

Stability and Phase Behavior of Acrylamide-Based Emulsions before and after Polymerization

Dan Zhang,[†] Ximing Song,^{*,‡} Fuxin Liang,[‡] Zhiying Li,[†] and Fengqi Liu^{*,†}

College of Chemistry, Jilin University, Changchun 130023, and School of Chemical Science and Engineering, Liaoning University, Shenyang 110036, China

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The stability and phase behavior of acrylamide-based emulsions, prepared with surfactants consisting of lipophilic Span80 and hydrophilic OP10, before or after polymerization were investigated. The research results indicated that the phase separation behavior of the W/O-type emulsions is related to the toluene/water ratio. When the water volume fraction was larger, the phase separation mechanism was mainly a penetration of aqueous molecules from the dispersed-phase droplets. When the water volume fraction was smaller, the phase separation mechanism was mainly a sedimentation of the separated aqueous droplets. At a fixed toluene/water ratio, the emulsion stability and the emulsion type are related not only to the ratio of the two surfactants but also to the acrylamide concentration, and the effect of increasing acrylamide concentration on the character of the emulsions is similar to that of increasing OP10 mass fraction (increasing HLB value), which determines the corresponding relationship between acrylamide concentration and HLB value in the most stable emulsion system. To obtain the most stable emulsion at a fixed acrylamide concentration, the emulsion with higher acrylamide concentration needs a lower HLB value for the emulsion systems.

1. Introduction

Polyacrylamide and acrylamide-based copolymers are important synthetic water-soluble polymers^{1,2} because of their use in many industrial applications, such as coagulants and flocculants^{3,4} in wastewater and potable water treatment, pushing fluids in enhanced oil recovery, drag reduction agents and drilling fluids, additives in paper making,^{5,6} superabsorbents⁷ in manufacturing and drug delivery, or biomaterials.^{8–11}

Special interest is focused on the polymerization of acrylamide in a water-in-oil dispersion because the molecular weight and reaction rate can be increased simultaneously in this process, which is attributed to the low viscosity of the reaction mass and good heat removal. Hunkeler et al.¹² have excellently summarized a large amount of literature before 1997 focused on the polymerization of acrylamide in a water-in-oil dispersion. In an inverse emulsion polymerization process, the water-soluble monomer is dispersed in a continuous organic medium using a water-in-oil emulsifier. The final product is usually a colloidal dispersion of hydrophilic polymer particles in a continuous oil phase. The inverse lattices are easily inverted and dissolved in water.¹³

Inverse emulsions are kinetically stable, and their stability is poorer than that of conventional lattices (O/W), because the low dielectric constant of organic compounds results in the electrostatic stabilization being ineffective.^{14,15} Furthermore, the very large density difference between the separated water phase and the continuous organic phase will promote the sedimentation of dispersions. Consequently, most inverse lattices settle on a time scale varying from a few hours to a few weeks or even months, and redispersion can be difficult.¹⁶ The stability of

inverse emulsions containing a monomer is very important for the polymerization processes, and can be adjusted through controlling the experimental conditions such as regulating the oil/water ratio, emulsifiers, and so on. Up to now, the majority of attention has been focused on the field of the polymerization mechanism and polymerization reaction dynamics etc. in the literature of inversion emulsion polymerization,^{17–24} but research on the stability and destabilization mechanism is limited.^{25–28}

To the best of our knowledge, a report concerning the phase separation mechanism and the cooperating effect of the HLB value and monomer concentration on the stability and character of acrylamide-based inverse emulsions has not been found. In this work, we reported two kinds of phase separation mechanisms caused by the ratio of toluene to water and an equivalence principle of the acrylamide concentration and HLB value. To perform this work, some experimental conditions such as the stirring speed, style of introducing surfactants, surfactant amount, etc. were maintained constant, while the aqueous-to-organic-phase ratio, monomer concentration, and HLB value were varied to explore their impact on the stability and phase behavior of such inverse emulsions. The primary purpose of the research outlined in this paper is to lay a foundation for optimizing a recipe of a stable acrylamide-based inverse emulsion by controlling these factors.

2. Experimental Section

2.1. Materials. Acrylamide was obtained from the Tianjing Fuchen Chemical Reagent Factory, China (AR grade), and recrystallized twice from acetone. Toluene was obtained from the Beijing Chemical Plant, China, and used without further purification. Sorbitan monooleate (Span80) from Shanghai Sanpu Chemical Co. Ltd., China (CP grade), and alkylphenol polyoxyethylene ether (OP10) from the Shenyang Xinxin Chemical Reagent Factory, China (CP grade), were used as received.

* To whom correspondence should be addressed. E-mail: xmsong@lnu.edu.cn (X.S.); liufengqi@jlu.edu.cn (F.L.).

[†] Jilin University.

[‡] Liaoning University.

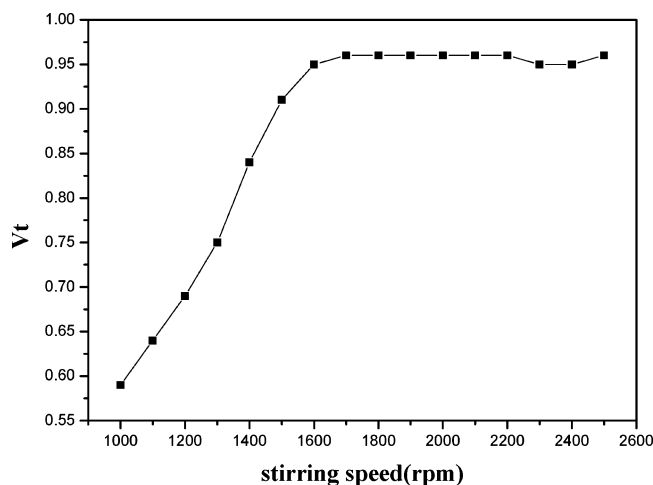


Figure 1. V_t of the inverse emulsions versus stirring speed in the course of the emulsion preparation. Recipe: 50 mL of toluene, 33.33% (w/w) acrylamide aqueous solution prepared with 40 mL of water, 6.0 g of Span80 + OP10, Span80/OP10 = 5.86 (w/w).

Azodiisobutyronitrile (AIBN) from the Beijing Chemical Plant (CP grade) was recrystallized from ethanol before use.

2.2. Emulsion Preparation and Polymerization. Emulsions were prepared as follows: Certain amounts of emulsifier and toluene were put into a 250 mL round flask and stirred with a motor stirrer at a high speed for 30 min. A certain amount of water phase containing acrylamide was added drop by drop (0.5 mL/min) to the toluene solution with stirring at a certain speed. The mixture was stirred for 1 h after mixing to give a white inverse emulsion. To obtain a polyacrylamide inverse latex, polymerization was carried out using AIBN as initiator at 50 °C for 6 h, and the conversions of acrylamide were above 97% for all systems.

2.3. Determination of Emulsion Type. The emulsion type (W/O or O/W) was determined by the phase dilution method on the basis of the following fact: an emulsion is very easily diluted with the liquid as a continuous phase but not easily diluted with the liquid as a dispersed phase.²⁹ In the experiment, a drop of the emulsion sample was added to two beakers, respectively, one containing about 100 mL of water and the other containing about 100 mL of toluene. The emulsion which could be dispersed rapidly in toluene is a W/O-type emulsion; conversely, the emulsion which could be dispersed rapidly in water is an O/W-type emulsion.

2.4. Evaluation of Emulsion Stability. The acrylamide monomer emulsions or polyacrylamide emulsions were put into test tubes with a height of 15 cm and a diameter of 1.2 cm to observe the emulsion instability phenomena in the placement course. The emulsion stability was evaluated by the ratio (V_t) of the emulsion volume left over after the tubes were placed in the water bath (25 ± 0.5 °C) for 84 h to the initial emulsion volume.

3. Results and Discussion

3.1. Selection of Experimental Conditions. **3.1.1. Stirring Speed.** V_t of inverse emulsions containing acrylamide monomer as a function of the stirring speed is shown in Figure 1. When the stirring speed is lower than 1000 rpm, the water phase is not dispersed effectively and thus the emulsions are all unstable, no matter how long the emulsification time is. When the stirring speed is higher than 1000 rpm, the emulsion rapidly becomes more and more stable with an increase of the stirring speed, up to 1600 rpm, where the emulsion stability does not change much

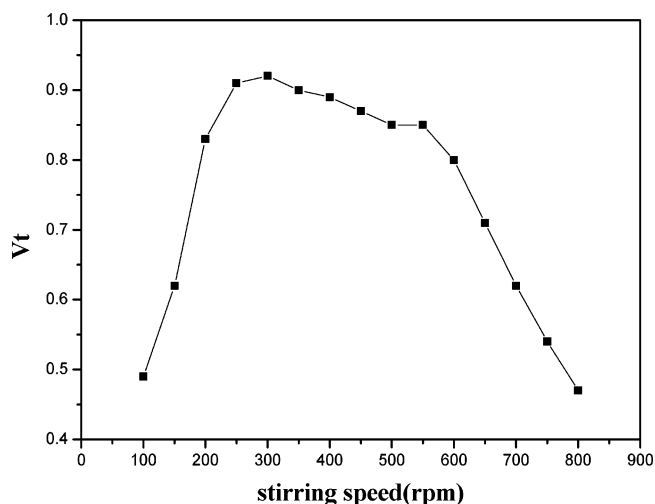


Figure 2. V_t of the emulsions with the recipe described in Figure 1 after polymerization versus stirring speed in the course of polymerization.

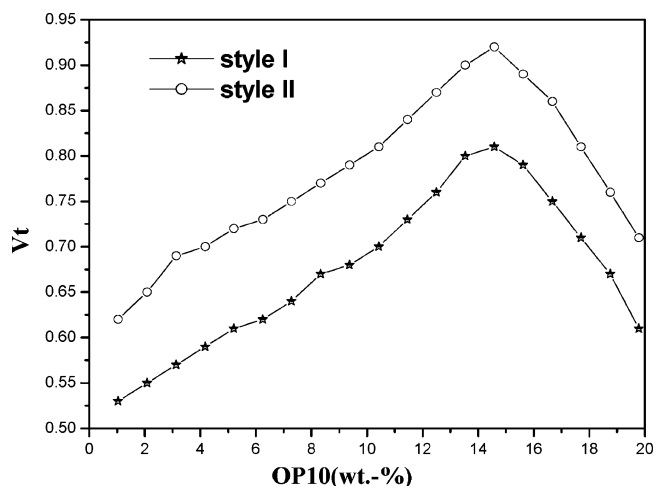


Figure 3. V_t as a function of OP10 mass fraction for the inverse emulsions. Recipe: 50 mL of toluene, 33.33% (w/w) acrylamide aqueous solution prepared with 40 mL of water, 6.0 g of Span80 + OP10. Style I is adding an acrylamide aqueous solution into a toluene solution containing Span80 and OP10 and style II is adding an acrylamide aqueous solution containing OP10 into a toluene solution containing Span80 in the preparation of the acrylamide monomer emulsions.

and V_t is above 95%. Therefore, 1800–2500 stirring speeds were used for the emulsification process in this work. Figure 2 shows the influence of the stirring speed in the polymerization process on the W/O emulsion stability. The results in Figure 2 indicate that the stirring speed should be lowered appropriately in the polymerization process to keep the stability of the emulsion. A fixed stirring speed of 300 rpm was used for the polymerization process in this work.

3.1.2. Style of Introducing Surfactants. The emulsions were prepared by two styles: adding an acrylamide aqueous solution as the water phase into a toluene solution containing Span80 and OP10 (style I) and adding an acrylamide aqueous solution containing OP10 as the water phase into a toluene solution with Span80 (style II). The influence of the surfactant blending styles on the V_t of emulsions before and after polymerization is shown in Figures 3 and 4, respectively. The emulsions obtained by style II have a higher stability at all ratios of the two surfactants, regardless of whether polymerization is carried out, and the stability of the emulsions before polymerization are higher than that after polymerization, i.e., lattices. These results indicate

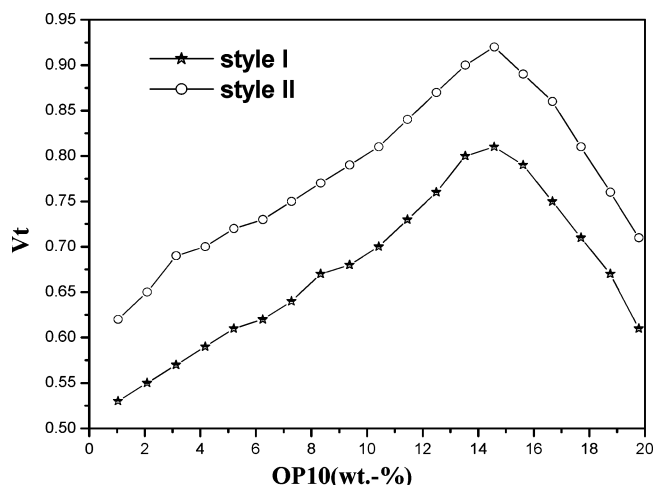


Figure 4. V_t as a function of OP10 mass fraction for the emulsions with the recipe described in Figure 3 after polymerization.

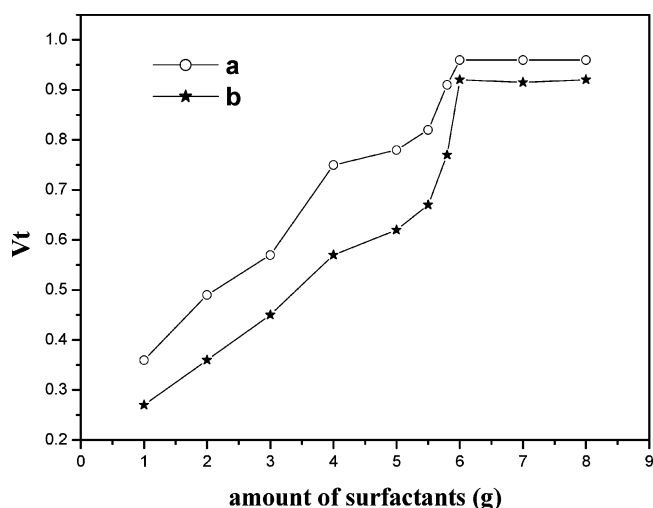


Figure 5. V_t as a function of surfactant amount (Span80 + OP10) for inverse emulsions before (a) and after (b) polymerization. Recipe: 50 mL of toluene, 33.33% (w/w) acrylamide aqueous solution prepared with 40 mL of water, Span80/OP10 = 5.86.

that the distribution and arrangement of the surfactants at the W/O interface in the emulsions are related to the surfactant blending style. In the case of style II, lipophilic and hydrophilic surfactants are dissolved in the oil and water phases, respectively, and enter the W/O interface in their respective ways, leading to the formation of a more compact and stronger interface membrane, and thus, the emulsions are more stable. Therefore, style II was used to prepare the emulsions in this work.

3.1.3. Surfactant Amount. The influence of the amount of the surfactants at a fixed mass ratio of the two surfactants (Span80/OP10 = 5.86) before and after polymerization on V_t is shown in Figure 5. The stabilities of the two inverse emulsion systems decrease with decreasing amount of the surfactants when the amount of the surfactants is less than 6 g, because a lower surfactant concentration cannot lower the interface tension effectively and the drop size of the dispersed phase is larger. When the amount of the surfactants is larger than 6 g, the stabilities of the two inverse emulsion systems do not change much with increasing amount of the surfactants. To make the observation of the instability phenomena easy and keep the stability of the polymerization process, we generally selected 6 g (Span80 + OP10) per 90 mL (toluene and water) in the emulsion preparation.

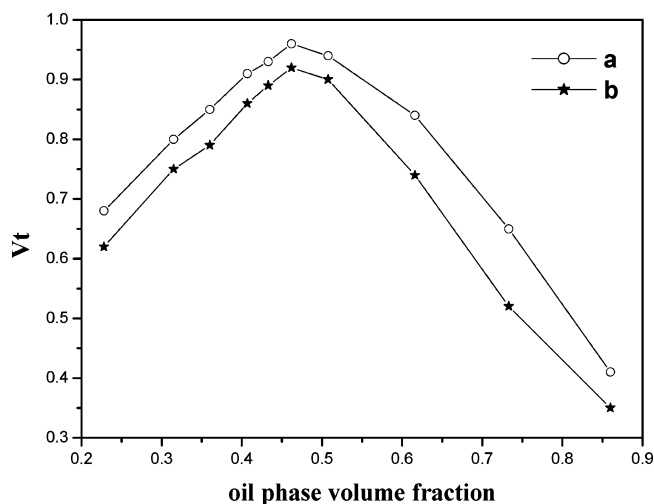


Figure 6. V_t as a function of oil-phase volume fraction for inverse emulsions before (a) and after (b) polymerization. Recipe: 90 mL of water + toluene, acrylamide concentration 33.33% (w/w) in the water phase, 6.0 g of Span80 + OP10, Span80/OP10 = 5.86 (w/w).

3.2. Influence of the Oil/Water Volume Ratio on the Instability Phenomena of the Emulsions. The influence of the oil/water volume ratio at a fixed amount of surfactants and acrylamide concentration on the V_t of inverse emulsions before and after polymerization is shown in Figure 6. The two inverse emulsion systems before and after polymerization have the same variation trends of stability when the oil/water ratio is varied, and the most stable emulsions occur at about 0.46 oil volume fraction, i.e., about the same oil- and water-phase volumes.

The emulsions showed two types of stratification (phase separation) behavior with the variation of the oil/water ratio. When the oil volume fraction was larger than 0.38, the emulsions were separated into two layers after a certain time of storage, a milky white W/O emulsion phase on the downside and a colorless (or yellow) transparent (or semitransparent) liquid with toluene as a major constituent on the upside. The volume fraction of the emulsion phase on the downside decreased gradually with prolongation of storage. When the oil volume fraction was smaller than 0.34, the emulsions were separated into two layers first in the placement course, a colorless transparent water phase on the downside and a milky white W/O emulsion on the upside. The water-phase volume fraction ($1 - V_t$) on the downside increased gradually with prolongation of storage, and after a certain time, a separated toluene phase appeared on the emulsion phase with further storage, resulting in a three-layer system with an emulsion layer sandwiched between the toluene and aqueous phases. The same separation behavior of three phases was also observed for inverse emulsion systems of mineral oil/water/Span surfactant.³⁰

Sedimentation and coalescence of dispersed-phase droplets can result in phase separation for emulsion systems. It was found that almost no phase separation was observed at stirring for the emulsion systems in which the oil volume fraction is larger than 0.38, uniform emulsion systems could be reobtained by stirring or oscillating the phase separation systems obtained after a certain time of storage, and the phase separation rate of the reobtained emulsions did not increase much in a period of further storage. Increasing the density of the continuous phase by adding CCl_4 to toluene could distinctly reduce the rate of phase separation. These results suggest that the floating of the toluene phase is mainly attributed to sedimentation of the dispersed-phase droplets.

For the emulsion systems in which the oil-phase fraction is smaller than 0.34, it was observed that the mobility of the aqueous phase separated from the emulsions is far larger than that of the emulsion itself. This fact implies that the mechanism of aqueous-phase separation is a deposition of water molecules which come from the inside of the dispersed droplets by penetrating through the interface membrane to the outside, rather than coalescence of the dispersed-phase droplets, although the droplets tend to pack tightly, because the aqueous phases separated from the emulsions after polymerization should be a more sticky polyacrylamide solution with approximately 33% concentration if coalescence of the dispersed phase had occurred.

After one month or more of storage, all emulsion systems will completely separate into two phases, an acrylamide or polyacrylamide aqueous solution phase and a toluene phase containing a small amount of other materials, with a visible surfactant layer at the interface.

We infer from these experimental results that sedimentation of the dispersed droplets occurs first, then the droplets are piled up at the bottom of the systems, and finally the accumulated droplets mix together to form the aqueous phases for these emulsion systems except the systems with an excessive water/oil ratio in which the aqueous phase comes from the water penetrating through the interface membrane at first.

For W/O-type emulsions, it is expected that increasing the volume fraction of water as a dispersed phase will increase the total area of the interface, so the amount of surfactants per unit interface area will be reduced with an increase of the ratio of water to toluene when the amount of surfactants is invariable, which causes the interfacial tension to increase especially for systems with a higher water/toluene ratio. Foye and Diane³⁰ have reported that the emulsion stability follows the same trends as the interfacial film strength (surface elasticity), and the interfacial film strength is reduced with an increase of the interfacial tension for W/O-type emulsions. From this, we could explain the instable phenomenon of the emulsion systems shown in Figure 6; i.e., the emulsion stability (V_t) should increase with decreasing relative amount of water, corresponding to interfacial tension, till the maximal value of V_t . The relative amount of surfactants is enough (see Figure 5) for the systems after the maximal V_t , but the distance between dispersed droplets tends to increase with decreasing water amount, and thus, the effect of sedimentation, which caused the decrease of V_t , will be more prominent.²⁸

3.3. Influence of the HLB Value of the Surfactant Blend on the Emulsion Stability. From Figures 3 and 4, we find that the ratio of lipophilic Span80 and hydrophilic OP10 has an effect on the emulsion stability. V_t as a function of the HLB value in a wider range of two surfactant ratios is shown in Figure 7, in which the HLB values were calculated with the following formula:

$$\text{HLB} = 4.3W + 13.9(1 - W)$$

Here W stands for the mass fraction of Span80. There are two maxima of V_t in Figure 7, and the stability of the emulsions is very poor at an HLB value of approximately 7.5. The emulsions are W/O type at HLB values lower than 7 while O/W type at HLB values higher than 7.6, according to our experimental results.

The introduction of OP10 should increase the strength of the oil–water interfacial layers because the hydrophilic polyglycol parts of OP10 can have an action with the polar carboxyl, carboxide, and ether of Span80 in the interface, and thus, proper matching of OP10 and Span80 will bring emulsion stability.

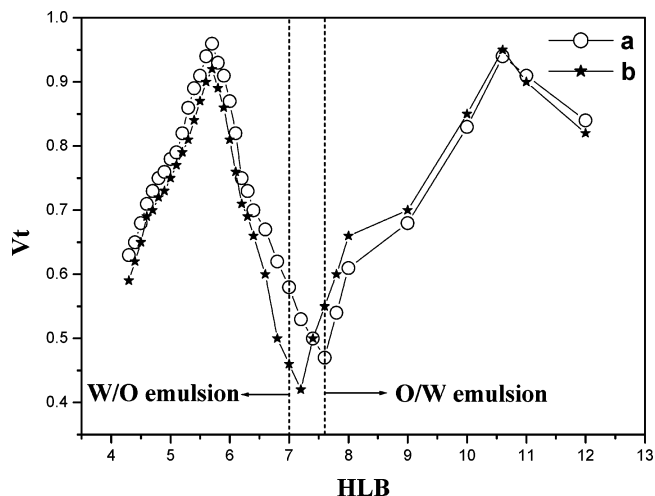


Figure 7. V_t as a function of HLB value for the emulsions before (a) and after (b) polymerization. Recipe: 50 mL of toluene, 33.33% acrylamide aqueous solution prepared with 40 mL of water, 6.0 g of Span80 + OP10.

On the other hand, from a thermodynamic viewpoint, OP10 with a bigger hydrophilic end group can change the curvature radii of the surfactant molecular film at the two-phase boundary.^{31,32} The curvature radii will increase with increasing amount of OP10 for the W/O-type emulsions, while the curvature radii will decrease with increasing amount of OP10 for the O/W emulsions. It is quite evident that the interfacial tension should have the lowest value when the radius of a dispersed-phase droplet and the thermodynamic curvature radius of the surfactant film at the phase boundary are well matched. Being considered a thermodynamic factor only, the radius of a dispersed-phase droplet in an equilibrium state will depend on the curvature radius of the surfactant layer. The variation trends of V_t with the HLB value in Figure 7 are easily understood from the viewpoint that the emulsion stability depends on the comprehensive effects of the interaction between the two surfactants and the curvature radius variation in an equilibrium state. The two maxima of V_t in Figure 7 should correspond to the best matching of the two surfactants in the W/O- and O/W-type emulsions, respectively.

The phase inversion behavior in Figure 7 is easily explained qualitatively according to the variation trends of the curvature radii of surfactant molecular layers with the HLB value. The radii of the dispersed-phase drops increase with an increase of the relative amount of OP10 in the W/O-type emulsion, and the W/O-type emulsion will undergo a transition to an O/W-type emulsion through a bicontinuous phase with a further increase of the relative amount of OP10 after a critical point.

The emulsion systems in Figure 7 all show the same appearance of instability, i.e., a milky white emulsion on the downside and a toluene phase on the upside, regardless of the emulsion type, W/O or O/W. It has been demonstrated above that the mechanism of the W/O emulsions is mainly a sedimentation of the dispersed aqueous droplets. Since the solution of acrylamide or polyacrylamide is a continuous phase in O/W-type emulsions, the floating of the toluene phase must be attributed to separation of a toluene molecule from the dispersed droplets or coalescence of the dispersed droplets.

The toluene layers separated from the emulsion systems in the nearby regions of the lowest V_t were more turbid than those in regions of much higher V_t . The volume of the 33.33% (w/w) acrylamide solution prepared with 40 mL of water is 58.2 mL, so we can deduce that the volume fractions of toluene in all

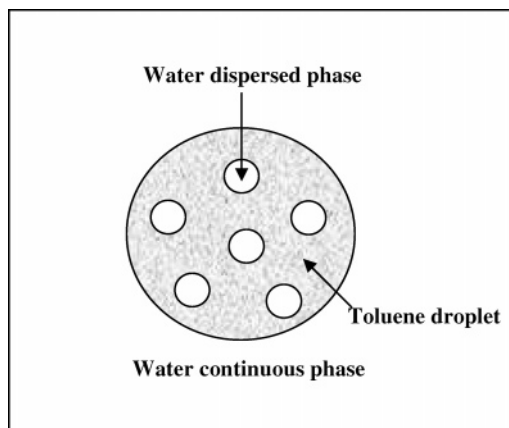


Figure 8. Schematic diagram for an O/W-type emulsion with a complex phase structure.

systems shown in Figure 7 are approximately 0.46. After 84 h of storage, the volume fraction of toluene layers separated from the emulsion systems in the nearby regions of the lowest V_t in Figure 7 was larger than the volume fraction of toluene added initially, and the emulsion systems did not completely separate to oil and water phases in this period. These results indicate that the toluene layer contains very small aqueous droplets. The system before polymerization at an HLB value of 7.6 (the lowest V_t) showed an O/W-type emulsion apparently. Because there were aqueous droplets in the toluene layer separated from the emulsion after storage, we could draw a conclusion that smaller water droplets must exist in the dispersed toluene phase before separation. Namely, the apparent O/W-type emulsions in the nearby region of the phase inversion actually have a complex phase structure sketched in Figure 8. Graillat et al.³³ have observed the existence of smaller droplets (15–20 nm) besides the conventional larger droplets in their acrylamide inverse emulsion systems by TEM with freeze-fracture technique treatment. If there are droplets with such small sizes in the systems in the nearby regions of the phase inversion, these droplets are easily embedded into the larger dispersed toluene droplets in the apparent O/W-type emulsions, so as coalescence of the dispersed toluene droplets occurs, these small aqueous droplets can be further brought into the separated toluene layers. Therefore, coalescence of the dispersed toluene droplets exists undoubtedly in the course of phase separation for the O/W-type emulsions, at least in the nearby regions of the phase inversion.

For the W/O-type emulsions, the volume of toluene layers separated from the emulsions after polymerization in the nearby regions of the phase inversion was also larger than the toluene volume added initially, which can also be explained by the bimodal distribution of the lattice particles; i.e., quite a large amount of smaller particles still resided in the toluene layer after sedimentation of conventional lattice particles in the bottom to form more concentrated W/O emulsions. As for the apparent W/O-type emulsions in the nearby regions of the phase inversion, whether smaller toluene droplets were embedded into the dispersed aqueous droplets we cannot verify in this work yet.

3.4. Influence of Acrylamide Concentration on the Emulsion Stability and Phase Behavior. Acrylamide plays a role of cosurfactant in an emulsion,^{31,32} which will enhance the strength of the W/O interface layer in the emulsion and make the emulsion stable. The W/O-type emulsions in Figures 3–7 before polymerization are more stable than those after polymerization at a fixed concentration of acrylamide (33.33%, w/w),

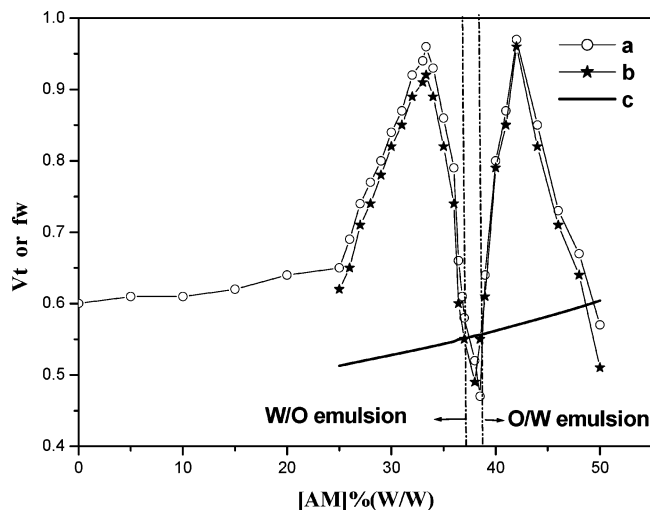


Figure 9. V_t as a function of acrylamide concentration for the emulsions before (a) and after (b) polymerization. Recipe: 50 mL of toluene, 40 mL of water, 6.0 g of Span80 + OP10, HLB = 5.7. (c) Volume fraction of acrylamide aqueous solution in the emulsions (f_w).

which may be due to the cosurfactant effect of acrylamide. Acrylamide as a cosurfactant tends to gather in the region of the interface layer before polymerization, while it will be pulled into the inside of the droplets after polymerization for W/O-type emulsions, which leads to emulsion instability. For the O/W emulsions (Figure 7), the cosurfactant effect of acrylamide on the emulsion stability (V_t) is partly offset because the motion of toluene as a dispersed phase is limited by a steep increase of the viscosity of the polyacrylamide aqueous solution as a continuous phase after polymerization.

The effect of acrylamide as a cosurfactant will enlarge the effective cross-sectional area of the surfactants at the interface,³¹ leading to an increase of the curvature radii of the droplets in an equilibrium state for W/O emulsions and a decrease of the curvature radii for O/W emulsions,³² which is similar to the effect of OP10 on the curvature radii. Therefore, it is expected that the increase of acrylamide concentration is equivalent to increasing the OP10 fraction for emulsion stability and phase behavior. The influence of acrylamide concentration on V_t and emulsion type at a fixed HLB value (5.7) is shown in Figure 9, which is indeed similar to that in Figure 7. The toluene volume fraction separated from the emulsions in the regions of the phase inversion is also larger than that added initially ($1 - f_w$), which indicates the separated toluene phases contain quite a large amount of smaller aqueous droplets. The data for the emulsion systems after polymerization in regions of acrylamide concentration lower than 25% are not given in Figure 9 because the emulsion systems were not stable in the course of polymerization. It was observed again here that the V_t value of the W/O emulsions after polymerization is smaller than that before polymerization.

The critical acrylamide concentration, in which the phase inversion takes place, should change with HLB value according to the equivalent influence of acrylamide concentration on the character of the emulsion systems and that of the hydrophilic OP10 fraction. Increasing the HLB value will lower the critical acrylamide concentration; i.e., the acrylamide concentration windows of forming acrylamide inverse emulsions are restricted by their HLB values. The phase diagram on the emulsion type at a fixed toluene/water ratio in the regions of 25–50% acrylamide concentration and 4.3 (pure Span80)–6.2 HLB value is shown in Figure 10. The systems in the zone under line 1 form W/O-type emulsions, the systems in the zone above line

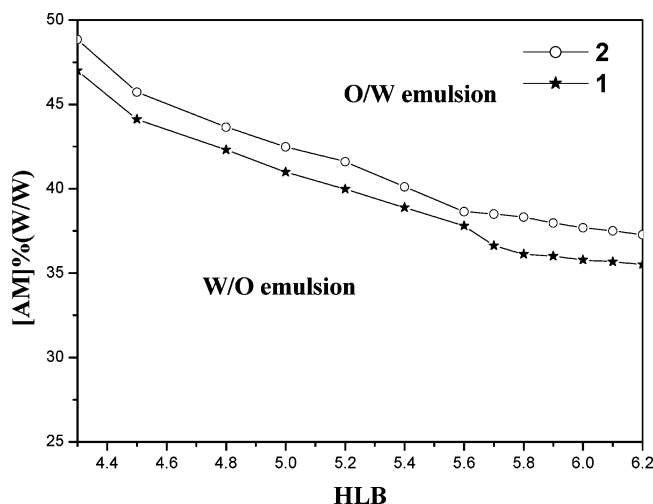


Figure 10. Phase diagram on the emulsion type. Recipe: 50 mL of toluene, 40 mL of water, 6.0 g of Span80 + OP10.

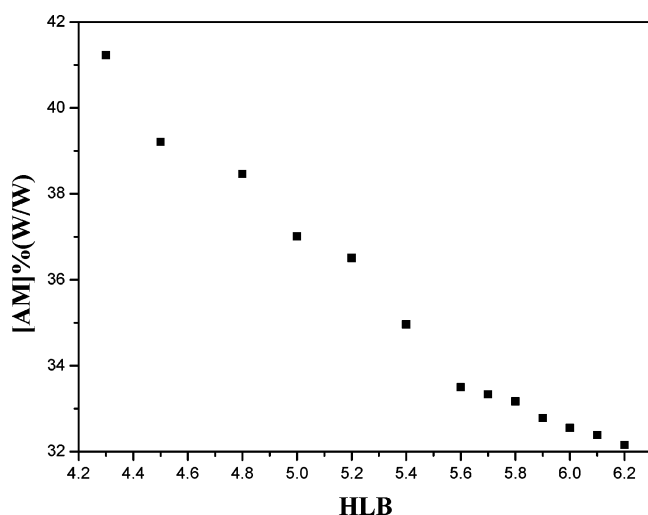


Figure 11. Corresponding relations between acrylamide concentration and HLB value for the most stable W/O emulsions. Recipe: 50 mL of toluene, 40 mL of water, 6.0 g of Span80 + OP10.

2 form O/W-type emulsions, and the zone between lines 1 and 2 is an interim zone of instable phase. The acrylamide concentration window of the inverse emulsion becomes wider with a decrease of the HLB value as expected.

Because of the effect of acrylamide as a cosurfactant, the emulsion stability depends not only on the HLB value but also on the acrylamide concentration. To obtain the most stable emulsion (maximum V_I), the best matching of acrylamide concentration is necessary for the type of emulsion. The above-mentioned equivalence principle of acrylamide concentration and HLB value provides a foundation for formulating a recipe to obtain a stable emulsion. The acrylamide concentration of forming the most stable W/O-type emulsion will become low with increasing HLB value. The corresponding relations between acrylamide concentration and HLB value in the most stable W/O-type emulsions at a fixed amount of the two surfactants and toluene/water ratio are shown in Figure 11, which reflects the above law.

4. Conclusions

In summary, we have investigated the stability and phase behavior of acrylamide-based emulsions, prepared with surfac-

tant blends consisting of lipophilic Span80 and hydrophilic OP10, before and after polymerization, elucidated two kinds of phase separation mechanisms caused by the toluene/water ratio, and found a rule of equivalence principle of acrylamide concentration and HLB value. All this work will provide a foundation for optimizing a recipe to obtain a stable acrylamide-based inverse emulsion by controlling these factors.

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