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Phase Inversion Temperature (PIT) Emulsification Process

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ABSTRACT: A quantitative analysis is made of the phase changes during the phase inversion temperature (PIT) emulsification process of an aqueous hexadecane emulsion stabilized by a tetra-ethylene glycol dodecyl ether surfactant. The mechanical dispersion part of the process takes place at the PIT, at which temperature the emulsion contains three phases: (1) water, with only minute fractions of surfactant and hydrocarbon; (2) an inverse micellar solution, with modest fractions of solubilized water; and (3) a bicontinuous microemulsion, with large concurrent solubilization of both water and hydrocarbon. After the mechanical action at the PIT, the emulsion is immediately cooled to temperatures beneath the PIT range, reducing the number of phases in the emulsion to two, an oil/water (O/W) microemulsion with moderate surfactant and hydrocarbon content, and an inverse micellar hydrocarbon solution with a significantly greater surfactant fraction. The emulsion is characterized by its large fraction of extremely small oil drops, significantly smaller than expected from the mechanical process. These drops are commonly assumed to emanate from the hydrocarbon fraction of the original bicontinuous microemulsion, the small size of the oil drops being a rational consequence of the colloidal dispersion prior to the phase separation. The quantitative analysis of the phase fractions versus temperature revealed this assumption to be premature. The original water phase is not the final aqueous phase in the emulsion; this phase is instead formed from the microemulsion phase by absorbing the original water phase, gradually modifying its own structure to become water-continuous with the originally large hydrocarbon fraction reduced to modest levels. In the process, a part of the original microemulsion is separated, forming the small oil drops.

INTRODUCTION

The essential elements of the phase inversion temperature (PIT) emulsification method[1] are shown in Figure 1. The mechanical part of the process takes place at the PIT, at which temperature the system contains three liquid phases: an aqueous phase (water), which consists of virtually pure water, an oil phase with some solubilized water as well as dissolved surfactant (oil), and a bicontinuous microemulsion (middle phase). In fact, one of the definitions of PIT is a temperature at which a maximum is found of the third phase. The mechanical dispersion at PIT is followed by an immediate reduction of the temperature to application level, at which temperature the formed two-phase emulsion is characterized by a large number of extremely small drops in addition to the micrometer-size drops formed in the mechanical emulsification. Intuitively, the features in Figure 1 suggest that the small and the larger drops in the final emulsion emanate from two sources. Larger drops stem from the original oil phase, which is mechanically dispersed in the emulsification process at PIT, while the small drops derive from the middle phase, which is disrupted in the cooling stage. The role of the water phase is viewed as the passive continuous phase.

The method has enjoyed huge popularity (a Google search gave 1.4 million references; http://www.google.com) as an energy-saving process from the time of its introduction,[1,2] over the years[3] to the present time[4] with special emulsification equipment even being introduced.[5] This unusual attention is at least partly owed to the nanoemulsions, an area with Solans et al.[6] as the leader. However, in spite of all this obvious importance, so far no information has been obtained as to the actual mechanism of the PIT process, except for the intuitive and qualitative opinion cited. The fact that the process has such wide utilization points to a strong need to provide a quantitative treatment of the process as a solid basis for its application.

The present contribution gives the quantitative changes during the cooling phase of the process, fully changing the entire perception of the elements of the emulsification. The facts are that the original water liquid does not form the aqueous phase after the cooling stage but is, instead, entirely absorbed into the original bicontinuous microemulsion. This diluted liquid now in turn partially forms the final aqueous phase and partially contributes to the ultrasmall drops observed. A brief review of the fundamental investigations into the colloidal phenomena is a useful and necessary introduction to comprehend the results and their ramifications for the process.

The basic studies were initiated by Shinoda and Arai,[7] whose interest was dictated by their scientific focus on solubility as such, and consequently their presentation centered on the variation of the temperature at which a low concentration of aqueous solution of a surfactant separates into two liquids, its cloud point. Solubilized aliphatic hydrocarbon in the aqueous solution increases the cloud point, and Shinoda's presentation, in Figure 2, using 5 % nonionic surfactant[8] reflects this fact and in addition shows a third phase to appear in a limited temperature range.

The focus on solubility was continued in the contributions by the Kahlweit−Strey group,[10−12] who approached the subject from the variation with temperature of the mutual solubility in a water/short chain oxyethylene alkyl ethers/hydrocarbon system.

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Realizing the effect of the temperature dependence of ethylene oxide adducts interaction with water,[13,14] a series of phase diagrams, in Figure 3 left, were established. The diagrams illustrate the fact that the solubility of the short-chain amphiphile shifts from water, Figure 3A, to hydrocarbon, Figure 3E, with increased temperature and that the system of long chain hydrocarbons changes from two phases to three during intermediate temperatures, Figure 3B—D, in the process.

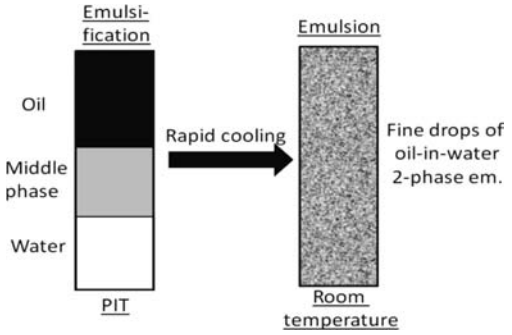

Figure 1. The PIT (phase inversion temperature) emulsification method, which consists of mechanical emulsification at the PIT (left) followed by rapid cooling to room temperature, where an emulsion with a large number of extremely small drops is found (right).

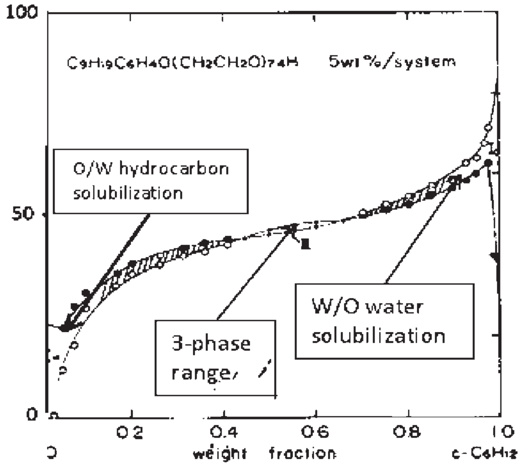

Figure 2. Shinoda presentation of the PIT phenomenon, temperature versus mass fraction,[9] reproduced with permission. The surfactant is an ethoxylated nonylphenol, $C_9H_{19}C_6H_4O(CH_2CH_2O)_{7.4}H$.

The sequel to these determinations included a careful study of the system water—ethylene glycol butyl ether (CAS Registry No. 111-76-2, EGBE)-dodecane by Strey et al.[15] The diagram at a selected temperature, Figure 3 right, illustrates the origin of the legendary "fish" shape. The continued research by the Strey group into colloidal structures of microemulsions[16,17] at the limit of their stability is relevant to the PIT process and the total scientific evidence[1−17] serves as an excellent primary source for the continued efforts to clarify the events of the procedure. Nevertheless, the material, in spite of its high quality, is not completely sufficient for the purpose, because the phase diagrams determined[10−12,15] are focused on short chain compounds.

This limited approach served well to outline the consequences of the temperature dependence of the mutual solubility per se, but for the type of surfactants used in commercial emulsions unadorned solubility is not the only determining factor for the phase behavior. An illustrative example is offered by the phase diagrams of commercial surfactants, nona-ethylene glycol nonylphenyl ether with two hydrocarbons, in Figure 4.[18] The diagrams accentuate the presence of a large number of association structure phases to the general pattern dictated by the difference in solubility between the surfactant and the hydrocarbons, Figure 3. Such details are not only of academic interest; in fact the lamellar liquid crystal, Figure 4 left, confers enhanced stability on an emulsion,[19] instead of commonly reduced stability[20] for emulsions at the PIT.

Applying the water/hydrocarbon 1:1 approach[10−12,15] to the system at right would lead to a series of six two-phase and five three-phase ranges following the initial one-phase range. Using the temperature variation of the phase diagram of a surfactant of this kind to clarify the PIT process would obviously lead to an unjustifiable huge amount of experimental effort. Instead the results from a simple but realistic surfactant with a 12 carbon hydrocarbon chain and 4 ethylene oxide groups will be utilized in the following analysis.

■ RELEVANT PHASE REGIONS

For commercial emulsions used at room temperature and with surfactants of greater molecular weight than in the present model

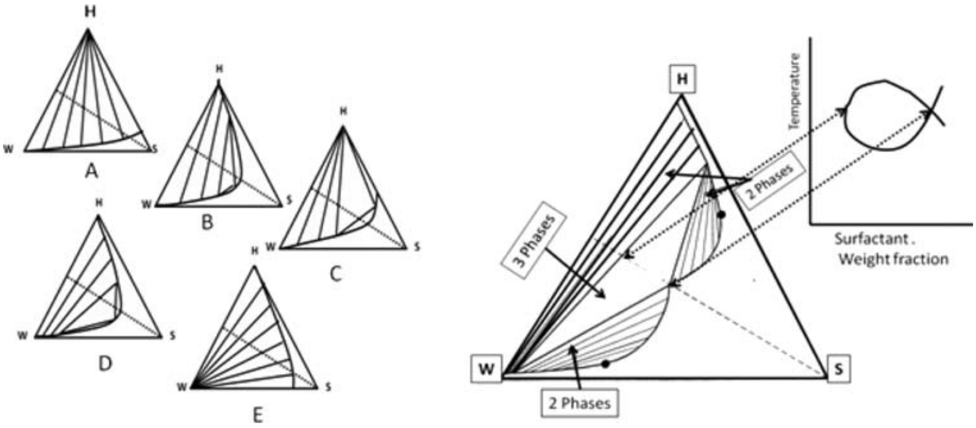

Figure 3. Left: phase diagrams of the system water (W), short chain poly(oxyethylene alkyl ether), C_mE_n (S), and hydrocarbon (H) with increasing temperature from A to E.[10−12] Right: phase diagram for selected temperatures gives the "fish" pattern to the right, adapted from the results in ref 15 with permission.

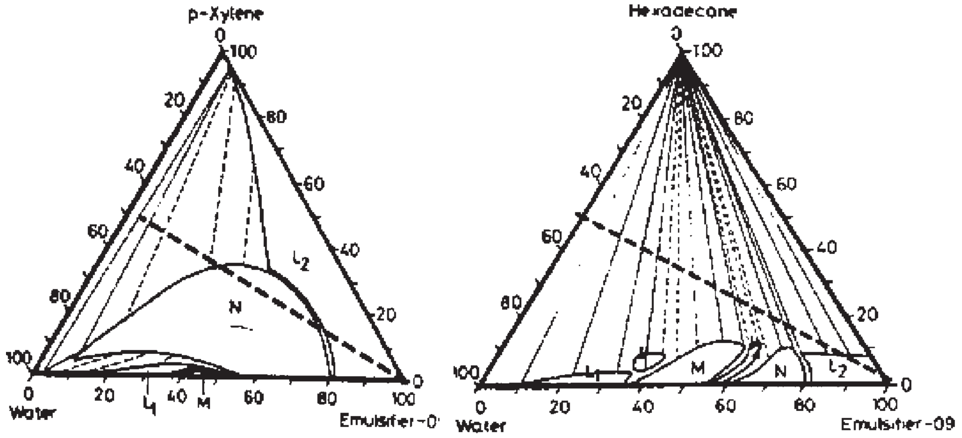

Figure 4. Phase diagram for the system water−commercial nonylphenol ethoxylate (CAS Registry No. 68412-54-4, Emulsifier-09) and *p*-xylene, left, and hexadecane, right,[19] reproduced with permission.

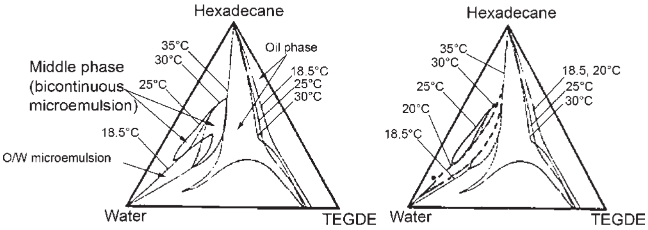

Figure 5. Essential phase regions at selected temperatures in the PIT range. (The middle phase region at 20 °C was not included in the diagram to the left, because of difficulties distinguishing the different areas.) The combination of the two diagrams gives a complete description of the areas. Adopted from Friberg et al.[21] with permission.

system, the PIT emulsification takes place at higher temperatures[2,3] followed by immediate cooling to room temperature. Information about the phase regions for such systems is not available, but the conditions in Figure 5 illustrate the development at a parallel temperature range and serve to illustrate the modification of phases, their areas, and equilibrium in the PIT range. The oil phase covers the entire hexadecane-tetra-ethylene glycol dodecyl ether (CAS Registry No. 5274-68-0, TEGDE, 3,6,9,12-tetraoxatetracosan-1-ol), the axis with content of solubilized water varying with temperature. The aqueous phase forms a sectorial microemulsion area from the water corner at 18.5 °C; for all other temperatures the aqueous phase consists of water with only insignificant amounts of surfactant and hydrocarbon. This phase is referred to as aqueous or water phase in the article depending on what aspect is emphasized. In addition to these two phases, there is a middle phase, a bicontinuous microemulsion in the PIT range (20 to 30) °C.

For this specific system the mechanical emulsification process takes place at 25 °C, the PIT, and the subsequent cooling reduces the temperature to 18.5 °C. The composition of the emulsion is marked with an x in Figure 6 and the composition of the phases with circles and is given as mass fractions (w_W, w_H, w_S; 0.80, 0.16, 0.04), of the three compounds.

The features in Figure 6 describe those in Figure 1 and support the opinion of the structure of the phases in Figure 1 and of the interpretation of the events during the emulsification. In addition, the features in Figures 5 and 6 offer intuitive guidance on the relationship between the surfactant concentration and the number of phases in the PIT range, in fact allowing some general conclusions about the emulsification state in the process, even without quantitative numbers. For the emulsion to remain two-phase in the entire range, sufficiently small surfactant concentrations are necessary. The exact numbers depend on the water/hydrocarbon ratio as illustrated in the inset, Figure 6 right. In the surfactant concentration range A to B the emulsion remains two-phase, while in the range B to C three phases are found in some of the range. Surfactant fractions in excess of C, in Figure 6, result in a one-phase bicontinuous microemulsion at PIT with complex emulsification behavior.

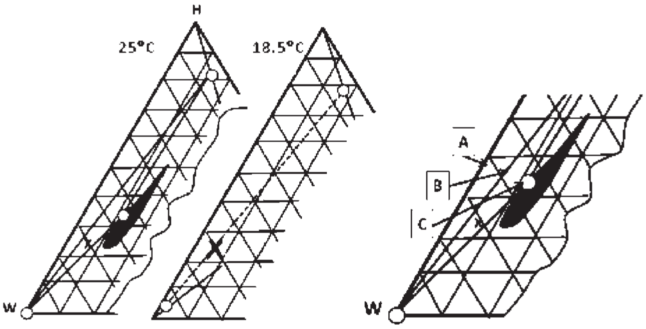

Figure 6. Phases of the emulsion (0.8, 0.16, 0.04) at (25 and 18.5) °C. The emulsion composition is marked by an X (exaggerated size at 18.5 °C for clarity) and the individual phase compositions by open circles. The area of the middle phase at 25 °C, the PIT, is black.

With this overview as a basis, a detailed analysis will be initiated on an emulsion with three phases in the entire PIT range of the system in Figures 5 and 6. As indicated earlier, the composition of the emulsion will be given as mass fractions of the compounds (w_W, w_H, w_S) with the obvious meaning of the subscripts. The changes in the phase composition and mass fractions will be described in order of reduced temperatures, since the emulsification process includes a reduction of temperature immediately after the mechanical emulsification. The range will be initiated at 35 °C, one temperature interval in excess of the upper limit of the PIT range and end at 18.5 °C as one interval lower than its lower limit. Furthermore, in spite of the fact that the PIT is at 25 °C, and the temperature range for the emulsification is limited to (25 to 18.5)° C, the numbers from 30 °C are included to illustrate the changes, when the system enters the PIT range from higher

Table 1. Composition in Mass Fraction, w_ν, of the Oil and Middle Phases in the Temperature Range (18.5 to 35) °C of the Entire System[a]

t	aqueous phase			oil phase			middle phase		
°C	w_W	w_H	w_S	w_W	w_H	w_S	w_W	w_H	w_S
18.5	(0.98)	(0.013)	(0.007)	0.066	0.759	0.175	(0.980)	(0.013)	(0.007)
20	1	0	0	0.040	0.864	0.096	0.845	0.105	0.050
25	1	0	0	0.042	0.823	0.135	0.558	0.340	0.102
30	1	0	0	0.045	0.782	0.173	0.273	0.573	0.154
35	1	0	0	0.213	0.630	0.157	not available		

[a] ν represents the components: water (W), hydrocarbon (H), and surfactant (S). The numbers differ to a small extent from earlier published information. The present ones are after a correction of an earlier minor miscalculation.

temperatures. At 35 °C the emulsion consists of two phases, in Figure 5, an inverse micellar solution, W/O microemulsion, Oi, and an aqueous phase, Aq, the latter virtually pure water. In the actual PIT range of (30 to 20) °C three phases are found for surfactant content of interest; an aqueous phase of pure water, an oil phase, and a middle phase, MP, a bicontinuous microemulsion, Figures 5 and 6. The composition of the aqueous phase is (1, 0, 0) in the entire temperature span, while the numbers of the oil and middle phases are given in Table 1.

In Table 1, the composition at 18.5 °C of the aqueous micellar solution and the middle phase are both within brackets, because the designation of the phase depends on the point of view. Observing the phases in Figure 6, right, the composition is evidently within the O/W microemulsion region in Figure 5, and a designation as an aqueous phase is justified. However, as will be apparent from the later results, the phase in question is identical to the middle phase at higher temperatures; that is, there is no phase change in the middle phase between (20 to 18.5) °C; therefore, the phase may be equally denoted as the middle phase.

A quantitative analysis of the cooling process will be made with the information in Table 1 and Figures 5 and 6, but in preparation for such an operation, a semiquantitative account of the variation in phase conditions is useful to establish a fundamental profile of the main elements and to envision the relative amounts of different phases versus temperature, Figure 7.

At 35 °C, Figure 7, the emulsion consists of two phases, of which the oil phase mass fraction equals $b/(a + b)$ and that of the water phase $a/(a + b)$. As the temperature subsides to levels below 35 °C, Figure 7 < 35 °C, a radical change occurs; a new phase, a bicontinuous microemulsion; the middle phase, MP, with greater content of water and surfactant is separated, while the composition of the oil phase is modified toward less surfactant and water. The mass fraction of water, $a/(a + b)$, is reduced, but actual numbers are needed before a conclusion can be made of the relative change of mass fractions of oil and middle phase, although expressions for their mass fractions are given as $c(1 - a)/(c + d)$ for the oil phase and $d(1 - a)/(c + d)$ for the middle phase. This trend is continued during the PIT range, (30 to 20) °C, Figure 7, with the composition of the middle phase moving along a trajectory toward the water corner and that of the oil phase continuing the earlier trend. Finally between (20 to 18.5)° C the temperature is reduced to a level below the cloud point for the system and the middle phase, and the remaining water is absorbed into the bicontinuous microemulsion, in Figure 5, 18.5 °C. This qualitative description of the events during a temperature reduction in a relevant temperature range provides an overview of the conditions, but quantitative information is necessary to comprehend the fundamentals of the emulsification process. This is provided in the next section using the algebraic system for extraction of information from phase diagrams of this kind.[22]

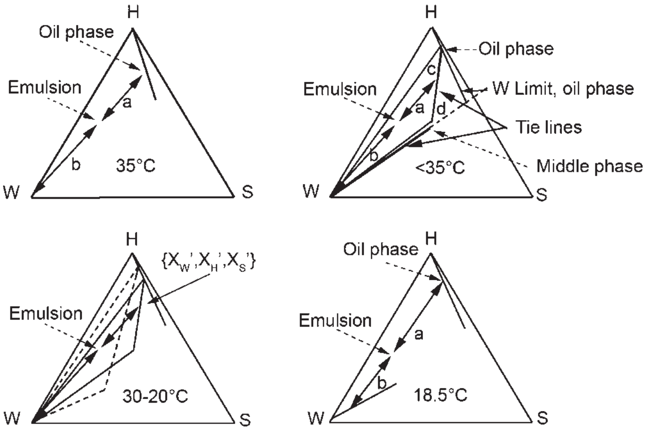

Figure 7. Variation of the location of the emulsion phases in the total PIT range. In the diagram for the range (30 to 20) °C the dashed lines represent temperatures lower than that of the solid line.

Table 2. Constants for Equations 1 and 2

t/°C	c_W	c_H
18.5, 20	0.275	0.655
25	0.230	
30	0.251	
35	0.575	

NUMERICAL CALCULATIONS

All of the calculations[22] are based on information of the maximum water solubilization in the oil phase for all temperatures and the corresponding hydrocarbon solubilization in the aqueous phase at 18.5 °C. Since the relevant conditions involve only limited surfactant fractions, both solubilization fractions are approximated as linear of the first order without significant loss of accuracy. Hence, the maximum water solubilization in the oil phase is

$$w_W = c_W(1 - w_H) \tag{1}$$

while the corresponding equation for oil solubilization into the O/W microemulsion is

$$w_H = c_H(1 - w_W) \tag{2}$$

Table 2 displays the values for c_W and c_H from the features in Figure 5.

The composition of the oil phase for the temperature 35 °C is obtained from the intersection of a line from the water corner through the emulsion composition (0.8, 0.16, 0.04).

$$w_w = 1 - 1.25 w_H \tag{3}$$

with the line for maximum water solubilization in the oil phase, eq 1 giving a composition of (w_W^I, w_H^I, w_S^I) equal to (0.213, 0.630, 0.157) for 35 °C.

Table 3. Mass Fractions of the Emulsion Phases in the Temperature Range (18.5 to 35) °C[a]

range	t/°C	w_{Aq} (1, 0, 0)	w_{MP}	w_{Oi}
<PIT	18.5	0	0.784	0.216
	20	0.306	0.597	0.097
PIT	25	0.631	0.317	0.052
	30	0.750	0.210	0.040
>PIT	35	0.746	0	0.254

[a] The composition of the middle phase is the aqueous O/W solution in Figure 6, middle, but the reason for the designation is to preserve a continuum in the curves in Figure 8.

The aqueous phase mass fraction is obtained

$$w_{\mathrm{Aq}} = \frac{(0.8 - w_{\mathrm{W}}^{\mathrm{I}})}{(1 - w_{\mathrm{W}}^{\mathrm{I}})} \tag{4}$$

For the three temperatures (30, 25, and 20) °C the mass fractions of the three phases are found from the relationships in Figure 7:

$$w_{\mathrm{Aq}} = \frac{(a)}{(a + b)}$$

$$w_{\mathrm{Aq}} = \frac{(w_{\mathrm{H}}^{\mathrm{I}} - 0.16)}{(w_{\mathrm{H}}^{\mathrm{I}})} \tag{5}$$

$$w_{\mathrm{MP}} = \frac{(c)}{(c + d)}$$

$$w_{\mathrm{MP}} = \frac{(1 - w_{\mathrm{Aq}})(1 - w_{\mathrm{H}}^{\mathrm{I}})}{(1 - w_{\mathrm{H}}^{\mathrm{MP}})} \tag{6}$$

$$w_{\mathrm{Oi}} = \frac{(d)}{(c + d)}$$

$$w_{\mathrm{Oi}} = \frac{(1 - w_{\mathrm{Aq}})(w_{\mathrm{H}}^{\mathrm{I}} - w_{\mathrm{H}}^{\mathrm{MP}})}{(1 - w_{\mathrm{H}}^{\mathrm{MP}})} \tag{7}$$

in which the superscript I denotes the mass fraction of the compound at the intersection between the tie line between the oil (Oi) and middle phases (MP) and the line from the water corner through the emulsion composition.

$$w_{\mathrm{H}} = 0.8(1 - w_{\mathrm{W}}) \tag{8}$$

The hydrocarbon mass fraction, $w_{\mathrm{H}}^{\mathrm{I}}$

$$w_{\mathrm{H}}^{\mathrm{I}} = \frac{(w_{\mathrm{H}}^{\mathrm{MP}} - w_{\mathrm{H}}^{\mathrm{Oi}})(1 - w_{\mathrm{W}}^{\mathrm{MP}})}{[1.25(w_{\mathrm{H}}^{\mathrm{MP}} - w_{\mathrm{H}}^{\mathrm{Oi}}) + w_{\mathrm{w}}^{\mathrm{MP}}]} \tag{9}$$

The mass fractions are given in Table 3.

The trends in Figure 8 offer a view of the quantitative changes in the fraction of phases within the PIT temperature range.

The most striking result is immediately obvious. It unquestionably disproves the intuitive notion of a disruption and vanishing of the PIT middle phase as responsible for the small drops in the final emulsion after cooling as premature. Instead of vanishing the microemulsion is increased forming the final aqueous phase. In the cooling process the entire original water phase is absorbed into the microemulsion, which causes its destabilization and expulsion of part of its hydrocarbon content.

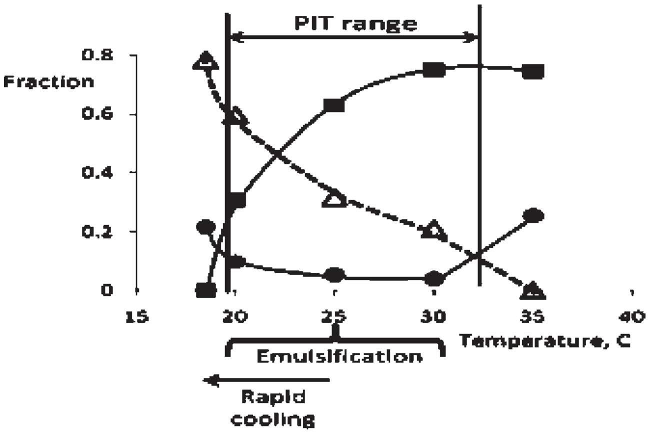

Figure 8. Mass fractions of the water phase, ■; the oil phase, ●; and the middle phase, △ of the emulsion (0.8, 0.16, 0.04). The emulsification temperature, 25 °C, (PIT) is marked as well as the rapid cooling to 18.5 °C.

The expelled hydrocarbon presumably forms the small oil drops. There is no indication of a phase change in the process, and the designation of the O/W microemulsion phase at 18.5 °C as the middle phase, in Tables 1 and 3 and Figure 8, is justified, when viewing the phase variation with temperature.

In addition to this major phenomenon, a series of minor features are central in Figure 8. At first the transfer of water is accelerated with reduced temperature, especially noticeable in the final step, when leaving the PIT range in the (20 to 18.5) °C temperature interval. Second, the diagram indicates a minor part of the accommodated water to be further transferred to the oil phase via the middle phase, a factor that will later be demonstrated to be more relevant than is directly realized. Third, the minor change in the water fraction, when the system entered the PIT range, may be noticed. According to the numbers in Table 1, the amount in the water phase should be increased, because the w_{W} of the oil phase is reduced; this change is compensated by increase of the w_{W} of the middle phase giving an increased $w_{\mathrm{W}}^{\mathrm{I}}$ (eq 5).

The emulsion (0.8, 0.16, 0.04) was chosen as a model to illustrate the phase changes in the PIT range in a commercial emulsion, but a comparison with the phase fractions at other surfactant concentrations is vital to fully understand the relation between the PIT emulsification and the phase pattern in the system. Figure 9 presents the conditions at reduced (left) and increased (right) surfactant fractions.

The most central consequence of a lesser surfactant concentration, 0.028, is a lowered temperature for the entry of the middle phase, Figure 9, left. The middle phase now emerges first at 25 °C and then as a small fraction. In an emulsion with the surfactant fraction reduced to 0.02, the middle phase emerged only in a most minute amount at 20 °C and with only inconsequential features, and the diagram was not included, the conditions for such a system having been examined in an earlier publication.[23] Conversely, an emulsion with increased mass fraction surfactant to 0.052, Figure 9 right, brings to light a completely new kind of emulsion. It actually remains two-phase in the entire range, but with rather critical phase changes, which will be examined in the Discussion section.

The results in Figures 8 and 9 are for an emulsion with a water mass fraction of 0.8, and it is of interest to see the extent to which the features are scalable. The traits of emulsion (0.8, 0.172, 0.028),

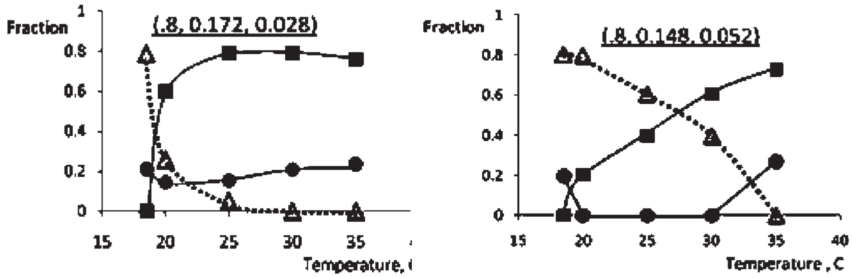

Figure 9. Variation of phase fractions (water phase, ■; the oil phase, ●; and the middle phase, △) with temperature.

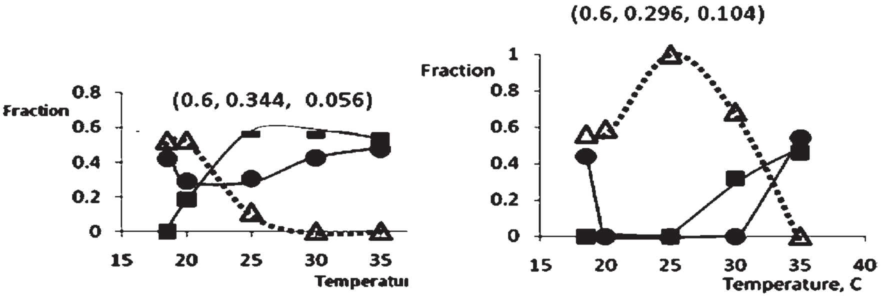

Figure 10. Variations of phase fractions, water phase, ■; the oil phase, ●; and the middle phase, △, for an emulsion (0.6, 0.344, 0.056), left and an emulsion (0.6, 0.296, 0.104), right.

Table 4. Relation between Temperature and Emulsion Configuration for Emulsion (0.6, 0.296, 0.104)

t	emulsions				
°C	0.8, 0.16, 0.04	0.8, 0.172, 0.028	0.6, 0.344, 0.056	0.8, 0.148, 0,052	0.6, 0.296, 0.104
35	O/W	O/W	O/W	O/W	W/O
30	O/MP/W	O/W	O/W	MP/W	W/MP
25	O/MP/W	MP/O/W	MP/O/W	W/MP	MP
20	(O + W)/MP	O/MP/W	(W + O)/MP	W/MP	MP
18.5	O/MP	O/MP	O/MP	O/MP	O/MP

in Figure 9 left, were considered the most interesting, and the phase fractions in an emulsion with identical surfactant content vis-à-vis the water fraction, (0.6, 0.344, 0.056) were calculated, in Figure 10.

It is interesting to note that in all cases the increase in the oil phase fraction occurs at the lower part of the temperature range. This is in agreement with the early results by Morris et al.[24] using a different model to explain the experimental results.

The main elements of the emulsion (0.8, 0.172, 0.024), in Figure 9 left, are remarkably reproduced for the emulsion with less water fraction (0.6, 0.344, 0.056), in Figure 10 left, with the modifications caused by the lesser water content. The entry of the middle phase slightly in excess of 25 °C is perfectly matched, while the patterns of the water and oil fraction reveal the same variation with temperature, but with the features modified due to the difference in water fraction. The emulsion (0.6, 0.296, 0.104), in Figure 10 right, with increased surfactant fraction corresponds to emulsion (0.8, 0.148, 0.052), in Figure 9. The emulsion now has sufficient surfactant content to exclude the water phase at the PIT forming a single middle phase, while the oil phase presents identical variation in the phase fraction with temperature. The variation in phase fractions give rise to a number of interesting inversions, with the rule of the phase with greatest fraction being the continuous phase. These results are given in Table 4, and although they formally are intriguing, they are not further examined, because the adopted rule denoting a specific phase as the continuous one is not truly realistic. However, the lower interfacial tensions to the middle phase make the difference between denoting an emulsion true double emulsion O/MP/W of oil drops in the middle phase drops dispersed in water and conversely (W + O)/MP as a combination emulsion of individual water and oil drops in the middle phase.

■ DISCUSSION

The aim of the investigation was primarily to clarify the relationship between the features in Figure 1 and the extremely small drops in the final emulsion prepared by the PIT method. A perfunctory inspection of the features of Figure 1 would suggest a simple and attractive interpretation. After the mechanical dispersion at the PIT, the emulsion consists of drops of the middle and oil phases, most probably in the form of a double emulsion arrangement of O/MP drops, because of the extremely low interfacial tension toward the middle phase. The subsequent temperature reduction causes a disruption of the middle phase parts of the drops into extremely small oil drops for the reason that the hydrocarbon is already colloidally dispersed in the middle phase. The aqueous phase remains the continuous emulsion phase after the mechanical dispersion. The present results proved this appealing interpretation to be premature; Figures 8 to 10 indisputably reveal that the aqueous phase at the PIT is not the aqueous phase in the final emulsion and the middle phase is not primarily disrupted. Instead its fraction increases by gradually absorbing the original water phase to become the final aqueous phase, while a significant part of it forms the ultrasmall oil drops. These are the evident results, and their unexpected nature indeed merits a further analysis.

However, prior to such examination, it is necessary to emphasize the limited significance of the current results for the experimental process. They provide the equilibrium phase conditions during the cooling stage of the emulsification process. They should be viewed as a thermodynamic basis on which the dynamic and kinetic factors serve as modifiers. Of these the mechanical treatment at the PIT is decisive for the size of the larger oil drops in the emulsion, while during the cooling part the kinetic and accompanying dynamic effects modify the overall pattern. The first phenomenon is certainly vital for the emulsion configuration, but contrary to traditional two-phase emulsions not the sole—nor even the major—factor for the small size of drops in emulsions from the PIT process. Experience has shown that an emulsion treated with similar energy per time unit, but without the presence of the third phase, does not contain drops of comparably small size. An additional limitation of the current results is their restriction to the specific system water/hexadecane/tetra-ethyleneglycol dodecyl ether, but the results as such have general relevance for aliphatic hydrocarbon emulsions with proper modifications.[18]

With these qualifications taken into consideration, the focus of the present contribution is to give a quantitative evaluation of the phase conditions in the PIT range to establish a fundamental basis for the PIT emulsification method. Additionally, the conditions in the PIT range are of decisive importance for the preparation and properties of microemulsions stabilized by nonionic surfactants of the ethylene oxide adduct kind. But an analysis of that facet of the PIT phenomenon was considered outside the present contribution. Instead the discussion will be limited to a quantitative evaluation of the phases in the entire PIT range.

Since the presence of the third phase obviously is central for the outcome of the emulsification, its role is examined based on the features in Figure 1, by the partial phase diagrams by Shinoda et al.[1,2] and Kahlweit,[8−10] by the complete phase diagrams of the water/ethyleneglycol monobutyl ether/dodecane[14] and by subsequent research by the Strey group.[16] This basis combined with the results from the present quantitative results from Figures 8 to 10 suffice for a quantitative analysis of the PIT emulsification process.

The main development is given by Figure 8, the features of which are directly connected to the factors in the introduction to this section. They unequivocally show that the water phase at the PIT does not remain to form the aqueous phase in the final emulsion and that the middle phase engages in more complex actions than a plain disintegration. In actual facts the original water phase is gradually taken up into the middle phase, until at the lower end of the PIT range all of the material from the original separate phase is incorporated and the middle phase is transformed to an O/W microemulsion, with no phase change in the process. As a summary of the results in Figure 8, the mass fraction of the aqueous phase, water, is reduced from 0.63 to 0 in the temperature interval from the PIT at 25 °C to the end of the PIT range at 18.5 °C, while that of the middle phase is increased from 0.31 to 0.78 and the oil phase from 0.05 to 0.22. The fact that the fraction of the middle phase increases is no contradiction to the early interpretation by Taisne and Cabane.[25] The change in the oil phase may seem of less significance, but as the continued examination shows, it is of vital interest.

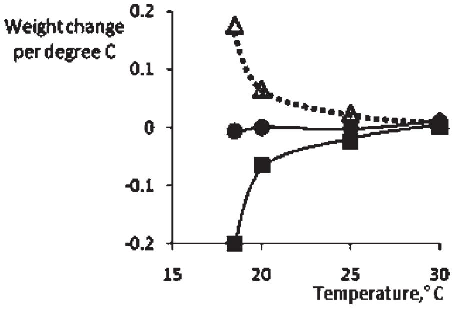

Figure 11. Rate of water lost or gained by the three phases in the interval preceding the temperature value. ■, water phase; ●, oil phase; and △, middle phase.

These are the main line of events, and with these as a basis the transferred quantities per se of compounds emerge as the key factor to understand the elements of the process. As is evident from Figures 8 to 10, the essential compound relocated is water, and the quantities reassigned during the temperature intervals are given in Figure 11 versus the lower temperature in each interval.

Figure 11 directly demonstrates the most apparent factor in the process; the major event is a relocation of water between the water and the middle phases. The oil phase content of water is small, as in Table 1, and its participation in the water shift seems inconsequential at a primary inspection. Furthermore, as has previously been indicated, the magnitude of the matter reassigned is increased with reduced temperatures. On the other hand, the results also prove the relocation of water per se not to emerge as the significant factor in creating the small oil drops, since the oil phase is not engaged in the actions in Figure 11. The attention instead must be directed to surfactant and hydrocarbon relocation involving the oil phase, and one distinct detail in Figures 8 to 10, the fact that the major change in the oil phase fraction occurs between (20 to 18.5)° C, is vitally essential to comprehend the origin of the small oil drops.

A first inspection of the numbers in Table 3 indicates the increase in the oil phase as emanating from the aqueous phase; its mass loss of 0.306 in the temperature range (20 to 18.5)° C corresponds exactly to the sum of the mass increases of the middle phase, 0.187, and the oil phase, 0.119. However, such an interpretation is incorrect, as proven by the weights of the individual compounds reassigned to the oil phase. Of these the majority is hydrocarbon 0.084 mass units with lesser amounts of water 0.004 and surfactant 0.009. This material obviously cannot stem from the water phase, which to all intents and purposes holds no surfactant or hydrocarbon. Instead the small drops are formed by material from the middle phase, of which in the order of 15 % form the drops in question.

The combined information from Figures 8 and 11 and the numbers quoted in the last paragraph enables a rational description of the events during the temperature reduction as schematically depicted in Figure 12.

The three main stages of the development of the emulsion during the cooling stage each present a transformation. At PIT,

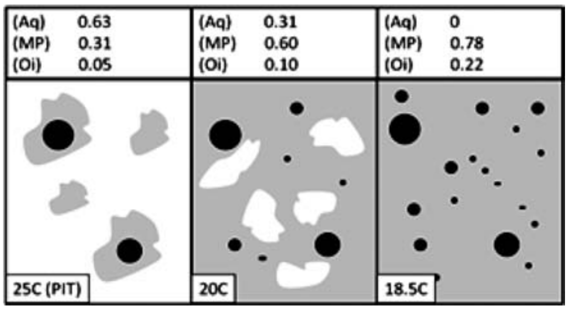

Figure 12. Schematic representation of the emulsion configuration during the cooling stage of emulsification. White (Aq) = water (W), gray = middle phase (MP), black (Oi) = oil (O).

Table 5. Ratio between the Mass Fractions of the Middle Phase at PIT, w_{MP}, and the Mass Fraction Small Drops in the Final Emulsion, w_{Oi}

w_S	w_{MP}/w_{Oi}
0.045	0.050
0.040	0.610
0.036	0.420
0.028	0.050
0.020	0

Figures 6 and 7, the mechanical emulsification gives an emulsion, the continuous phase of which is water with drops of the middle phase and of the oil phase. The size of the drops is determined by the mechanical treatment in this primary emulsification step, and their shape most likely deviates from the spherical, because of the low interfacial tension.[26] Furthermore, the lower tension at the MP/O and MP/W interface compared to the O/W value causes a large fraction of the drops to be in a double emulsion, an O/MP/W, arrangement. The size of the drops is determined by the mechanical action, and although the low value of interfacial tension should result in small drops, they are large in comparison with the ones spontaneously formed in the subsequent step. The pronounced increase of the middle phase fraction from (25 to 20) °C supports an inversion from the double emulsion O/MP/W to a combination emulsion (O + W)/MP. At this temperature, as a contrast to the case at 25 °C, the difference in the level of interface tension actually disfavors a double emulsion, and the combination emulsion is more likely.

The inversion would probably give small and irregular water drops, but this factor was neglected, being immaterial for the arrangement of the final emulsion. The features in Figure 9 indicate an increase—albeit small—of the oil phase fraction in the range (20 to 18.5) °C. The material for this increase stems from the middle phase, and the drops *formed from this material* are small and located within the middle phase with no obvious connection to the existing oil drops except for the separation of oil at the surface of the existing drops. They are formed by the microemulsion partly disintegrating and are not per se connected to the transfer of the material to the existing oil phase. These small drops[16] are included in the drawing in addition to the original drops, for which there is no basis to assume a change in size except the potential of growth through “condensation” of oil on their surface. In the final stage, (20 to 18.5) °C, the entire water drops are absorbed into the continuous middle phase, and the emulsion now becomes a plain O/W emulsion. In this step the oil phase fraction is significantly increased by the addition of the small drops; a more marked feature at greater surfactant fractions in the emulsion, as in Figures 9 to 11.

Finally, it is useful to cite an obvious consequence of the opinion of the original water phase being retained to form the final aqueous phase, while the entire middle phase disrupts to form the small final oil drops. If this were the case, there would be a simple relation between the fraction of the original middle phase and the fraction of small drops in the final emulsion. The numbers in Table 5 show the ratio of mass fractions of the original middle phase and of the final small drops versus the surfactant fraction in the emulsion.

The outcome plainly shows the lack of correlation, which is a rational result. The small oil drops are an ultimate consequence of a complex series of events, of which the water uptake of the original middle phase is essential, as is the fact that the drops in question are formed only in the lowest part of the PIT range. It should be noted that the kinetic factors during a temperature quench may produce different results[27] from those indicated by the phase equilibria.

CONCLUSIONS

A quantitative analysis was made of the events during the cooling part of the PIT emulsification process using the phase diagram of a model system. The results showed the process to include the following steps. When entering the PIT range from higher temperatures, the original oil phase separates into a middle phase bicontinuous microemulsion and a retained oil phase with less surfactant and water. As the temperature is reduced, the middle phase incorporates the entire original water phase, and at the lowest temperature interval before the system leaves the PIT range, the middle phase spontaneously disintegrates partly, resulting in extremely small oil drops inside the phase.

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