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TOWARDS CUSTOM-MADE MICROEMULSIONS

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With the goal of finding the optimal properties of soaps used for tertiary oil recovery we show which properties control the position and shape of the three-phase regime in ternary mixtures of oil, water, and soap. We determine the conditions for the existence of large and multiple three-phase regimes in the phase prism formed by the Gibbs triangle of compositions and the temperature axis.

If tertiary oil recovery by means of microemulsions is ever to be successful, we must learn how to control the shape and position of the three-phase regime in ternary mixtures of oil, water, and soap. We want a regime which stretches over a large range in temperature and salinity, consumes little soap, and lies at any desired position in the parameter space characterizing the oil well.

A useful property of three-phase regimes is that as long as they are small they have quasi-universal features, being controlled by a near-lying tricritical point [1-4]. In its neighbourhood it is easy to obtain excellent fits to experimental data [5-9]. For applications, however, we have to move into regions of large three-phase regimes, far away from the tricritical point. Then quasi-universality is lost and we need specific models to study the phenomena.

The purpose of this Letter is to point out that important information can be derived from the simplest possible lattice model of ternary mixtures [10]. The model allows for three occupations per site, water (W), oil (O), or soap (S) and its mean-field free energy, as a function of the concentrations, is

$$x_1 = x_\mathrm{W}\ ,\quad x_2 = x_\mathrm{O}\ ,\quad x_3 = x_\mathrm{S}\ ,$$

$$\sum_{i=1}^{3} x_i = 1 \quad (i, j, k = \text{cyclic}):$$

$$g = \sum_{i=1}^{3} (a_{jk} x_j x_k + x_i \log x_i)\ . \qquad (1)$$

The coefficients $a_{jk} = a_{kj}$ parametrize the binary interactions between WO, OS and WS. The important feature of the model is that all properties of the ternary system are completely determined by the three binary subsystems (if there were terms of the type $x_1 x_2 x_3$ this would not be the case).

Focusing attention on non-ionic soaps we shall, for simplicity, study the model in the phase prism formed by the Gibbs triangle of concentrations x_i and the temperature axis.

Since the phenomena take place in a small temperature range compared to the absolute temperature, we expand the coefficients a_{ij} in the neighbourhood of the critical values ($a_{ij}^c = 2$) as

$$a_{ij}(T) = 2[1 + w_{ij}(T_{ij}^c / T - 1)]\ . \qquad (2)$$

Here the T_{ij}^c are the critical temperatures of the binary subsystems and the w_{ij} parametrize the widths of the corresponding solution boundaries. One should note that this interpretation of w_{ij} and T_{ij}^c holds only if T is close to T_{ij}^c. Now the oil–water and oil–soap systems have miscibility gaps with critical temperatures far above and below the three-phase regimes [6,11] to be studied, so that for $a_{12} = a_\mathrm{WO}$, $a_{23} = a_\mathrm{OS}$, (2) are only effective linear parametrizations. Near the three-phase regime only T_WS^c is close to the actual temperature. The water–soap system usually has a miscibility gap in the form of a closed loop and the three-phase regime lies close to the lower critical point (the cloud point) [6,12]. We therefore use $w_\mathrm{WS} < 0$ to parametrize a_WS near this temperature.

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In order to explain the experimental situation, the model needs one refinement. As it stands it is completely symmetric in the composition variables. The oil–soap upper critical point, however, usually lies on the oil-rich side [6,13]. More importantly, the cloud point is found at low soap concentrations. The asymmetry increases with the chain length and can reach 1 wt% [6,14]. Therefore, for good soaps, the variables x_i require a strong distortion. As a somewhat artificial prescription, to be justified by the results, we relate the true weight fractions g_i to the model fractions x_i by [15]

$$g_W = x_W r_O / N , \quad g_O = x_O r_W / N , \quad g_S = x_S r_W r_O / N , \tag{3}$$

where $N = x_W r_O + x_O r_W + x_S r_O r_W$. Now, the critical concentrations on the water–soap and oil–soap sides $g^c_W = (1+r_W)^{-1}$ and $g^c_O = (1+r_O)^{-1}$ are to be fitted to experiment (note that the rescaling does not allow for an independent fit of the oil–water miscibility gap).

For small r_O, r_W the entire ternary x_i composition space is dragged into the regime of small soap concentration which is precisely what is needed experimentally (and has been achieved by other ad hoc methods before [16]. We do not use these methods since they violate the desirable feature that the ternary system is determined by the binary subsystems).

The general thermodynamics of (1) has been described in great detail [17,18] so we can directly study the specific properties of the distorted model.

First we explain the behaviour of the size of the three-phase regime (upper minus lower critical temperature) as the tricritical point is approached. Experimentally, Kahlweit et al. [6–8] vary the chain length k of the carbon atoms of the stretched *n*-alkanes (using as a soap various fixed compounds C_iE_j with $i \in (4, 12)$, $j \in (1, 7)$). Obviously only w_{OS}, T^c_{OS}, w_{WO}, T^c_{WO} depend on k while w_{WS}, T^c_{WS} which characterize the water–soap system remain fixed. For solutions of C_iE_j in *n*-alkanes the critical temperatures show a linear dependence [6,11] $T^c_{OS}(k) \approx T^c_{OS} + kT'_{OS}$ with $T'_{OS} \approx 6.5\,^{\circ}\mathrm{C}$. From the phase boundaries of C_6E_5 in *n*-alkanes [6] we find that w_{OS} falls with increasing k and we use $w_{OS}(k) = w_{OS} - kw'_{OS}$. For the oil–water system we take $T^c_{WO}(k) = T^c_{WO} + kT'_{WO}$ with $T'_{WO} = 50\,^{\circ}\mathrm{C}$. Lacking experimental information on the k dependence, we take $w_{WO}(k) = w_{WO}$, independent of k. For $k = 14$ we use $T^c_{OS} = 225$ K, $T^c_{WS} = 330$ K, $T^c_{WO} = 1200\,K$, $w_{OS} = 0.2$, $w_{WS} = 1.5$, $w_{WO} = 1$ and $w'_{WO} = 0.03$. The resulting upper and lower critical points of the three phase regime are given in fig. 1a. They show the same cusp shape as the experimental data of fig. 1b [8]. The overall slope and the curvature of the cusp boundaries are very sensitive to the k dependence of w_{OS}. If we had taken $w_{OS}(k) = w_{OS}$, the slope of the cusp would have turned out much smaller.

Let us now turn to the shapes of the three-phase regime. We know from the systematic analysis of Kahlweit et al. [6] that this forms a flat fish-shaped body with the nose pointing in the direction of low soap concentration. Fig. 2 shows three cuts through this body as obtained in our model (a) in comparison with a typical experimental result (b) [6]. The parameters used were

$$T^c_{OS} = 225\ \mathrm{K} , \quad T^c_{WS} = 320\ \mathrm{K} , \quad T^c_{WO} = 1000\ \mathrm{K} ,$$

$$w_{OS} \approx 0.345 , \quad w_{WS} = 3.1 , \quad w_{WO} \approx 0.674 ,$$

$$r_W = r_O = 1 .$$

Since the model correctly reproduces the main features of the phase diagram (employing r_W, $r_O < 1$ improves the agreement) we are encouraged to use it to find conditions for the most desirable shapes of three-phase bodies. Given the six parameters w_{ij}, T_{ij} we know all $a_{ij}(T)$. At any T we can use $a_{OS}(T)$, $a_{WO}(T)$ to calculate the range $a^{\ell}_{WS}(T) < a_{WS}(T) < a^{u}_{WS}(T)$ for which a three-phase body exists [18]. If $a_{WS}(T) > a^{u}_{WS}$, there are two phases with the soap mainly in the upper oil-rich phase ($=\bar{2}$), for $a_{WS} < a^{\ell}_{WS}$ the same thing holds with the soap in the lower water-rich phase ($=\underline{2}$) [19]. Thus in order to

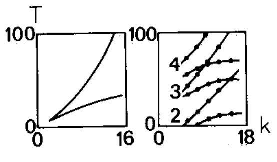
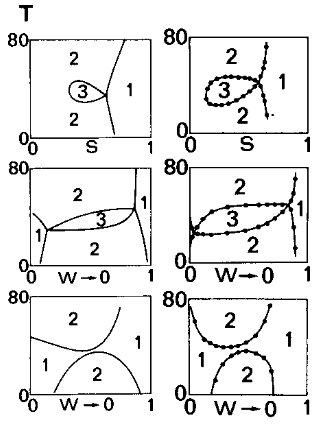


Fig. 1. Upper and lower temperatures of the three-phase regimes as functions of the number k of carbon atoms in the *n*-alkanes. (a) Results of the model with parameters given in the text. (b) Fits by eye through the experimental results for C_iE_j with $j = 2$, 3, 4 from ref. [8].



a) b)

Fig. 2. Cuts through the three-phase bodies. 1, 2, 3 denote the numbers of coexisting phases. (a) Results of the model with the parameters of eq. (4). (b) Fits by eye through the experimental results for C_4E_1–decane–water from ref. [6]. The cuts in the first row are taken at $x_W=x_O$ (a) and $g_W=g_O$ (b). The horizontal axis denotes the amphiphile concentration x_S (a) and g_S (b). In the second row the cut plane contains the critical points at T_ℓ and T_u. The horizontal axis gives the oil/water ratio in (a) x space and (b) g space. The cuts in the third row are taken at constant amphiphile fraction (a) $x_S=0.62$ and (b) $g_S=0.61$.

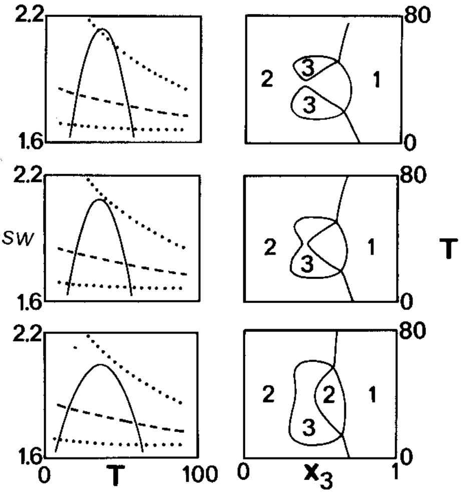


Fig. 3. The left-hand part shows the T dependence of $a_{WS}(T)$ (full line) which produces the exotic three-phase regimes described in the text. If the curve $a_{WS}(T)$ cuts the boundary lines $a^{u}_{WS}(T)$, $a^{\ell}_{WS}(T)$ (dotted lines) twice, there are two separate fish bodies. If $a_{WS}(T)$ does not quite reach the upper boundary, the fish bodies merge. The dashed line shows $a_{OS}(T)$. $a_{WO}(T)$ is too high to be visible in the figures.

improve the quality of a microemulsion we have to find soaps for which $a^{\ell}_{WS}(T)<a_{WS}(T)<a^{u}_{WS}(T)$ is as large as possible for a range of temperatures.

As an interesting special effect, it is possible to produce two fish bodies on top of each other (see fig. 3). All we have to do is to find a soap for which $a_{WS}(T)$ crosses the strip $a^{\ell}_{WS}(T)$, $a^{u}_{WS}(T)$ twice, for instance:

$$a_{WS}(T)=\bar{a}_{WS}-(\bar{a}_{WS}-1)(T-\bar{T})^2/\Delta^2 .$$

With $\bar{T}=310$ K, $\Delta=10$°C and $\bar{a}_{WS}=2.12$, fig. 3 shows the resulting three-phase bodies consisting of two fishes. By letting $\bar{a}_{WS}=2.11$ and 2.05, their bodies merge harmoniously with each other.

By realizing the importance of the parameter $a_{WS}(T)$ of the binary water–soap miscibility gap, we have come considerably closer to our goal of producing custom-made microemulsions for exhausted oil wells. The reduction of the problem to an analysis of the binary systems can be of help in classifying and manufacturing the optimal soaps.

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