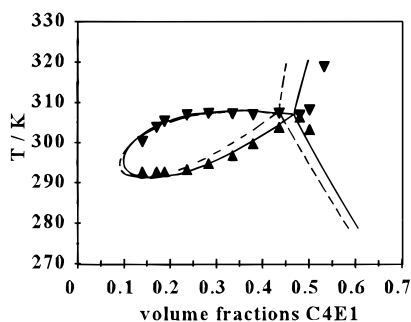


Figure 6. Comparison of the predictions using the definition of the order parameter x of Kleinert and of this work. (\blacktriangle , \blacktriangledown) Experimental points; (—) this work; (---) Kleinert.

of 1:1 is the term “balanced microemulsion” justified. This is not the case at atmospheric pressure for the systems investigated here. With increasing oil-chain length and with increasing hydrophilicity of the surfactant the inclination of the “fish” increases. This gives a reason for the assumption that by variation of the oil-chain length and of the surfactant hydrophilicity a balanced microemulsion can be induced.

The large extension of the three-phase region at high and low oil-to-water ratios proves that even for systems containing such small surfactants as C₄E₁ and C₄E₂ the excess water or oil phase is almost free of oil and water, respectively. The solubilization of the water and the oil using these short-chained surfactants is comparable to the solubilization using the long-chained more efficient surfactants.

The description of the experiments by the modified Landau-type model is satisfying. Fitting the parameters for a pseudo-binary cross section at a constant oil-to-water ratio results in a very good representation of the experimental results. The introduced modification allows the use of the adjusted parameters to predict the phase behavior of other oil-to-water ratios for the same system. Here the results are less impressive, but still in quite good agreement with experimental findings. Omitting the introduced coefficient ($z^2 + z + 1$) leads to a less satisfying representation. As an example, the results of the predictions of the “fish” for the system nonane + water + C₄E₁ at the oil-to-water ratio of 0.747 using the original definition of the order parameter x as given by Kleinert^{1,2} and the definition introduced in this work are depicted in Figure 6.

A striking point is the fact that the “fishes” at around $\alpha \approx 0.9$ could not be reproduced very well by the model. Neither using the parameters obtained at other oil-to-water ratios nor fitting the model directly to the experimental results for $\alpha \approx 0.9$ leads to a satisfying description of the experimental results. This is probably caused by the shift of the maximum of the X-point surfactant concentration away from the oil-to-water ratio of $\alpha = 0.5$.

Another point worth noting is the less good description of the phase transitions from the one-phase to the two two-phase

regions. The predicted “tail” is more or less symmetrical to the line describing the inclination of the “fish” (line connecting the X-point and the “mouth” of the “fish”). The experimental points are rather symmetrical to a line of constant temperature which is equal to the X-point temperature. The opening angle of the experimentally found “tails” increases from $\alpha \approx 0.1$ to $\alpha \approx 0.9$. This is not reproduced by the model since the values of the parameters a_1 and a_2 depend on the tilt of the “body” of the “fish”.

The model cannot be used to make predictions from one system to another. This is based on the fact that the predictions of the model are in some respect extrapolations from experimental data of the same system.

The deviations between the experimental and predicted phase equilibrium data are based on the assumptions of the model. First, the classical theory of Landau is developed for the description of symmetrical phase behavior close to tricritical points.¹⁰ We omitted this limitation by a new definition of the “idealized” order parameter x and obtained better results than without this modification. Second, it is assumed that the surfactant concentration is quadratic depending on the order parameter x and shows its maximum at $\alpha = 0.5$. Considering experimental data of the X-point surfactant concentrations for different oil-to-water ratios, this is reasonable, although the maximum is usually not found at $\alpha = 0.5$. A better description should be found for a slightly shifted parabola with its maximum at $\alpha \neq 0.5$. To adjust such a parabola, lots of experimental data at different oil-to-water ratios would be necessary.

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