

## Influence of Temperature on the Phase Inversion of Chlorinated Polypropylene

Xiaoyang Ma,<sup>1</sup> Zemin Qiao,<sup>1</sup> Zhifeng Huang,<sup>1</sup> Xinli Jing,<sup>1</sup> Chaohui Gu,<sup>2</sup> Hanliang Tang<sup>3</sup>

<sup>1</sup>Department of Applied Chemistry, School of Science, Xi'an Jiaotong University, Xi'an 710049, People's Republic of China

<sup>2</sup>Zhejiang Desoul Chemical Technology Co., Ltd., Huzhou 313216, People's Republic of China

<sup>3</sup>Guangzhou Haoyu Chemical Industry Technology Co., Ltd., Guangzhou 510540, People's Republic of China

Correspondence to: X. L. Jing (E-mail: rgfp-jing@mail.xjtu.edu.cn)

**ABSTRACT:** In this study, the maleic anhydride modified chlorinated polypropylene (MCP) resin was emulsified by mixed ionic surfactants comprising sodium dodecyl sulfate (SDS) and sulfonated castor oil (SCO). The influence of temperature on the morphology of emulsion was studied through transitional and catastrophic inversion methods. The transitional inversion of emulsion from water-in-oil (W/O) to oil-in-water (O/W) was triggered by decreasing the temperature and the catastrophic inversion was achieved by increasing the weight fraction of water. The results of transitional and catastrophic inversion both indicated that the phase inversion of "ionic surfactant-MCP-water" system is easier to trigger at low temperatures than at high temperatures, which could be interpreted by the thermodynamic and hydrodynamic theory. Incomplete phase inversion occurred at low temperatures when the volume of water phase was small and emulsions with small particle size and narrow particle size distribution could only be obtained at an intermediate temperature. These results are of great importance for the preparation of stable polymer emulsions in food, cosmetics and paints industry. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40325.

**KEYWORDS:** coatings; colloids; morphology; phase behavior; surfactants

Received 1 August 2013; accepted 16 December 2013

DOI: 10.1002/app.40325

### INTRODUCTION

Adhesion to untreated polypropylene (PP) plastics is usually poor due to their low surface energy and thus the painting of PP requires a chemical or physical surface treatment procedure or the use of a special adhesion promoter to improve coating adhesion. Most adhesion promoters are based on solvent-borne chlorinated polypropylene (CPP), which are applied as adhesion promoting additives or primers.<sup>1–4</sup> Because of a large amount of volatile organic compounds (VOC) in the solvent-borne CPP, the environment-friendly water-borne CPP is becoming more and more popular in PP coating industry. The water-borne CPP is usually prepared through the emulsification of the solvent-borne CPP resin with additional surfactants, such as the blend of sodium dodecyl sulfate and sulfonated castor oil, for the spontaneous emulsification of the CPP resin which has few or no hydrophilic groups is almost impossible.

The water-borne CPP emulsion, a finely dispersed oil-in-water emulsion, is usually prepared by phase inversion method. Emulsion phase inversion is a process in which the curvature of the oil-water interface swaps its bending from one way to the other, and then the type of the emulsion changes in the "surfactant-

oil-water" (SOW) system. Generally, emulsion phase inversion can be achieved through two different patterns, either due to a shift in physicochemical formulation (such as temperature, salinity, oil properties, etc.), which is called transitional phase inversion, or by increasing the volume of continuous phase, which is called catastrophic phase inversion.<sup>5–7</sup> Phase inversion is a low-energy emulsification method, for the decrease in interfacial tension of the SOW system at phase inversion point tends to enhance the efficiency of stirring-mixing process and thus tends to produce small droplets.<sup>8</sup> The phase inversion method is widely used in food, cosmetics and paints industry to produce emulsions, which is especially useful in the emulsification of high-viscosity materials such as CPP resin, epoxy resin and other polymeric components to produce concentrated aqueous emulsions.<sup>9–13</sup>

There are two main viewpoints to explain the driving force of phase inversion, namely the thermodynamic theory and hydrodynamic theory. According to the thermodynamic theory, the phase inversion of SOW systems essentially depends on the relative affinity of the surfactant for the oil and water phase,<sup>14</sup> which is triggered due to the change of the hydrophilic-

lipophilic deviation (HLD) of surfactant, and the curvature of the oil-water interface determines the type of the emulsion. When  $HLD > 0$ , the surfactant exhibits a stronger affinity for oil and the emulsion morphology tends to be W/O. When  $HLD < 0$ , the surfactant exhibits a stronger affinity for water, and the emulsion morphology tends to be O/W. When  $HLD = 0$ , the surfactant exhibits an equal affinity for water and oil, and the emulsion morphology tends to be lamellar (such as W/O/W/O ...).<sup>15,16</sup> However, the thermodynamic theory can not explain all phase inversion phenomena and the hydrodynamic factors are sometimes considered to be the driving force of phase inversion. The kinetic modeling of phase inversion by hydrodynamic theory is based on the breakup and coalescence of the droplets.<sup>10</sup> According to the hydrodynamic theory, the viscosities of water and oil have great influence on the phase inversion process, and the phase with higher viscosity tends to be the dispersed phase. As has been pointed out by Salager,<sup>11,17</sup> the inversion mechanism and the fraction of dispersed phase at which the phase inversion is triggered are both affected by the viscosity of oil and water. When the viscosity of water phase is much higher than that of oil phase, the phase inversion from O/W to W/O emulsion occurs through the formation of pseudo-fibrous structure. When the viscosity of water phase inversion is equivalent to that of oil phase, the phase inversion occurs via the formation of a multiple emulsion.

It is well-known that the temperature has a great influence on the HLD of the surfactants. The ionic surfactant will change from lipophilic to hydrophilic when the temperature is increased for the effective fraction dissociation of the counterion will increase with the temperature.<sup>17–21</sup> So at low temperatures the thermodynamic factors make the “ionic surfactant–CPP–water” system tend to be W/O emulsion. However, at low temperatures, since the viscosity of the CPP resin is several orders of magnitude higher than that of water, the emulsion tends to be O/W according to the hydrodynamic theory. At high temperatures the thermodynamic and hydrodynamic factors both make the system tend to be O/W emulsion however the hydrodynamic driving will be weakened for the difference in viscosity between the CPP resin and water will be smaller under this condition. Thus, the influence of temperature on the morphology and stability of “ionic surfactant–CPP–water” emulsions still needs to be explored.

In this study, maleic anhydride modified chlorinated polypropylene (MCP) was emulsified by the ionic surfactants mixture comprising sodium dodecyl sulfate (SDS) and sulfonated castor oil (SCO) and stable water-borne polypropylene adhesion promoter was prepared. The transitional and catastrophic phase inversion methods were performed respectively to reveal the influence of temperature on the phase inversion of “ionic surfactant–MCP–water” system.

## EXPERIMENTAL

### Materials and Equipments

SCO (industrial products, 40 wt %) and SDS (AR) were obtained from Guangzhou Chuangsheng Chemical Technology of China and Tianjin Chemical Reagent Company of China, respectively. SCO and SDS were mixed in a 1 : 2 mass ratio and

used as surfactants. Xylene (AR) and MCP resin (industrial products, approximately 40 wt % solid content and viscosity 4.28 Pa·s at 25°C) came from Tianjin Hongyan Reagent Factory of China and Zhejiang Desoul Chemical Technology of China, respectively. The MCP resin was diluted to viscosity  $\sim 1$  Pa·s at 25°C and used as oil phase. Ammonia (28 vol %) and pH test paper were from Xi'an Sanpu Fine Chemical Industry of China and Shanghai Sansi of China, respectively. The ammonia was diluted to 5 vol % with distilled water and used as neutralizer.

Rotational viscometer SNB-1 and conductivity meter DDS-307 fitted with a DJS-1C cell were produced by Shanghai Precision Instrument of China. The stirring energy was supplied by a constant speed mixer S312-90 produced by Shanghai Shensheng Technology of China. Centrifuge TGL-16C and precision electronic balance BS110S were produced by Shanghai Anting Instrument of China and Sartorius Instrument of Germany, respectively.

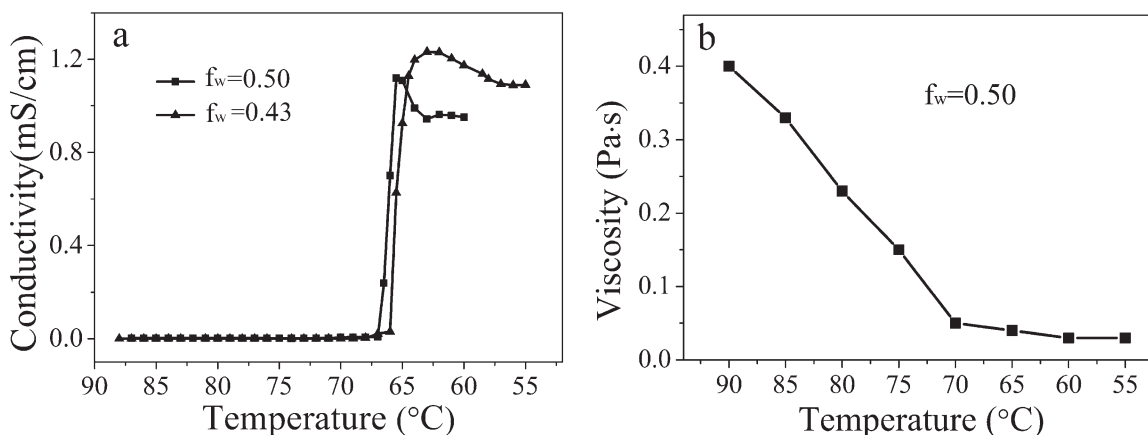
### The Emulsification of MCP

**Transitional Inversion.** The transitional inversion method was adopted to study the influence of temperature on the emulsion type of “ionic surfactant–MCP–water” system. Firstly, 80.00 g MCP resin (viscosity  $\sim 1$  Pa·s at 25°C) and 6.40 g surfactant were charged into a 500 mL capacity four-neck flask equipped with mechanical stirrer, conductivity meter cell, condenser, and thermometer. Secondly, the flask was placed in a 90°C oil bath and agitated at a stirrer speed of 800 rpm for 1 h. Then the water was added gradually into the four-neck flask until the mass fraction of water ( $f_w$ ) reached the preconcentrated value (0.43 and 0.50). Finally, the temperature of the emulsion was decreased at a constant rate of 1°C/min until the phase inversion took place. The conductivity and temperature of the emulsion were monitored during this process.

**Catastrophic Inversion.** Catastrophic inversion could be triggered by increasing the weight fraction of water. 80.00 g MCP resin (viscosity  $\sim 1$  Pa·s at 25°C) and 6.40 g surfactant were charged into a 500 mL capacity four-neck flask equipped with mechanical stirrer, conductivity meter cell, condenser and thermometer. The system was heated to the preconcentrated temperature (61, 71, 76, 81, and 86°C) while agitated at a stirrer speed of 800 rpm. After the MCP and surfactant were mixed adequately, 120.00 g water was dropped into the flask gradually at a rate of 2.00 g/min, and the catastrophic inversion was triggered during this process. The temperature was kept constant and the conductivity of the system was monitored. After all the water was added the O/W emulsion was agitated for 3 h at the preconcentrated temperature. Finally, the flask containing emulsion was placed in an ice bath and cooled down to room temperature quickly. The pH of the emulsion was adjusted to 8–9 by adding ammonia.

### Characterization

**Conductivity.** The conductivity of the SOW system was continuously monitored using a conductivity meter DDS-307 fitted with a DJS-1C cell dipped in the emulsion. All conductivity values measured at temperature  $T$  were transformed to conductivity at 25°C by the following equation (JJG376-2007, Verification Regulation of Electrolytic Conductivity Meters)



**Figure 1.** Conductivity (a) and viscosity (b) evolution of the “ionic surfactant–MCPP–water” system as the temperature decreases (from left to right) with surfactant/oil weight ratio 0.08.

$$\gamma_{25} = \frac{\gamma_T}{1 + \alpha(T - 25)}$$

where  $\gamma_T$  and  $\gamma_{25}$  are the measured value of conductivity at  $T$  and the calculated value of conductivity at 25°C, respectively.  $\alpha$  is a constant, which is taken as 0.02 (the value of pure water) in this article.

**Viscosity.** The viscosity of “ionic surfactant–MCPP–water” system during the procedure of transitional and catastrophic phase inversion were determined by Rotational viscometer SNB-1. About 5 mL sample was taken out of the flask every 10 min and the viscosity of the sample was determined immediately using rotor 4. The sample was put back to the flask immediately after the viscosity test.

**Droplet Size and Size Distribution.** Emulsion droplet size and size distribution were determined by dynamic laser light scattering instrument Zetasizer Nano ZS90 (Malvern Instrument). Measurements were carried out at 25°C with a scattering angle of 90°. The sample was prepared by diluting the emulsion to 1 wt % solid content with distilled water.

**Stability.** The stability of emulsion was tested by a centrifuge (TGL-16C). 5 mL emulsion was poured into a 5 mL centrifugal tube and centrifuged for 30 min at a speed of 3000 rpm. The appearance of the emulsion was observed and emulsion without flocculation and delamination phenomena meant excellent stability which demonstrated that the emulsion could be stored for more than six months stably. Poor stability of emulsion would cause flocculation and delamination phenomena after centrifugation.

## RESULTS AND DISCUSSION

### Transitional Inversion of the Emulsion

In this study, the viscosity of the MCPP resin at room temperature is three orders of magnitude higher than that of water while the conductivity of the MCPP resin is a few orders of magnitude smaller than that of water. When the phase inversion from W/O to O/W is triggered, the conductivity of the system shows precipitous increase to a very high value and the viscosity decreases to a very low value. So the distinct change of viscosity

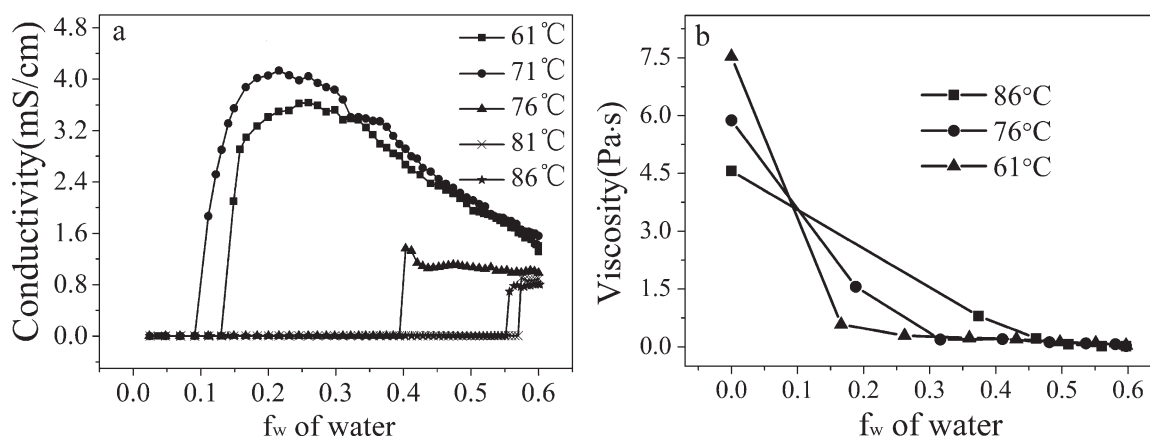
and conductivity can be used to characterize the process of phase inversion of the emulsion.

The transitional phase inversion of “ionic surfactant–MCPP resin–water” system was triggered by decreasing the temperature. While the temperature of the “ionic surfactant–MCPP resin–water” system was decreased regularly at a constant stir speed, phase inversion occurred and the type of the system changed from W/O to O/W, which indicated that the hydrodynamic factor played a major role. The evolution of the conductivity and viscosity as the temperature decreased from 90 to 60°C is shown in Figure 1. The conductivity of the emulsion rose precipitously and the viscosity decreased to a low value (about 0.04 Pa·s) when the temperature was decreased to ~67°C and simultaneously the emulsion split out abruptly. The low viscosity and sudden increase of conductivity indicated that the phase inversion from W/O to O/W had occurred.

Although the phase inversion had occurred when the viscosity and conductivity of the emulsion changed precipitously, it was not always complete. After the phase inversion occurred, when a small aliquot of the emulsion was withdrawn and poured immediately into water, it could be seen that a part of emulsion dispersed readily in water and the rest floated on water. This phenomenon might be attributed to the incomplete phase inversion of the emulsion. Phase inversion merely occurred in the location where the  $f_w$  is higher than the average  $f_w$  of the emulsion or the location where the temperature was lower than the average temperature of the system caused by fluctuations, and the O/W part dispersed in water while the W/O part floated on the water.<sup>14</sup> When the emulsion was cooled further, the conductivity tended to be constant after a small drop and the viscosity tended to be constant, meanwhile, the W/O part disappeared and the emulsion could be fully dispersed in water, which demonstrated that complete phase inversion was achieved. Thus the evolution of conductivity could be used to determine whether the phase inversion is complete.

### Influence of Temperature on the Catastrophic Inversion

The above results of transitional phase inversion indicated that the temperature had a great effect on the emulsion type. This conclusion was further verified by the catastrophic inversion



**Figure 2.** Variation of the conductivity (a) and viscosity (b) as water is added (from left to right) at different temperatures, with surfactant/oil weight ratio 0.08 and addition rate of water 2.0 g/min.

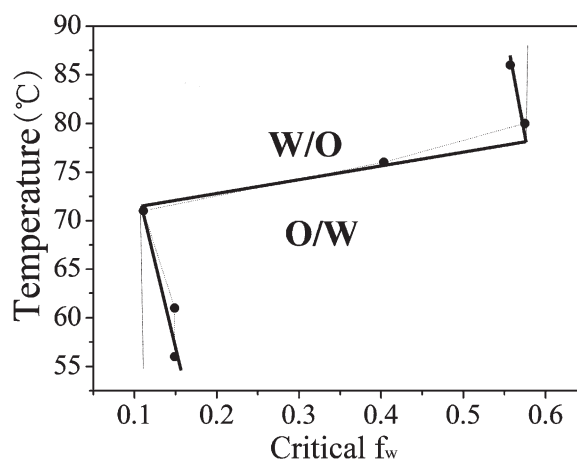
which was triggered by increasing the weight fraction of water. Figure 2 shows the variation of conductivity and viscosity as the water was added at different temperatures with surfactant/oil weight ratio 0.08 and addition rate of water 2.0 g/min. The phase inversion point corresponded to a critical mass fraction of water (critical  $f_w$ ) when the conductivity rose precipitously to a very high value and the viscosity decreased to a low value. Figure 3 shows the relationship between the critical  $f_w$  and temperature. The critical  $f_w$  increased with the temperature (Figures 2 and 3), which indicated that the O/W emulsion was easier to form at lower temperature.

The temperature range from 55 to 90°C could be divided into three regions due to the critical  $f_w$  (Figure 3), namely low temperature region, high temperature region, and the transitional temperature region. The temperature had little influence on the critical  $f_w$  in the low and high temperature regions, but had a great influence in the transitional temperature region. In general, the critical  $f_w$  s at high temperatures were much bigger than those at low temperatures, which indicated that the O/W emulsion was easier to form at low temperatures.

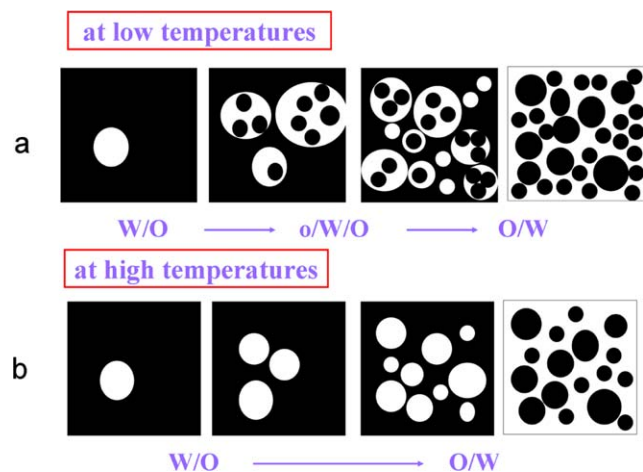
The phase inversion triggered at lower temperature needed smaller critical  $f_w$ , which might result from the formation of o/W/O multiple emulsion. At low inversion temperature such as 61 and 71°C, the conductivity of the emulsion increased suddenly [Figure 2(a)] and the viscosity decreased to a low value [Figure 2(b)] when the  $f_w$  was small, which indicated that the phase inversion had taken place and water had become the continuous phase. When a small part of emulsion at the phase inversion point was withdrew and dropped immediately into water, it could be seen that part of the emulsion dispersed readily in water and the rest floated on water, which was the feature of incomplete phase inversion. When more water was added after the phase inversion took place, the conductivity of the system decreased while the fraction of water-dispersible part of the emulsion increased and the floating part of emulsion decreased. The decrease of conductivity after the phase inversion point could be attributed to the incomplete phase inversion of the system. Density of conductive ions formed during the incomplete phase inversion in o/W/O emulsion region were high

which caused high conductivity. As water was added further, o/W/O part changed to O/W and the density of conductive ions decreased which caused the decrease of conductivity. When o/W/O emulsion disappeared the conductivity became constant. All those above phenomena indicated that the phase inversion continued during the addition of water after the phase inversion point.<sup>22</sup>

The incomplete phase inversion in the preparation of polymer emulsions has been widely studied. Yang et al.<sup>12</sup> found that the morphology of waterborne dispersions of epoxy resin was greatly effected by emulsification temperature and emulsifier concentration and incomplete phase inversion was easier to occur at low emulsifier concentration or high emulsification temperature. In our research when we focused on the influence of emulsification temperature on the morphology of MCPPE emulsions during the process of emulsification, we found that incomplete phase inversion was easier to occur at low temperatures which was proved by the dispersing property and conductivity evolution of the emulsion.



**Figure 3.** Critical  $f_w$  s at phase inversion point at different temperatures, with surfactant/oil weight ratio 0.08 and addition rate of water 2.0 g/min.



**Figure 4.** Possible morphology evolution of phase inversion process while water is added gradually at low (a) and high (b) temperatures. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

The critical  $f_w$  was much smaller at low temperatures, which could be explained by the hydrodynamic theory. Since the viscosity of MCPP was much higher than that of water, the MCPP resin phase tended to be the dispersed phase and the phase inversion took place through an emulsion morphology evolution of W/O to o/W/O and eventually to O/W emulsion [Figure 4(a)]. Thus, at low temperatures a small amount of water was enough to trigger the phase inversion because the O/W drops formed in the early stage could also be part of the dispersed phase.

When the inversion temperature was 76°C, the phase inversion occurred as soon as the  $f_w$  reached 40%, which was larger than the critical  $f_w$  at lower temperature. Under this condition the conductivity and particle size of the emulsion hardly changed when more water was added after the phase inversion occurred (Table I), which was the feature of complete phase inversion.

The critical  $f_w$  at higher temperatures was much larger than that at lower temperatures, which indicated that there might be no o/W/O emulsion formed before phase inversion occurred [Figure 4(b)]. When the emulsion temperature was high (such as 81 and 86°C), the inversion was not triggered until the  $f_w$  reached 55%, which was much higher than the critical  $f_w$  at lower temperatures. Tyrode<sup>23</sup> pointed out that when the SOW system was far from the optimum formulation, whether there was o/W/O emulsion or not, the inversion was found to take

**Table I.** The Particle Size of MCPP Emulsions with Different  $f_w$ s at 76°C

Sample	$f_w$	Average particle diameter (nm)	Polydispersity index
1	0.40	396	0.145
2	0.50	336	0.128
3	0.55	374	0.116
4	0.60	392	0.143

**Table II.** The Effect of Temperature on MCPP Emulsion Particle Size and Size Distribution ( $f_w = 0.6$ )

Sample	Dispersion temperature (°C)	Average particle diameter (nm)	Polydispersity index	Stability
5	61	892	0.307	Poor
6	71	388	0.384	Poor
7	76	126	0.204	Nice
8	81	604	0.327	Poor

place when the dispersed phase fraction reached a critical value. At high temperatures, the dispersed phase before inversion was water drops, while at low temperatures the dispersed phase before inversion included O/W drops and water droplets. So comparing with the phase inversion at low temperatures, the phase inversion at high temperatures could not be triggered until more water was added and the critical  $f_w$  was much larger. In addition, in the process of the catastrophic phase inversion triggered at high temperatures, the conductivity hardly changed after the phase inversion point and the emulsion could be dispersed in water immediately, which indicated that the phase inversion at phase inversion point was complete.<sup>22</sup>

The temperature not only affects the  $f_w$  of phase inversion, but also affects the particle size, polydispersity and stability of emulsion. When the inversion was triggered at 86°C, the emulsion product flocculated rapidly and delaminated in a few hours. When the inversion was triggered at 61, 71, or 81°C, the particle diameter and polydispersity index of emulsion were much larger and the stability of emulsion was also poor (Table II). While the inversion was triggered at 76°C, the particle diameters and polydispersity index of emulsion were smaller and the emulsion was stable. It is not difficult to understand. At high temperatures (81 and 86°C), the particles had strong mobility and were easier to coalesce which caused big particle size and polydispersity. While at low temperatures, due to the formation of o/W/O emulsion, the particle size and polydispersity were also big. As a result emulsion with small particle size and polydispersity could only be obtained at intermediate temperature.

#### Driving Force of Phase Inversion

In the “ionic surfactant–MCPP resin–water” system, the thermodynamic factors make the emulsion tend to be O/W at high temperatures and W/O at low temperatures, while hydrodynamic factors make the emulsion tend to be O/W all the time. The results of transitional phase inversion and catastrophic phase inversion demonstrate that the phase inversion of “ionic surfactant–MCPP resin–water” system could be explained by both the hydrodynamic theory and the thermodynamic theory. At low temperatures, the viscosity of MCPP was much higher than that of water and the hydrodynamics were the main driving force of phase inversion, while at high temperatures the difference of viscosity between MCPP resin and water became small and the influence of hydrodynamic factors was weakened, and as a result the thermodynamics became the main driving force.

According to Figure 3, the temperature range from 55 to 90°C was divided into three regions, and in the transitional temperature region the influence of temperature on critical  $f_w$  was much greater than that in the other two regions. The particle diameter and the polydispersity index of emulsion prepared at 76°C were much smaller than the emulsion prepared at other temperatures. This may be because that 76°C is the phase inversion temperature (PIT) of the system at which the efficiency of stirring–mixing process was high. So stable emulsion could only be obtained at appropriate intermediate temperature, which might result from the combined action of the hydrodynamic and thermodynamic factors.

## CONCLUSION

In the emulsification process of the “ionic surfactant–MCP–water” system, the temperature has a great influence on the type and particle size of emulsion. Both transitional inversion and catastrophic inversion indicate that the phase inversion of the “ionic surfactant–MCP–water” system from W/O to O/W is easier to trigger at low temperatures. Stable water-borne MCP emulsion with small particle size and narrow particle size distribution can only be obtained at appropriate intermediate temperature, which may result from the combined action of the hydrodynamic and thermodynamic factors.

## REFERENCES

1. Hintze-Brüning, H.; Borgholte, H. *Prog. Org. Coat.* **2000**, *40*, 49.
2. Schellekens, M.; Twene, D.; van der Waals A. *Prog. Org. Coat.* **2011**, *72*, 138.
3. Tang, S. Y.; Liu, D. Z.; Fan Z. L. *Phys. Chem. Liq.* **2006**, *44*, 531.
4. Tomasetti, E.; Vandorpe, S.; Daoust, D.; Boxus, T.; Marchand-Brynaert, J.; Poleunis, C.; Bertrand, P.; Legras, R.; Rouxhet, P. G. *J. Adhes. Sci. Technol.* **2000**, *14*, 779.
5. Solans, C.; Izquierdo, P.; Nolla, J.; Azemar, N.; Garcia-Celma, M. *J. Curr. Opin. Colloid Interface Sci.* **2005**, *10*, 102.
6. Iliá Anisa, A. N.; Nour, A. H.; Nour, A. H. *J. Appl. Sci.* **2010**, *10*, 3076.
7. Silva, F.; Peña, A.; Miñana-Pérez, M.; Salager, J.-L. *Colloids Surf.: A* **1998**, *132*, 221.
8. Galindo-Alvarez, J.; Boyd, D.; Marchal, P.; Tribet, C.; Perrin, P.; Marie-Bégué, E.; Durand, A.; Sadtler, V. *Colloids Surf.: A* **2011**, *374*, 134.
9. Jahanzad, F.; Saha, B.; Sajjadi, S.; Brooks, B. W. *Macromolecules* **2007**, *40*, 4182.
10. Xu, J.; Jamieson, A. M.; Qutubuddin, S.; Gopalkrishnan, P. V.; Hudson, S. D. *Langmuir* **2001**, *17*, 1310.
11. Galindo-Alvarez, J.; Sadtler, V.; Choplin, L.; Salager, J.-L. *Ind. Eng. Chem. Res.* **2011**, *50*, 5575.
12. Yang, Z. Z.; Xu, Y. Z.; Zhao, D. L.; Xu, M. *Colloid Polym. Sci.* **2000**, *278*, 1164.
13. Yang, Z. Z.; Xu, Y. Z.; Zhao, D. L.; Xu, M. *Colloid Polym. Sci.* **2000**, *278*, 1103.
14. Allouche, J.; Tyrode, E.; Sadtler, V.; Choplin, L.; Salager, J.-L. *Langmuir* **2004**, *20*, 2134.
15. Salager, J.-L.; Márquez, L.; Peña, A. A.; Rondón, M.; Silva, F.; Tyrode, E. *Ind. Eng. Chem. Res.* **2000**, *39*, 2665.
16. Sajjadi, S. *Langmuir* **2006**, *22*, 5597.
17. Rondón-González, M.; Madariaga, L. F.; Sadtler, V.; Choplin, L.; Márquez, L.; Salager, J.-L. *Ind. Eng. Chem. Res.* **2007**, *46*, 3595.
18. Salager, J. L.; Morgan, J. C.; Schechter, R. S.; Wade W. H.; Vasquez, E. *SPE J.* **1979**, *19*, 107.
19. Chen, S. H.; Chang, S. L. *J. Phys. Chem.* **1990**, *93*, 1907.
20. Anton, R. E.; Garces, N.; Yajure, A. *J. Dispers. Sci. Technol.* **1997**, *18*, 539.
21. Antóna, R.; Rivasb, H.; Salager, J.-L. *J. Dispers. Sci. Technol.* **1996**, *17*, 553.
22. Yang, Z.; Zhao, D.; Xu, Y.; Xu, M. *Chem. J. Chin. U (in Chinese)* **1999**, *20*, 809.
23. Tyrode, E.; Mira, I.; Zambrano, N.; Márquez, L.; Rondón-Gonzalez, M.; Salager, J.-L. *Ind. Eng. Chem. Res.* **2003**, *42*, 4311.