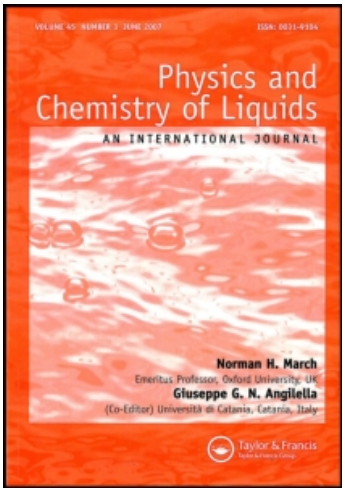

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Study on a novel oil-in-water-type microemulsion system of water/Triton X-100/Tween80/*n*-hexyl alcohol/*n*-octane

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First published on: 25 November 2009

To cite this Article Duan, Guorong , Li, Aimei , Yang, Xujie , Lu, Lude and Wang, Xin(2010) 'Study on a novel oil-in-water-type microemulsion system of water/Triton X-100/Tween80/*n*-hexyl alcohol/*n*-octane', Physics and Chemistry of Liquids, 48: 1, 19 — 28, First published on: 25 November 2009 (iFirst)
To link to this Article: DOI: 10.1080/00319100802623912
URL: http://dx.doi.org/10.1080/00319100802623912

Physics and Chemistry of Liquids
Vol. 48, No. 1, February 2010, 19–28

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Study on a novel oil-in-water-type microemulsion system of water/Triton X-100/Tween80/*n*-hexyl alcohol/*n*-octane

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(*Received 5 June 2008; final version received 13 November 2008*)

A novel oil-in-water-type microemulsion system (water/Triton X-100/Tween80/*n*-hexyl alcohol/*n*-octane) has been studied. The results of investigations of the mechanism of formation of this system have indicated that the mixture of Triton X-100, Tween80 and *n*-hexyl alcohol acts as a surface layer. Further studies have shown that by controlling the *n*-octane content of this system, it is possible to change its cloud point. Furthermore, variation of the environmental temperature has been shown to affect the maximum *n*-octane content of this system, the maximum *n*-octane content increases with increasing environmental temperature.

Keywords: microemulsion system; cloud point; oil-in-water-type emulsion

1. Introduction

Microemulsion technologies have hitherto been widely applied in many fields, including material science and engineering [1,2], because of microemulsion's transparent, homogeneous and thermodynamical stability [3,4]. Numerous researchers have reported the preparation and characterisation of nanoparticles made using the reverse microemulsion method [5–7]. Three-component microemulsion systems (MESs) of surfactant, oil and water have many important features and have attracted the attention of many researchers [8,9]. The most important property of a MES, besides thermodynamic stability, is its microstructure; thus, much work has been focussed in this particular direction [10–12]. The structure of a ternary microemulsion is generally one of the three types, namely oil-in-water (O/W), water-in-oil (W/O) or a 'bicontinuous' structure [13,14], and the O/W-type structure has an important application as a template in the preparation of hollow materials. In this work, we report a novel O/W-type structural microemulsion.

Microemulsions based on water/Triton X-100/*n*-octane have been extensively studied [15,16]. In some experiments, we found that when some Tween80 was added to the above system, the maximum *n*-octane content increased and the corresponding thermal stability was improved. Thus, we have now studied the novel microemulsion of water/Triton X-100/Tween80/*n*-hexylalcohol/*n*-octane. The results of a study of the formation mechanism of this system have indicated that the mixture of Tween80, Triton X-100 and *n*-hexyl alcohol acts as a surface layer. Further studies have indicated that controlling the *n*-octane content of the system changes its cloud point. Furthermore, variation of the

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ISSN 0031–9104 print/ISSN 1029–0451 online

DOI: 10.1080/00319100802623912
http://www.informaworld.com

environmental temperature also affects the maximum *n*-octane content of this system and the maximum *n*-octane content increases with increasing environmental temperature. This work primarily reports these new findings.

2. Materials and methods

2.1. *Materials*

Triton X-100 (TX-100, $C_{45}H_{64}O_{11}$, $\rho = 1.055$) and *n*-octane, both of chemical reagent grade, were purchased from China Jiangsu Yonghua Chemistry Co. Ltd. Tween80 ($C_{34}H_{64}O_{11}$, $\rho = 1.10$) and *n*-hexyl alcohol, both of chemical reagent grade, were purchased from the China National Medicine Group Shanghai Chemical Reagent Company.

2.2. *Preparations*

All preparations and measurements were carried out at room temperature. A ternary phase diagram was used to characterise the O/W-type MES of water/Tween80/TX-100/*n*-hexyl alcohol/*n*-octane, the content of water ranges from 100 to 0.0 vol.%, surfactant from 0.0 to 100 vol.% and *n*-octane from 0.0 to 33.3 vol.%. In this system, *n*-octane was employed as the oil phase, and the mixture of TX-100, Tween80 and *n*-hexyl alcohol acted as the surfactant layer (the volume ratio was 5 : 3 : 2). TX-100, Tween80 and *n*-hexyl alcohol were added sequentially to the water, the content of water in the system changes from 100% to 0.0 (it is given as 0.0–1.0 in Figure 1), with magnetic stirring. After the mixture had become a transparent solution, a proper *n*-octane was added dropwise from a glass injector (such as the components of an example of microemulsion are 40 mL of water, 10 mL of surfactant and 2.5 mL of *n*-octane). Eventually, a thermodynamically stable O/W-type microemulsion was spontaneously formed after continuous stirring.

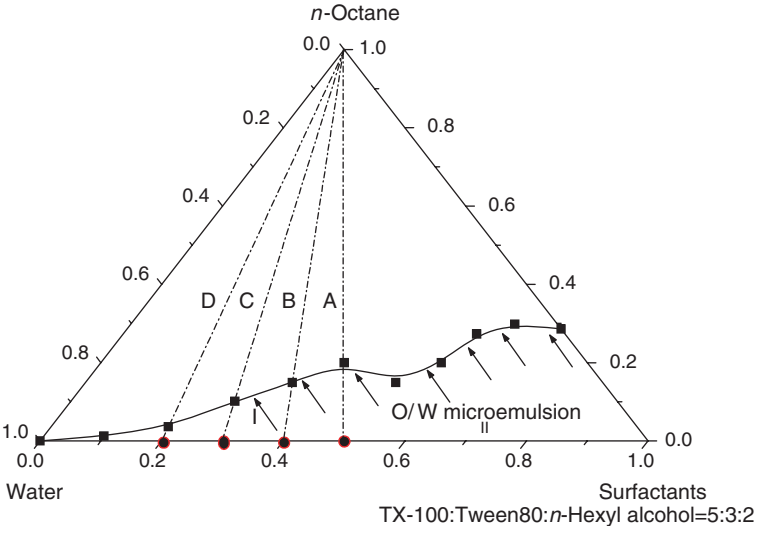

Figure 1. Ternary phase diagram for the O/W microemulsion system of water/Triton X-100/Tween80/*n*-hexyl alcohol/*n*-octane.

3. Results

In order to ascertain the solubilisation capability of the oil phase in the present system, the oil/water/surfactant ternary phase diagram was recorded. In this experiment, a microemulsion with a specific ratio of water to the mixture of surfactants was first prepared. Then, *n*-octane was added dropwise until the microemulsion became turbid. Depending on the volume and concentration of each species, the composition in terms of each component – that is, *n*-octane, water and the surfactant mixture – could be determined. Subsequently, a series of experiments were performed following a similar procedure, systematically changing the composition in terms of the relative amounts of water and the mixture of surfactants, which allowed us to obtain the ternary phase diagram shown in Figure 1.

The boundary between the microemulsion region and the non-microemulsion region was determined on the basis of clear/turbid observations. When the sizes of the oil-phase domains (swollen micelles of *n*-octane) are in the range 10–100 nm, which is lower than the wavelength of white light and does not cause substantial light scattering, the system appears clear and transparent. Increasing oil-phase content in the oil/surfactant/water mixture will result in a crossing of the microemulsion/non-microemulsion boundary, and this will lead to the formation of oil-phase domains of colloidal dimensions (200 nm–10 μm), which cause light scattering [2]. Therefore, the system becomes translucent yet turbid. The type of MES was determined by the dilution method [17], that is to say, microemulsion droplets were titrated into water; if the droplet scattered on the water surface, then the microemulsion was of the O/W-type; however, if the droplet floated on the water surface, then it was of the W/O-type.

Figure 1 shows the ternary phase diagram of the MES. In this system, distilled water acted as the aqueous phase, the mixture of TX-100, Tween80 and *n*-hexyl alcohol (volume ratio 5 : 3 : 2) acted as the surfactant phase, and *n*-octane acted as the oil phase. From Figure 1, it can be seen that the present system has two distinct characteristics. On one hand, the maximum content of the oil phase increases slowly with increasing content of the surfactant phase in the water-rich region. When the *R*-value (*R* is the volume ratio of aqueous phase to the surfactant phase) is increased to 1.0, the maximum content of the oil phase reaches a maximum value of 20 vol.%. Thereafter, the increase in the maximum content of the oil phase is very small, undulating on a wave-like line. On the other hand, in the surfactant-rich region and in the neighbourhood of the boundary line, the microemulsion is very viscous and unsuitable as a soft template for preparing nanosized hollow capsule structures [3–5]. Arrowheads in the ternary phase diagram denote the direction of increasing viscosity.

Importantly, the boundary point of the microemulsion region and the non-microemulsion region are distinct when the *R*-value is below 1.0. However, when the *R*-value is above 1.0, the boundary point becomes fuzzy, because the transition of the MES type from O/W to W/O is continuous in microemulsion extension.

4. Discussion

4.1. *Effect of the surfactant content on the oil phase content*

Figure 2 shows the effect of the TX-100 content on the maximum *n*-octane content. In this experiment, we first added 2 mL of *n*-hexyl alcohol to 40 mL of water, because an

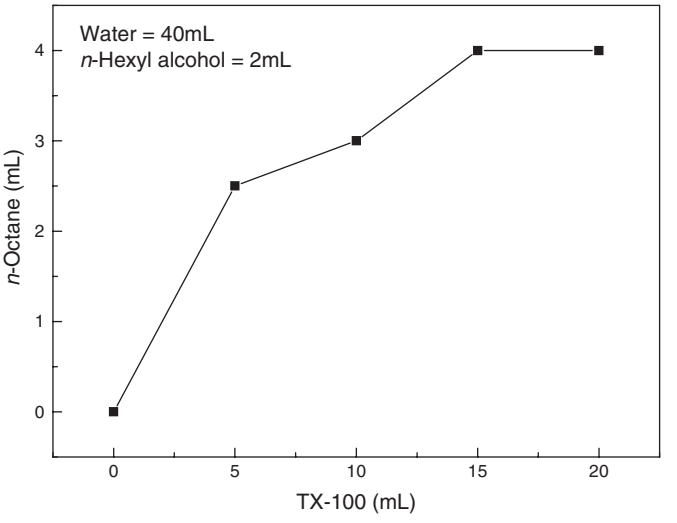

Figure 2. Effect of the TX-100 content on the maximum *n*-octane content.

O/W-type microemulsion could not be obtained if there was no *n*-hexyl alcohol in the system [17–20]. Then, a microemulsion with a specific ratio of TX-100 to water was prepared, to which *n*-octane was added dropwise until turbidity appeared. Depending on the volume and concentration of each species, the composition in terms of each component, that is, *n*-octane, water and TX-100, could be determined. Subsequently, a series of experiments were performed following a similar procedure, systematically changing the composition in terms of the relative amounts of TX-100 and water, which allowed us to obtain Figure 2.

From Figure 2, it can be seen that the maximum *n*-octane content generally increases with increasing TX-100 content. Importantly, however, the rate of increase varies with the different TX-100 contents; when the TX-100 content is below 5.0 mL (the corresponding volume of water is 40 mL), the rate of increase of the *n*-octane content is fastest; when the TX-100 content is in the range 5.0–15.0 mL, the rate of increase becomes slower. In particular, when the TX-100 content exceeds 15.0 mL, the maximum *n*-octane content remains constant at a level of 4.0 mL, thus indicating that the optimum TX-100 content in this system is in the range 10.0–15.0 mL.

Figure 3 shows the effect of the *n*-hexyl alcohol content on the maximum *n*-octane content. In this experiment, we first added 10.0 mL of TX-100 to 40 mL of water, because a number of experiments had shown that an O/W-type microemulsion could not be obtained if there was no TX-100 in the system [17–20]. The method of acquiring Figure 3 was the same as that used to acquire Figure 2. From Figure 3, it can be observed that the maximum *n*-octane content generally increases with increasing *n*-hexyl alcohol content. However, the rate of increase again falls into three distinct ranges. From 0 to 1.0 mL, the rate of increase is slow; from 1.0 to 2.0 mL it is at its fastest and from 2.0 to 3.0 mL it becomes slow once more. As in the case of TX-100, when the *n*-hexyl alcohol content exceeds 3.0 mL, the maximum *n*-octane content remains constant at a level of 5.0 mL. These results indicate that the optimum *n*-hexyl alcohol content in this system is in the range 3.0–4.0 mL.

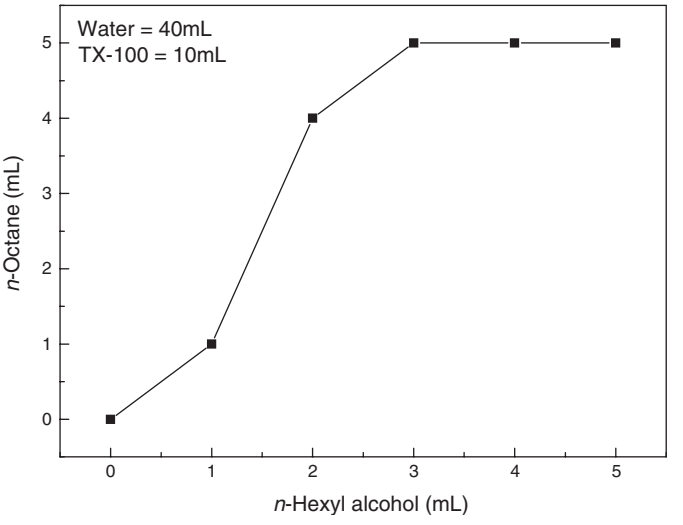

Figure 3. Effect of the *n*-hexyl alcohol content on the maximum *n*-octane content.

From the above two experiments, it can be concluded that this O/W-type MES must include both TX-100 and *n*-hexyl alcohol, and the optimal ratio of TX-100 to *n*-hexyl alcohol is 5 : 2 (by volume). Interestingly, we found that when some Tween80 was added to this system, the maximum *n*-octane content increased. Therefore, we further studied the effect of Tween80 on the maximum *n*-octane content. In this experiment, we first added 10 mL of TX-100 and 4.0 mL of *n*-hexyl alcohol to 40 mL of water; the experimental methods used were the same as those used to acquire Figures 2 and 3. From Figure 4, it can be observed that the maximum *n*-octane content again generally increases with increasing Tween80 content. However, when the Tween80 content exceeds 4.0 mL, the maximum *n*-octane content remains constant at a level of 8.0 mL. This experiment indicates that the optimum ratio of TX-100, Tween80 and *n*-hexyl alcohol is 5 : 3 : 2.

4.2. *Formation mechanism of the MES*

The stability of a MES depends on the integrity and compactness of the surfactant membrane; when the surfactant membrane is more cohesive, the stability is higher, and the corresponding solubilisation capability is greater [17–20]. The type of MES depends on the Hydrophile–Lipophile Balance (HLB) value of the surfactant; a high HLB value is propitious for the formation of an O/W-type MES and a low HLB value is propitious for the formation of a W/O-type MES. The HLB value of a surfactant can be calculated according to the method of Davies [18]. Such calculations yield values of 6.1, 15.0 and 13.5 for *n*-hexyl alcohol, Tween80 and TX-100, respectively. The ratio of TX-100, Tween80 and *n*-hexyl alcohol in the present system is 5 : 3 : 2, from which an HLB value for the surfactant mixture of 12.47 may be calculated by additive theory [19]. This value indicates that the surfactant mixture is soluble in the aqueous phase and is propitious for the formation of an O/W-type microemulsion by the theory of Bancroft [20]. The hydrophobic groups of the three kinds of surfactants (TX-100, Tween80 and *n*-hexyl alcohol) are all soluble in *n*-octane, while their hydrophilic groups are soluble in the aqueous phase [18]. Thus, it may be postulated that these three surfactants are probably arranged in the

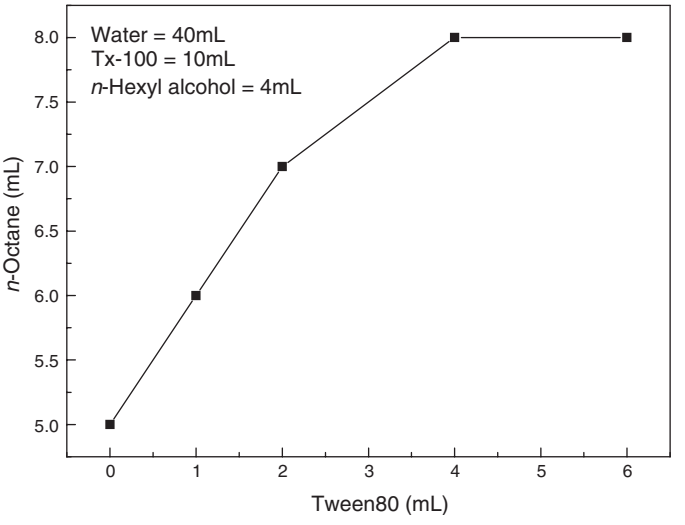

Figure 4. Effect of the Tween80 content on the maximum *n*-octane content.

manner shown in Figure 5(B) to form the surfactant membrane. Clearly, the diameter (*R* was indicated in Figure 5(A)) will increase when more material is dissolved in the oil phase, and then the requirement for integrity of the surfactant membrane will be higher, otherwise the MES will be destroyed. Thus, when the integrity of the surfactant membrane is higher, the solubilisation capability of the microemulsion will be greater. The presence of *n*-hexyl alcohol adds the tightness of the surfactant membrane, so this kind of surfactant membrane is very stable and that the stability of such a MES is very good.

In addition, the hydrophilic group of Tween80 adopts a spherical form and its volume is very large, which is propitious for the formation of a stable 'wedge' structure [17–20]. Such a 'wedge' structure enhances the stability of the surfactant membrane, leading to the formation of a stable O/W-type microemulsion according to the 'orientation wedge' theory of surfactant membranes [17]. The volume of the hydrophilic OH group of *n*-hexyl alcohol is small and it may form hydrogen bonds with H_2O molecules, and so the cohesion between the OH group of *n*-hexyl alcohol and the H_2O molecules is very strong, which also enhances the stability of the surfactant membrane. Furthermore, the cross-sectional area of a stearic acid molecule is 0.21–0.25 nm^2, while that of an oleic acid molecule is 0.28–0.55 nm^2; a molecular membrane comprised of Tween80, which incorporates oleic acid, is very tousy [20]. As a result, there is charge repulsion between the double bonds of the oleic acid moieties because of the extensive electron clouds, and some holes may form; oil-phase micro-droplets may then easily cross the surfactant membrane, leading to destruction of the stable microemulsion. *n*-Hexyl alcohol can occupy these holes and thereby enhance the stability of the surfactant membrane. The above propositions can be verified experimentally, in that only a white macroemulsion can be obtained when there is no *n*-hexyl alcohol in the system.

4.3. *Cloud-point study*

The maximum *n*-octane content is dependent on the size of the oil-phase domains, which, in turn, is dependent on the stability of the microemulsion, as reflected by its cloud point.

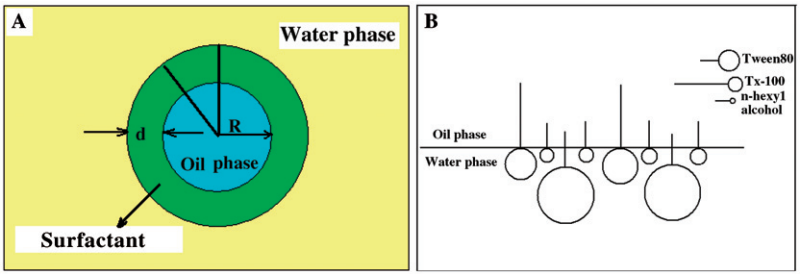

Figure 5. Illustration of the structure of an O/W microemulsion.

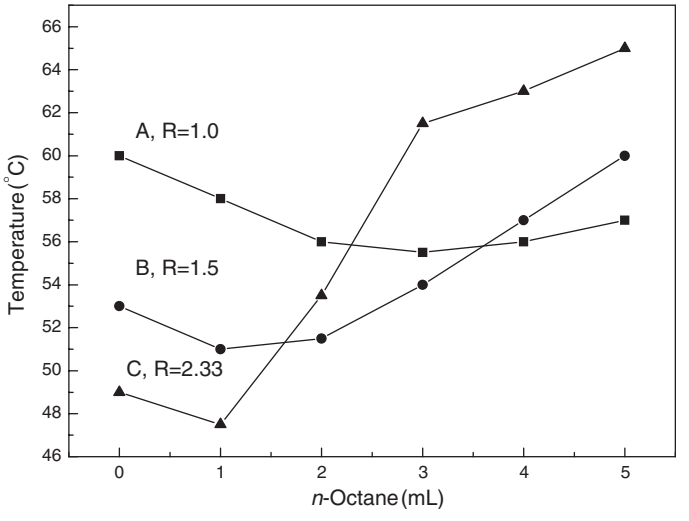

Figure 6. Relationship between the *n*-octane content and the cloud point of the microemulsion.

Thus, we further studied the effect of the maximum *n*-octane content on the cloud point of the microemulsion. We selected three components, designated by lines A, B and C in Figures 1 and 6, with *R*-values of 1.0, 1.5 and 2.33, respectively, *R* being the ratio W/S (where W is the volume of water and S is the volume of the surfactant mixture). In these experiments, the *n*-octane content was gradually increased from 0 mL to the maximum content in increments of 1.0 mL, and the corresponding cloud point of the MES was recorded. Subsequently, a series of experiments were performed following a similar procedure, systematically changing the *n*-octane content, which allowed us to obtain Figure 6. From Figure 6, it can be seen that there is a common character, in that the curves show a U-shape. However, there are some differences: on the one hand, the minimum point of each U-shaped curve moves towards lower *n*-octane content with increasing *R*-value; on the other hand, beyond the minimum point, the rate of increase of the cloud point with increasing *n*-octane content becomes more pronounced with increasing value of *R*. These features suggest that the properties of the different components in the present MES are different.

The results presented above show that the *n*-octane content could effect the corresponding cloud point. Thus, we further studied the effect of the environmental temperature on the maximum *n*-octane content at temperatures above room temperature,

using the component corresponding to line B as an illustrative example. In these experiments, the temperature was systematically increased and the corresponding maximum *n*-octane content was recorded, allowing us to obtain Table 1 and Figure 7. From Figure 7, it can be seen that the experimental points are almost situated on a straight line. Thus, unitary linear regression analysis may be carried out in industry to predict and control this technological parameter.

If the regression equation between the variable X (°C) (denoting environmental temperature) and the variable Y (mL) (denoting the *n*-octane content) is [21]:

$$\hat{Y} = \hat{a} + \hat{b}\,X.$$

Then, $n = 10$, $\bar{X} = 64.65$, $\bar{Y} = 10.5$

$$L_{XY} = \sum X_i Y_i - n\bar{X}\bar{Y} = 6845.5 - (10 \times 64.65 \times 10.5) = 57.25$$
$$L_{XX} = \sum X_i^2 - n\bar{X}^2 = 41836.25 - (10 \times 64.65^2) = 40.025$$
$$L_{YY} = \sum Y_i^2 - n\bar{Y}^2 = 1185 - (10 \times 10.5^2) = 82.5$$

then, $\hat{b} = L_{XY}/L_{XX} = 1.43036$, $\hat{a} = \bar{Y} - \hat{b}\bar{X} = 10.5 - 1.43036 \times 64.65 = -81.97$.

The linear correlation coefficient of the equation is $\mathrm{Re} = L_{XY}/\sqrt{L_{XX}L_{YY}} = 0.99628$, $\mathrm{Re}_{0.05} = 0.632$, indicating that the linear correlation between the variables X and Y is very reliable and that the linear regression equation is effective. Hence, the practical linear

Table 1. Effect of temperature on the *n*-octane content ($W = 24$ mL, $S = 16$ mL).

Item	1	2	3	4	5	6	7	8	9	10
Temperature (°C)	61.5	62.5	63	63.5	64	65	65.5	66.5	67	68
n-Octane (mL)	6	7	8	9	10	11	12	13	14	15

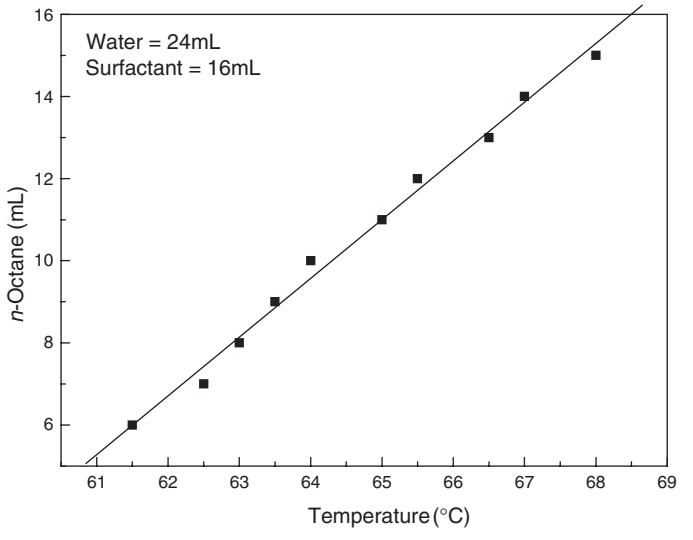

Figure 7. Effect of the environment temperature on the *n*-octane content.

regression equation is: $\hat{Y} = -81.97 + 1.43036X$ $(68 > X > 61.5)$, the total deviation is $Q = (1 - \mathrm{Re}^2)L_{YY} = 0.612$, and the remainder standard deviation is $S = \sqrt{\frac{Q}{n-2}} = 0.27661$, then the 95% predictive scale is $(\hat{Y} - 1.96\,S, \hat{Y} + 1.96\,S)$, or $(\hat{Y} - 0.54, \hat{Y} + 0.54)$.

In some experiments, we found that not only above the cloud point, but also below a certain temperature, the transparent microemulsion would become turbid. This result suggested that there were two cloud points, that is, an upper and a lower point. Thus, we further studied the effect of the *n*-octane content on the lower cloud point of such an O/W-type microemulsion by employing the same experimental methods as used to obtain Figure 6, which allowed us to obtain Figure 8. In Figure 8, plots a and b refer to the cloud-point properties of lines C and D marked in Figure 1, respectively. From Figure 8, it can be seen that there is a series of lower cloud points accompanying the upper cloud points. Furthermore, the relationships between the *n*-octane content and corresponding upper and lower cloud points are similar, both values increasing with increasing *n*-octane content. Importantly, the experimental points relating to the lower cloud points are almost situated on a straight line, as is the case for the upper cloud points, indicating that unitary linear regression analysis may be carried out in industry to predict and control this technological parameter. The relevant results are shown in Table 2. From Table 2, it can be seen that the linear correlation coefficients are above $R_{0.05}$ (0.632), suggesting that the linear correlation is very reliable and that the linear regression equation is effective. The practical linear regression equations are shown in Table 2 and the corresponding regression lines are shown in Figure 8. From Figure 8, it can be seen that the slopes of the regression lines of

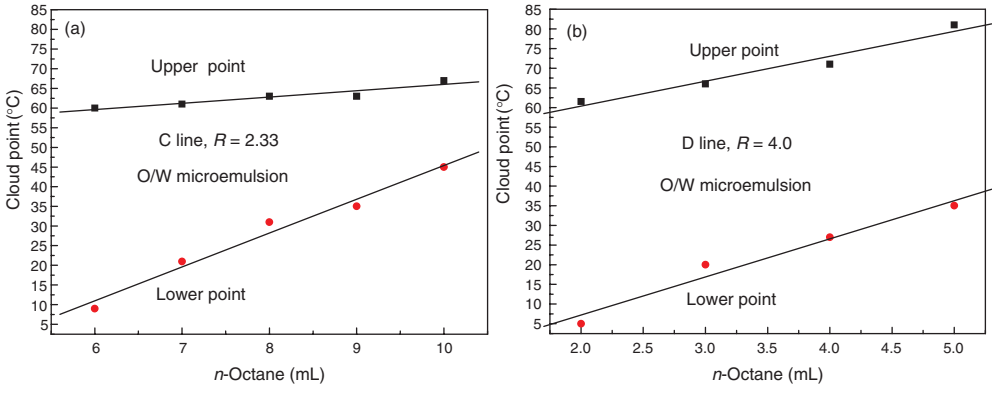

Figure 8. Relationship between the *n*-octane content and cloud points.

Table 2. Linear fitting analysis of the relationship between the *n*-octane content and the cloud point.

	$W/S = 2.33$		$W/S = 4.0$	
Item	Upper point	Lower point	Upper point	Lower point
$\hat{b}$	1.6	8.6	6.35	9.7
Re	0.943	0.989	0.979	0.983
Linear regression	$Y = 50 + 1.6X$	$Y = -40.6 + 8.6X$	$Y = 47.65 + 6.35X$	$Y = -12.2 + 9.7X$

the lower cloud points in plots a and b are different, suggesting that the properties of the different components in the ternary phase diagram (as shown in Figure 1) are distinct, and that the properties of the D line component are more stable than those of the C line component.

5. Summary

A water/Tween80/TX-100/n-hexyl alcohol/n-octane O/W-type MES has been successfully obtained by using a mixed surfactant of TX-100, Tween80 and n-hexyl alcohol in a volume ratio of 5 : 3 : 2. Experiments indicated that the cloud points of this MES could be adjusted by controlling the *n*-octane content. These features suggest that such a MES could have a number of potential applications.

Acknowledgement

The High Technical Foundations of Jiangsu Province (Nos. BK2008520, BG2007047) supported this work. The authors are grateful for the grants.

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