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Emulsion Inversion in the PIT Range: Quantitative Phase Variations in a Two-Phase Emulsion[†]

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The phase-inversion temperature (PIT) phenomenon is for the first time given a quantitative treatment for systems having a sufficiently small surfactant content to be limited to two phases at the PIT. The results show that the early opinion of a phase transfer of the surfactant as the major event in the transversal of the temperature range is not entirely correct; the major phenomenon is instead an expulsion of water from the low-temperature aqueous micellar solution. In addition, the results unexpectedly give an indication of the existence of three phases at temperatures beneath the PIT, in spite of the the fact that system consists of only two phases at the actual PIT.

Introduction

Inversion is a central process in emulsion technology, both as an integral part of the manufacturing technology[1,2] and as an inevitable component in a large number of emulsion applications, especially those involving evaporation, since the evaporation path with necessity leads to inversion when the evaporation takes place predominantly from the continuous phase. Even with the exception of the evaporation process, inversion is critically essential in economically massive fields, such as the removal of water from water-in-bitumen and water-in-crude-oil emulsions, in which area extensive research has taken place with the Ugelstad Laboratory at the Norwegian University of Technology,[3] the University of Alberta,[4] and Rice University[5] as the leading institutions.

As expected from the wide significance of the process, its fundamental aspects have been the focus of comprehensive reviews,[1,2] which have divided the process into two main groups: transitional and catastrophic inversions. The latter are caused by an increase in the dispersed phase volume, which results in a pronounced increase in the coalescence rate until inversion happens and the continuous phase is engulfed by the coalescing drops of the dispersed phase. Knowledge about the coalescence process per se has recently seen significant progress with the investigation by Bremond et al.[6] Their investigation using a microfluidic device revealed that the decisive event in the coalescence of two colliding drops happens during the separation stage instead of during their approach. The separation induces the formation of two facing nipples in the contact area that increase the connection of the interfaces prior to fusion. Catastrophic inversion is decisively important for emulsion manufacturing, and a number of investigations have outlined the essential factors, such as the surfactant hydrophilic−lipophilic balance (HLB)[7] and the effect of the size of an incremental addition of one component.[8]

As a contrast, the former inversion is a more gradual process that in some cases involves intermediate stages of additional structures, of which Brooks[1] mentions microemulsions. Their participation in emulsion transitional inversion was introduced early by Shinoda, who used the shift with increased temperature in the solubility of nonionic surfactants of the ethylene oxide adduct type from water to hydrocarbon to cause emulsion inversion from oil/water (O/W) to water/oil (W/O)[9] and found a bicontinuous microemulsion as the third phase.[10] Shinoda presented his results for systems with constant surfactant fraction (Figure 1, left), giving diagrams of the general shape of Figure 2.

The diagram in Figure 2 illustrates the shift of a two-phase system consisting of an aqueous solution containing solubilized oil in contact with oil at low temperatures to a system consisting of oil containing solubilized water in equilibrium with water at high temperatures, with a transitional three-phase arrangement at intermediate temperatures. This transition was later investigated by Kahlweit and Strey[11−13] using systems with a water/hydrocarbon ratio of 1/1 (Figure 1, right), which resulted in the much acclaimed “fish” pattern to indicate the presence of the third phase (Figure 3).

This approach was also used by Allouche et al.[14] to show the variation of viscosity and conductance as functions of temperature (Figure 4). Brooks achieved identical results by varying the HLB number of the surfactant instead of the temperature.[15]

The most important information about phase structures in the phase-inversion temperature (PIT) range was offered early by Miller and collaborators.[16] Other examples of inversion of some relevance to the phenomena happening in the PIT range are “abnormal emulsions” (e.g., emulsions in which the surfactant is preferentially located in the dispersed phase). Sajjadi et al.[17] followed the inversion of an abnormal emulsion into a normal emulsion in a system by changing the surfactant and in fact could pursue reinversion to an abnormal emulsion by continued change of the surfactant. Another special case of transitional inversion is found in emulsions stabilized by particles,[18] in which the inversion is brought about by a gradual change of the hydrophilic−hydrophobic balance of the particles, shifting their location toward the opposite side of the interface.

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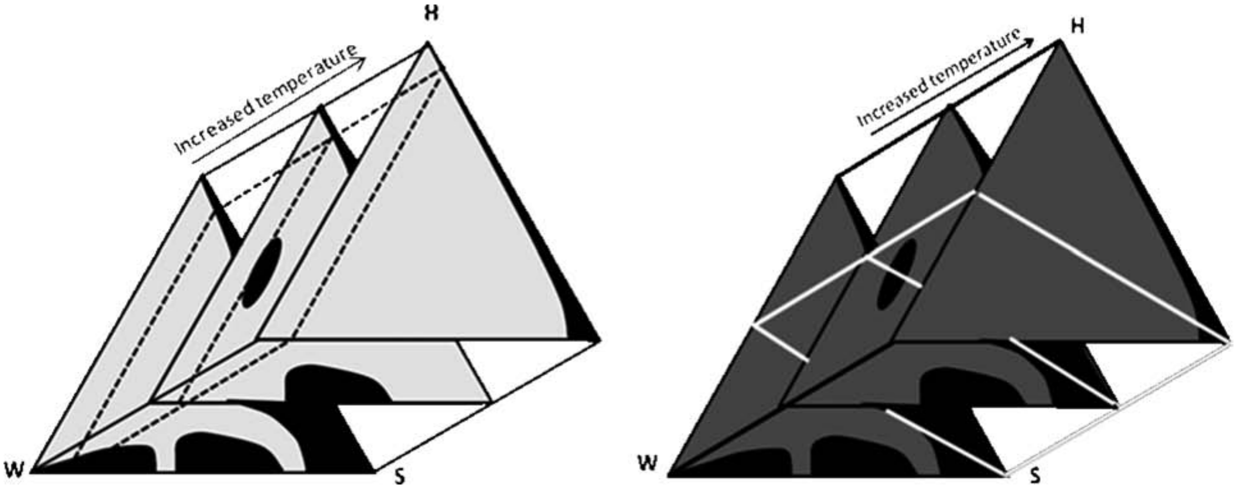

Figure 1. Shift of the surfactant association structures from aqueous-micellar to a bicontinuous phase to inverse-micellar with increased temperature: (left) the Shinoda approach of emulsions with constant surfactant concentration[9,10] and (right) the Kahlweit−Strey representation with a water/hydrocarbon ratio of unity.[11−13]

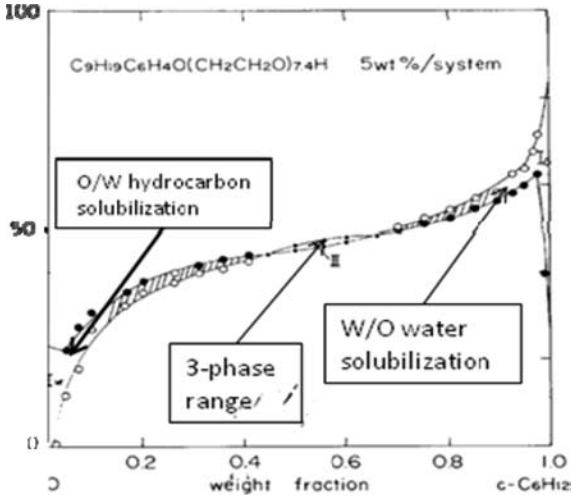

Figure 2. Experimental representation by Shinoda. Adopted from Shinoda et al.[10] with permission.

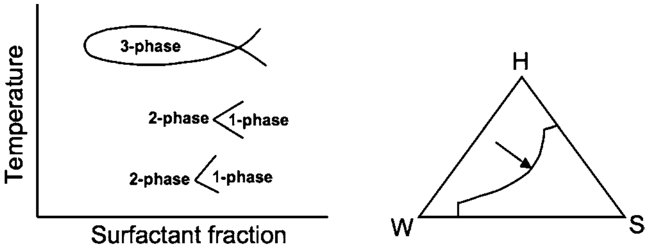

Figure 3. (left) Kahlweit−Strey presentation with the “fish” pattern. (right) Path of the third phase.

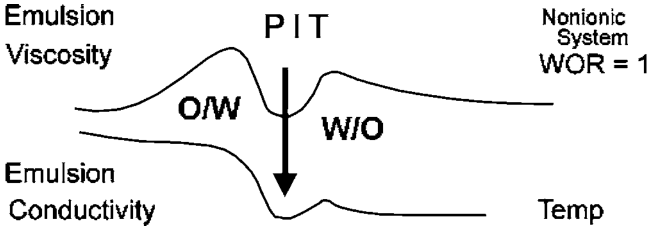

Figure 4. Viscosity and conductance in the PIT range. Adopted from Allouche et al.[14] by permission.

One fundamental aspect of the inversion is the degree to which there is mutual penetration between two phases when they are in contact under nonequilibrium conditions. Such states were treated early by Miller and Neogi,[19−23] whose efforts were continued by Masliyah,[24] Al-Bawab,[25] and Laughlin[26,27] from a different perspective. Essential information, albeit of an indirect nature, can also be found in the reports on spontaneous emulsification.[28−34]

In regard to PIT inversion, the general view is of a strong or even necessary connection to a third phase, and some discussion has been focused on the potentially active role of such a phase in the process[35] in addition to the original Shinoda identification of ultralow interfacial tension. The action of the third phase is unquestionably of primary importance for the performance of a large number of commercial emulsions; however, the third phase requires a certain level of surfactant content, and inversion undoubtedly takes place in emulsions with a smaller surfactant fraction. The only explanation for this conduct that has been offered to date is the changed solubility of surfactant from Shinoda’s original investigations,[9,10] which is in line with the definition of transitional inversion.[1,2]

However, since quantitative information about the fraction of the phases involved has not been published, the present authors, realizing the advantage of such information for the formation of a sound basis for the evaluation of the inversion process, found a quantitative analysis of the volume fractions in the PIT range for a model emulsion to be attractive because the necessary material is available in the literature.[11−13,36,37] The analysis was primarily initiated with the purpose of distinguishing between transitional and catastrophic inversion in the PIT range for emulsions having concentrations of surfactant sufficiently small to avoid formation of three phases at the PIT. All the same, the results of the investigation unexpectedly indicated the potential for a third phase to exist at temperatures below the PIT, leading to plans for future investigations in the lower temperature range. In the present contribution, the phase fractions in the system water + tetraethylene glycol dodecyl ether (TEGDE) + hexadecane are calculated from the results in refs 36 and 37, the reliability of which has repeatedly been verified.

Phase Diagram Background

The system for this study is shown in Figure 5.[36]

The values from Figure 5c (for the equilibrium compositions) are not easy to distinguish, so the values for the oil and middle

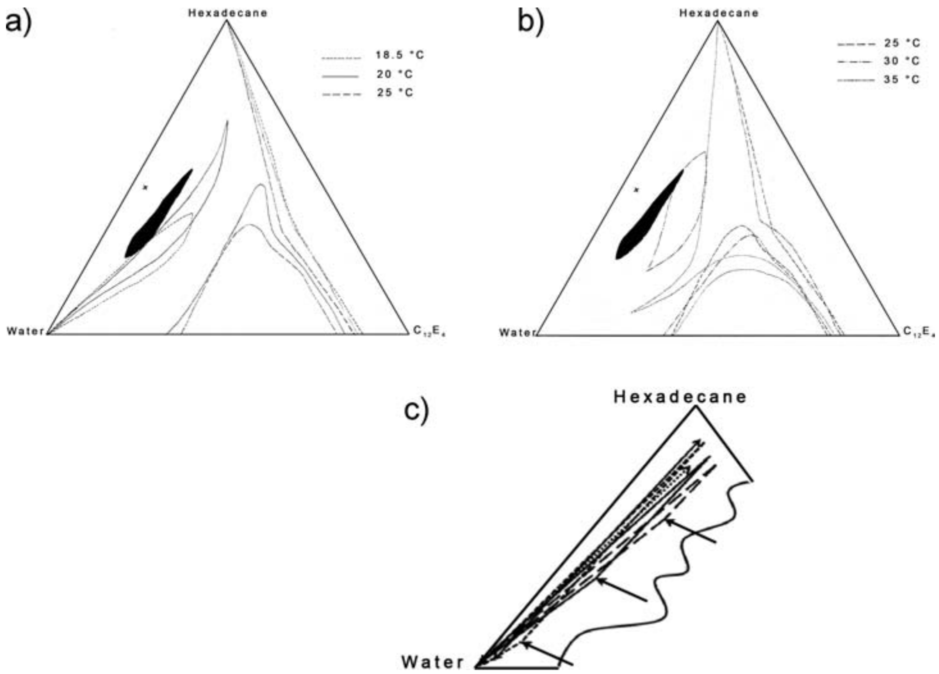

Figure 5. (a, b) Liquid regions in the system water + tetraethylene glycol dodecyl ether (TEGDE) + hexadecane over the temperature range (18.5 to 35) °C, adopted from Friberg and Lapczynska[36] by permission. The composition of the emulsion is marked by the × symbols, and the microemulsion region at 25 °C is shown in black for ease of viewing. (c) Tie lines for the microemulsion areas at 20 °C (dotted line), 25 °C (solid line), and 30 °C (dashed line). The composition of the third phase is indicated by single-headed arrows. The equilibrium tie lines between the aqueous and oil phases at 18.5 °C (solid double-headed arrow) and 35 °C (dotted double-headed arrow) are included for an emulsion with weight fractions of 0.50, 0.45, and 0.05 for water, hexadecane, and surfactant, subsequently written as (0.50, 0.45, 0.05)−see Table 1 for equilibrium composition values.

Table 1. Equilibrium Compositions for the Emulsion Systems According to Figure 5

	oil phase			middle phase		
T/°C	X_W	X_H	X_S	X_W	X_H	X_S
18.5	0.039	0.876	0.085	(0.941)[a]	(0.042)[a]	(0.017)[a]
20	0.040	0.864	0.096	0.845	0.105	0.050
25	0.042	0.823	0.135	0.558	0.340	0.102
30	0.045	0.782	0.173	0.273	0.573	0.154

[a] Values in parentheses are for the aqueous phase at 18.5 °C.

phases over the range (20 to 30) °C are given in Table 1, which also includes the composition of the aqueous phase at 18.5 °C as values in parentheses in the columns for the middle phase. There was no middle phase at 35 °C and no three-phase equilibrium.

Phase Fractions

The results provide the basis for establishing the relationship between the surfactant fraction X_S and the number of phases under the PIT conditions using the algebraic system.[38,39] The prerequisite for an emulsion to remain as two-phase is evidently an emulsion with a surfactant fraction smaller than that corresponding to the system's tie line between (1,0,0) and $(X_W,X_H,X_S)^{oil}$. According to Table 1, the tie line for the PIT at 20 °C is

$$X_S \leq 0.111X_H \tag{1}$$

The value for $X_H = 0.45$ is $X_S = 0.05$, proving that an emulsion (0.50, 0.45, 0.05) contains only two phases at the PIT value. However, while this is true at 20 °C, the results did not reveal the conditions for intermediate temperatures over the range (18.5 to 20) °C. If it is assumed that the separation of water was initiated at a small temperature increase in excess of 18.5 °C and that the minimum surfactant and hydrocarbon content of the aqueous phase (now the middle phase) in equilibrium with the formed liquid water was extremely small, the condition would read

$$X_S \leq 0.097X_H \tag{2}$$

giving a value of $X_S = 0.044$ for $X_H = 0.45$ and revealing the emulsion (0.500, 0.450, 0.050) actually to be of the three-phase variety. This result was unexpected, and calculating the weight fraction of the middle phase at this temperature would be instructive; however, this has been postponed until reliable information can be obtained for the temperature range in question. Instead, the compositions in Table 1 were used to calculate the phase fractions for two emulsions (0.500, 0.450, 0.050) and (0.625, 0.335, 0.040) in order to evaluate the potential for a phase inversion for two-phase emulsions in the PIT range. These calculations were based on the equilibrium compositions

Table 2. Equilibrium Compositions for the Two Emulsions at 18.5 °C

	aqueous phase			oil phase		
emulsion	X_W	X_H	X_S	X_W	X_H	X_S
(0.500, 0.450, 0.0505)	0.956	0.033	0.011	0.044	0.870	0.086
(0.625, 0.335, 0.040)	0.909	0.068	0.023	0.049	0.856	0.075

Table 3. Composition of the Equilibrium Oil Phase in the Emulsions Investigated

	(0.500, 0.450, 0.050)			(0.625, 0.335, 0.040)		
T/°C	X_W	X_H	X_S	X_W	X_H	X_S
20	0.0840	0.8640	0.0960	0.0430	0.8558	0.1012
25	0.0279	0.8750	0.0971	0.0299	0.8666	0.1035
30	0.0220	0.8802	0.0978	0.0238	0.8721	0.1041
35	0.1066	0.8041	0.0893	0.1132	0.7922	0.0946

Table 4. Equilibrium Volume Phase Fractions for the Two Emulsions

	(0.500, 0.450, 0.050)			(0.625, 0.335, 0.040)		
T/°C	$X_{\mathrm{aq}}^{\mathrm{vol}}$	$X_{\mathrm{oil}}^{\mathrm{vol}}$	O/W	$X_{\mathrm{aq}}^{\mathrm{vol}}$	$X_{\mathrm{oil}}^{\mathrm{vol}}$	O/W
18.5	0.443	0.557	1.26	0.616	0.384	0.623
20	0.599	0.401	0.67	0.599	0.401	0.669
25	0.573	0.427	0.75	0.573	0.427	0.746
30	0.570	0.430	0.75	0.570	0.430	0.754
35	0.613	0.387	0.63	0.613	0.387	0.632

of the phases given in Tables 2 and 3, which in turn were obtained from algebraic functions describing the maximum water solubilization in the oil phase and vice versa (these are available from one of the authors at stic30kan@gmail.com).

The phase weight fractions could then be directly obtained[39,40] from the compositions in Tables 2 and 3. The fractions are

$$X_{\mathrm{aq}} = \frac{X_{\nu}^{\mathrm{oil}} - X_{\nu}^{\mathrm{emul}}}{X_{\nu}^{\mathrm{oil}} - X_{\nu}^{\mathrm{aq}}} \qquad (3)$$

in which ν represents W, H, or S.

The weight fractions for the oil phase obey $X_{\mathrm{oil}} = 1 - X_{\mathrm{aq}}$ and were not separately calculated. The actual computations were restricted to $\nu = \mathrm{W}$ and $\nu = \mathrm{H}$ because the small numbers for X_{S} made the accuracy less than acceptable, and the results in Table 4 are averages of the results for $\nu = \mathrm{W}$ and $\nu = \mathrm{H}$. The average of the differences between the numbers was 0.7 %, including an outlier of 5.5 %, and the accuracy was considered acceptable. The weight fractions were subsequently employed in the computation of volume fractions using a simple approximation for the density:

$$\rho = \frac{1}{\sum (X_n/\rho_n)} \qquad (4)$$

where ρ_n is the density of compound n. The assumption inherent in eq 4 that each molecule occupies a volume in solution equal to that in the pure compound is supported by recent results[40] demonstrating the accuracy of the method to be better than 0.5 % for similar surfactant systems. The volume fractions and values for the O/W volume ratios are given in Table 4.

Discussion

The values in Table 4 form the basis for assigning the kind of emulsion inversion in the PIT range for the two-phase water + TEGDE + hexadecane emulsions, but prior to that analysis, it is useful to qualify Shinoda's original premise that the PIT range is characterized by a change in the preferential solubility of the surfactant from water to hydrocarbon. Although Shinoda did not explicitly clarify his statement, it is obvious that the term "surfactant solubility" in water and hydrocarbon in this context does not represent the solubility in the liquids per se but rather the solubilitiy in their mutually saturated solutions, also including all association structures. With this definition, the hydrocarbon and surfactant are mutually completely soluble over the entire range, while the solubility of the latter in water is most significantly reduced. Further to belabor the point, the molecular solubility of the surfactant in water is truly nominal, and although it cannot be determined for micellar surfactant systems below the cloud point, there is no reason even to expect a substantial change in the surfactant solubility in water in the PIT range. As a related issue, the common definition of the cloud point as the temperature at which the solubility of the surfactant in water is strongly reduced is not adequate; in point of fact, the cloud point phenomenon signifies a reduction of water solubility in the micellar solution from infinite to a finite value. Spontaneous expulsion of water from an aqueous micellar solution has been previously reported for an oil + water + surfactant system at (or near) the nonionic surfactant cloud point temperature.[41]

With these qualifications, an evaluation of the values in Table 4 shows that the volume changes for two-phase emulsions of this kind in the PIT range do not support the view of a catastrophic inversion and instead support Shinoda's original interpretation[10] of a transitional inversion, i.e., an inversion due to transfer of the surfactant from the aqueous phase to the oil phase. Nevertheless, the values establish a vital proviso to Shinoda's interpretation of the essential factor in the inversion. In actual fact, the values in the present contribution indicate that the transfer of surfactant from the aqueous phase in the PIT range is less than that of the hydrocarbon and that both of these transfers have a magnitude less than that of water. There is an obvious need for quantitative information about the transfer of all of the compounds versus the temperature over the entire PIT range, but such an evaluation was not considered central to the current theme and was postponed to a later analysis of the phase conditions during PIT emulsification.

The results also give a first indication of the appearance of a third phase at temperatures only slightly in excess of 18.5 °C. It is vital to realize that at present there is only an indication of the existence of this phase; there is no information about the phase conditions in this narrow temperature range (i.e., the minimum temperature for water separation to begin is not available). However, if a separation of water is initiated close to 18.5 °C, the potential for the third phase exists. Admittedly, this is only an indication built on unproven assumptions, but it is sufficiently intriguing for future investigations to be planned.

Conclusion

A quantitative treatment of the phase conditions in a water + tetraethylene glycol dodecyl ether + hexadecane system has been given at surfactant fractions sufficiently small that the system contains only two phases at the actual phase inversion temperature (PIT) of 20 °C. The results indicate the potential of the system actually to form three phases at temperatures less than the exact PIT value.

The results have also confirmed the original opinion that the phase inversion in the PIT range is of the transitional kind, but contrary to earlier conclusions that the interphase transport of surfactant is the relevant factor for the process, the present results have shown that water is by far the dominating compound in the interphase transport.

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