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Emulsion Polymerization of P (MMA-AA-EA) and Its Demulsifying Performance in Water/Oil Emulsion

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Abstract

Stable water-in-oil emulsions are produced in oil exploitation and cause many environmental and operational issues. In this paper, a co-polymer demulsifier is reported in detail; an emulsion polymerization method is used to prepare nano-P (MMA-AA-EA) with MMA, AA and EA as the monomers, DVB as the cross-linker and APS as the initiator. The resulting products are characterized by FT-IR. Furthermore, the surface tension and particles size analysis is investigated. The results show that the surface tension reduction is 10.66 mN/m at 20°C when the concentration of co-polymer is 1000 ppm and the average size is 76.99 nm. Moreover, the HLB of polymer is discussed specifically by changing the amount of AA. With the increase of AA, the HLB value of the polymer is increased accordingly. Besides, the demulsification performance of the co-polymer is also evaluated at different synthesis and demulsification conditions. It is showed that the maximum demulsification efficiency is 96% at 70°C for 60 min. The optimum concentration of demulsifier is 400 ppm when the amounts of AA and DVB are 1.4 g and 0.1 g, respectively. At last, the process of demulsification is showed under a microscope; the coalescence process of water droplets is indicated under the action of the demulsifier.

Keywords

Emulsion Polymerization, Polymer Demulsifier, W/O Emulsion,
Demulsifying Efficiency, Process of Demulsification

1. Introduction

Enhanced oil recovery (EOR) using water injection is gradually getting mature

in most of the oilfields worldwide. Although water and crude oil are two immiscible phases, highly stable water-in-oil (W/O) emulsions are likely to be produced due to the presence of interfacially active materials and fine solid particles accompanying with shear [1] [2] [3]. Crude oil produced in the form of emulsions causes a series of operational issues and oily wastewater [4] [5]. Therefore, it is of the utmost importance to demulsify the produced emulsions. These techniques are mainly chemical, biological, and physical demulsifications [6] [7] [8] [9] [10].

Chemical demulsification is a technique in which the film-thinning rate is enhanced and emulsion stability is lowered by using some chemicals called demulsifiers. According to their chemical structures and their applications, chemical demulsifiers will be classified into three different categories: polymeric surfactant, ionic liquids and nanoparticles [11] [12] [13]. Shehzad *et al.* reported that dendrimers have been considered widely because they are effective in various emulsions [14]. It is well known that nanoparticles modified polymeric surfactants are more effective compared with counterpart polymeric surfactants. Nanoparticle-based demulsifiers showed a great potential to break an emulsion, but it has not been researched drastically. Abdel-Raouf *et al.* synthesized various ethoxylated sugar based amine surfactants and studied various factors which affect the performance of demulsification [15]. The demulsification efficiency can be influenced by temperature, concentration of demulsifier and other factors. The hydrophilicity or lipophilicity of a demulsifier is the determining factor in the identification of its optimum dosage for breaking an emulsion [16]. Alsabagh *et al.* synthesized polymeric surfactants of alkene oxide diesters with different Hydrophile-Lipophile Balance (HLB) values and molecular weights [17]. The HLB of a polymer was varied by altering the degree of propoxylation and ethoxylation.

In this paper, poly (methyl methacrylate-ethyl acrylate-acrylic acid) demulsifier was synthesized by emulsion polymerization. The optimum demulsification condition was performed to investigate the demulsifier performance. In detail, the influence of HLB and cross-linker of polymer on demulsification were discussed. Furthermore, optical microscope was used investigated demulsification process.

2. Experimental

2.1. Materials

Methyl methacrylate (MMA), Methyl acrylate (EA), and Acrylic acid (AA), (AR grade) bought from National Chemicals Co., Ltd., are kept in brown bottles and stored in a refrigerator at below 5°C. Ammonium persulfate (APS), divinylbenzene (DVB), methylbenzene all are bought from Tianli Chemicals Co., Ltd (Tianjing, China). Sodium alkylphenol ether sulfosuccinate (MS-1) and po1yoxyethylene octylphenol ether (OP-10) are supplied by Hainan Petrochemical Company (Jiangsu, China).

2.2. Synthesis of P (MMA-AA-EA)

An emulsion polymerization method is used to prepare P (MMA-AA-EA) with MMA, AA and EA as the monomers, DVB as the cross-linker and APS as the initiator. First of all, 0.20 g MS-1 and 0.20 g OP-10 are added to 70 g deionized water in a 250 mL three-mouth flask which is properly assembled for heating under reflux, dropping funnel, thermometer. Afterwards, the flask is heated to 75°C, 10 mL APS initiator solution is gradually added into the flask which is prepared by dissolving 0.2 g APS into 20 mL deionized water. Subsequently, the mixture of 0.5 g EA, 8.0 g MAA, and a certain amount of AA and DVB are dropped into flask with a constant pressure funnel. Finally, the reaction temperature is maintained at 75°C for 3 h, and then gradually cooled to room temperature. And the correspond products is purified by using deionized water and vacuum freeze-drying. Figure 1 shows reactions schematic of as-prepared P (MMA-AA-EA).
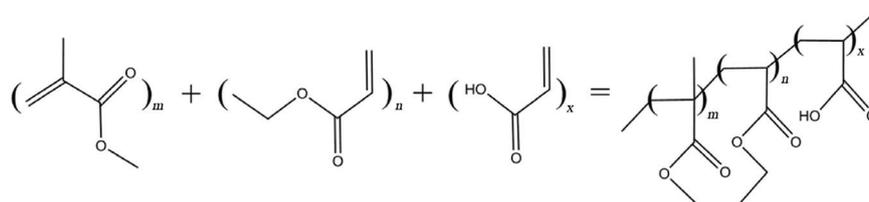

Figure 1. Synthesis of P (MMA-AA-EA).

2.3. Preparation of W/O Emulsion

Crude oil is supplied by Block115 in Fushan Oilfield. And the physical analysis of the crude oil was shown in Table 1. W/O emulsion is prepared by adding 70-vol% water to the crude oil and then the two phases are mixed at 50°C. And then crude W/O emulsion is completely stirred at high speed for 30 min by CJSS-B12K type frequency conversion high-speed mixer. At last, the emulsion is kept stable for 24 h without water or oil separated.

Table 1. Physical analysis date of crude oil.

Viscosity/(mPa·s^{-1})	Freezing point/°C	Asphaltene/%	Colloid/%	Microcrystalline wax/%	S/%	Water content/%
200.4	25	16.5	9.3	16.8	0.12	1.56

2.4. Demulsification Performance Test

The demulsification performance test is evaluated according to SY/t5281-2000 (Industrial standard). The polymer is dissolved in an organic solvent and prepared into a demulsifier solution with concentration of 10 g/L. The test is carried out in 25 ml graduated prescription bottles. Firstly, an amount of demulsifier is added into 20 mL of emulsion, and then the bottles are shaken vigorously 200 times by hand within 2 minutes. Afterward, the bottles are immediately returned into the as-settled water bath. The demulsifying efficiency is measured by calculating the amount of water removed from the emulsion sample.

$$DE = \frac{C_o - C_d}{C_o} \times 100\% \tag{1}$$

where C_o is initial water concentration before water separation, C_d is water concentration after water separation.

3. Results and Discussion

3.1. IR Spectra Analysis

The infrared spectrometer is equipped with a 15 cm optical path and a ZnSe gas pool. The scanning spectrum range is 4000 - 400 cm^{-1}. Each sample is scanned by mid-infrared DTG detector for 16 times. The samples are made by KBr compression. The IR spectra of the copolymer are shown in **Figure 2**. It is obvious that the absorption peaks at 2952.35 cm^{-1} and 2848.36 cm^{-1} are ascribed to the C-H stretching vibrations of -CH$_2$. The characteristic peaks of the ester at 1739.32 cm^{-1} (C=O stretching) and 1145.00 cm^{-1} (C-O stretching) are ascribed to carbonyl groups in MMA and EA. In addition, the peaks at 1450.10 cm^{-1} and 1224.83 cm^{-1} belong to bending vibration absorption peak of C-H and the asymmetric stretching peak of C-O-C, respectively. The absorption peak at 987.86 cm^{-1} is the characteristic peak of ethyl acrylate. These results have confirmed that the polymerization of vinyl monomers occurs.
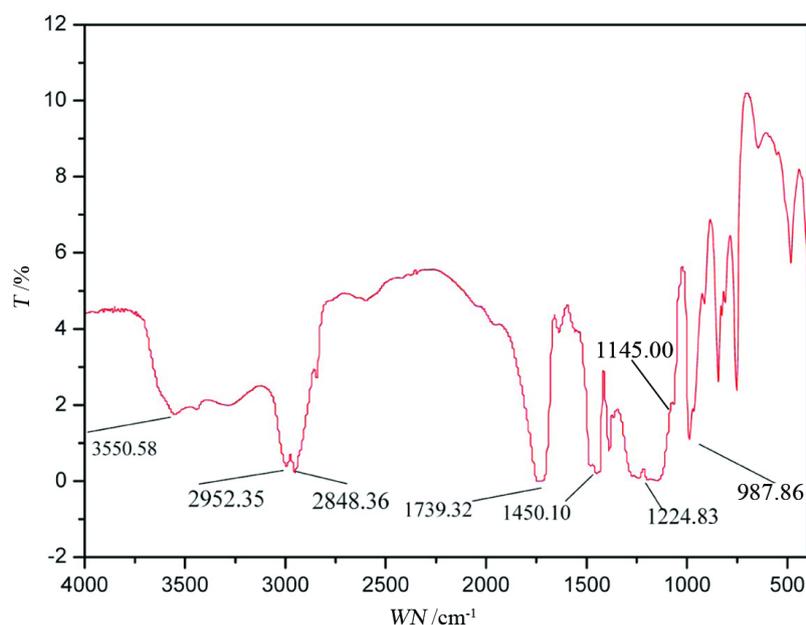

Figure 2. FT-IR spectrum of P (MMA-AA-EA).

3.2. Test of Surface Tension

The surface tension of the polymer is tested by hanging piece methods (platinum plate size: 19.9 mm × 10 mm × 0.2 mm, accuracy: 0.01 mN/m) at 20°C. The sample is synthesized by using 1.4 g AA, 8.0 g MMA and 0.5 g EA as monomers. The relationship of surface tension and concentration of P (MMA-AA-EA) is

shown in **Figure 3**. The surface tension is reduced with the increase of the amount of polymer. When the amount of polymer is critical micelle concentration (CMC), the surface tension will no longer be changed. With the increase of the amount of polymer, the polymer molecule is gathered into micelles. The interaction between molecules is equilibrium. The surface tension reduction (π_{cmc}) is 10.66 mN/m ($\pi_{cmc} = \gamma_0 - \gamma_{cmc}$). It means that the surface tension of a solution was reduced by the polymer. The parameters such as Gibbs free energy of micellization (ΔG_{mic}) and Gibbs free energy of adsorption (ΔG_{ads}) can be obtained by Gibbs absorption equations [18]. The result of calculations indicates that ΔG_{mic} is −26.79 KJ/mol and ΔG_{ads} is −37.83 KJ/mol.It means that the polymer tends to be adsorbed to the interface of emulsion rather than micelle. Then the adsorption will be accompanied with micellization at last. This means that the micellization of these polymeric esters in the solution is inhibited more than the adsorption at the liquid/air interface, or the adsorption is facilitated more than micellization.
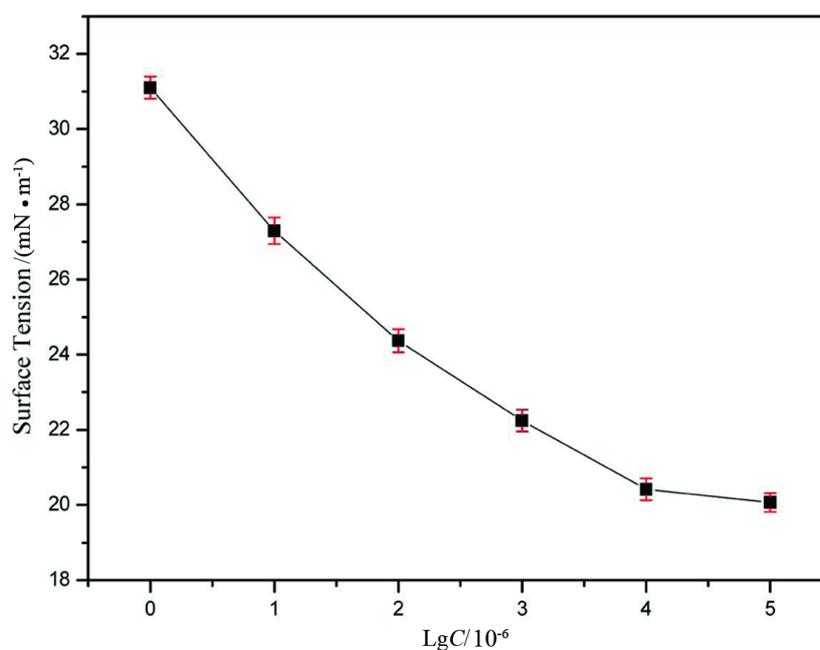

Figure 3. Surface tension versus Lg C of P(MMA-AA-EA) in toluene solution at 20°C.

3.3. Particle Size Distribution

The size of the polymer is tested at Malvern nano ZS laser particle size analyzer at 25°C. The particle size distribution of P (MMA-AA-EA) is shown in **Figure 4**. The polymer is distributed at the size of 30 - 210 nm. And the average size is 76.99 nm. It is believed that the particle size and distribution of the polymer are smaller and narrow. Therefore, it has larger surface area, and it would improve the solubility of polymer. Furthermore, the polymer can be dispersed in the emulsion more uniformly and adsorbed on the water/oil interface rapidly to replace the nature emulsifiers.
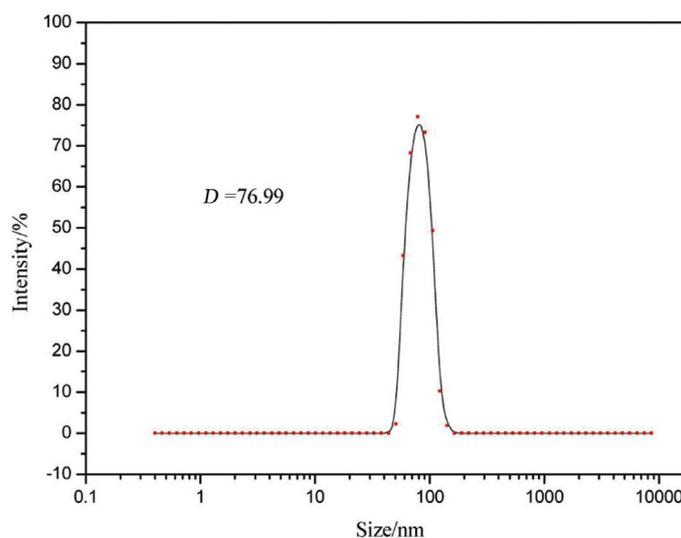
Figure 4. Size distribution of P (MMA-AA-EA).

Effect of Concentration of Polymer on Demulsifying Performance

When the amount of AA is 1.4 g, different amount of demulsifiers are added into the W/O emulsion at 70°C. The results are shown in **Figure 5**. When the concentration of emulsifier is 100 ppm, there is no demulsifying phenomenon because the emulsifier is not enough to replace the nature emulsifiers. Therefore, the interfacial film cannot be ruptured and the coalescence of oil droplets cannot be triggered. With the concentration of emulsifier increasing from 200 to 400 ppm, demulsification efficiency also increases. Furthermore, the adsorption rate of emulsifier increases with its amount at the same time. When the concentration of emulsifier is 400 ppm and the emulsion is heated for 60 min, the demulsification efficiency is 96%. With the increase of the concentration of emulsifier, more natural emulsifiers are replaced. And then the demulsification efficiency is increased.
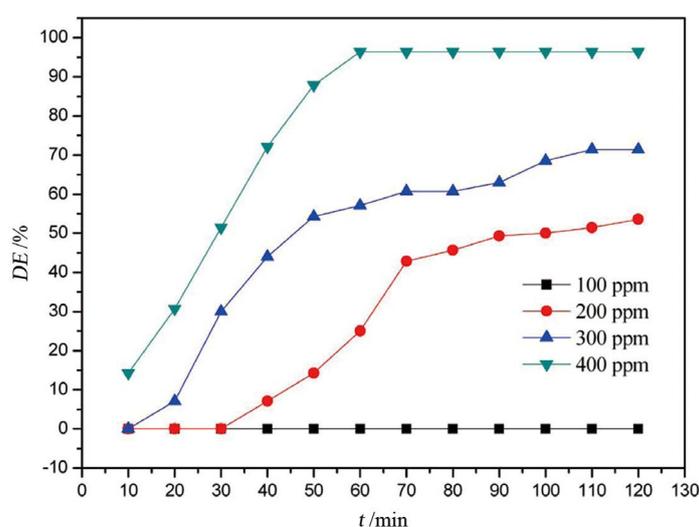

Figure 5. The effect of different concentrations of polymer on the demulsifying performance.

3.4. Effect of Demulsification Conditions

The demulsification of different amount of polymers in W/O emulsion is shown in Figure 6. The definition of water phases is influenced by different amount of polymers. The most clear water phase separated from emulsion is the cylinder in Figure 6(d). Kokal *et al.* pointed that demulsifiers was also surface-active agents like the emulsifier [19]. And high concentration of demulsifier may prone to overdosing. It is obvious that the water phase of Figure 6(e) was less clear than Figure 6(d).
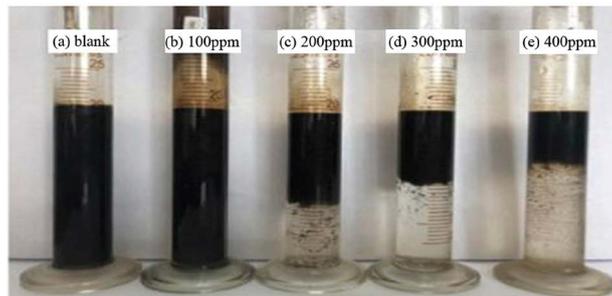

Figure 6. The effect of concentration of polymer on demulsifying performance ((a): blank; (b): 100 ppm; (c): 200 ppm; (d): 300 ppm; (e): 400 ppm).

Effect of Temperature on Demulsifying Performance of Polymer

It is shown in Figure 7 that the demulsification efficiency presents an obvious increasing trend with the demulsification temperature increased from 60°C to 75°C. As the result demonstrates that the demulsifying efficiency is only 58.26% at 60°C. In contrast, as the temperature is reached up to 70°C, it is found that the efficiency of demulsification is about 94.78%. On the one hand, the rise of the temperature would cause the reduction of viscosity and the mechanical strength of oil/water interface. One the other hand, the rise of the temperature would promote the kinetics of water dropt and increase the difference of water-oil phase density (Brownian motion). It is demonstrated that the above consequence may contribute for effective coalesce and aggregation of water drops and the separation of crude oil emulsions.
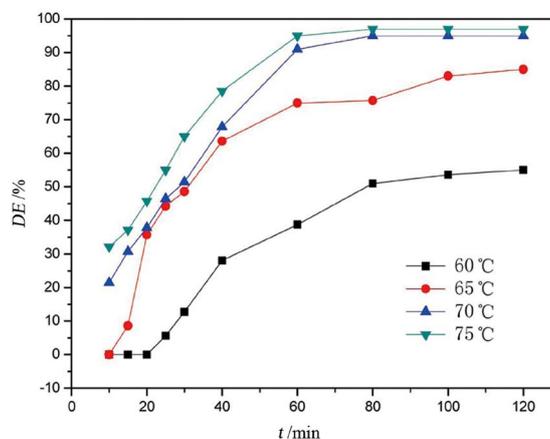

Figure 7. The effect of temperature on demulsifying performance of polymer.

3.5. Effect of Synthesis Conditions

3.5.1. Effect of AA on Demulsifying Performance of the Polymer

The demulsifying performance of polymer in W/O emulsion is tested by using the same synthesis conditions with different amount of AA at 70˚C under the concentration of 400 ppm. It indicates that the demulsification efficiency is influenced by the different amount of AA (Figure 8). As shown in Figure 8, the efficiency of demulsifiers with different doses of AA increases gradually at first and becomes almost constant. As for the AA of 1.4 g, demulsification efficiency increases gradually to 91% after 60 min, while AA of 0.6 g is almost constant after 80 min. It indicates that the demulsification speed of demulsifiers with 1.4 g AA is much more rapidly compared with others. It means that the speed of demulsification but not the demulsification efficiency was influenced by the amount of AA.
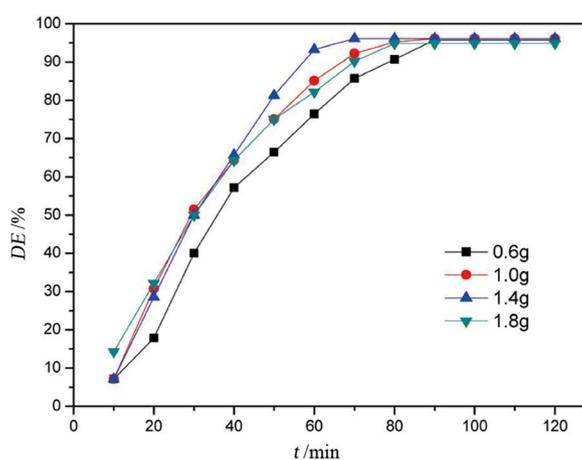

Figure 8. The effect of AA on demulsifying performance of the polymer.

The HLB of the emulsifier is the most important parameter, which shows its simultaneous attraction to oil and water [20]. When the natural emulsifiers (aspartames, resins, carboxylic acid, clay and waxes) in W/O emulsion are replaced by a polymer, the emulsifier with high HLB has a strong attraction to the water phase. It is very attractive to water in W/O emulsion, which is conducive to water separated from the emulsion [21]. The HLB of polymer is changed by different amount of AA. When the HLB of the polymer is increased, more polymers are dissolved in aqueous phase and increased the interface concentration between aqueous phase and oil phase. It indicates that oil in emulsion is more likely to be moved up to oil phase.

Alsabagh *et al.* pointed out that the HLB value was estimated by:

$$w(\mathrm{HLB}) = 20\left[\frac{m(\mathrm{MH})}{m(\mathrm{MH}) + m(\mathrm{ML})}\right] \qquad (2)$$

where $m(\mathrm{MH})$ is formula weight of the hydrophilic portion of the molecules and $m(\mathrm{ML})$ is the formula weight of the lipophilic (hydrophobic) portion of the molecules [17].

The *w*(HLB) of the polymer of different amount of AA is shown in Table 2. When the amount of AA is increased, the *w*(HLB) value of the polymer is increased accordingly.

Table 2. *w*(HLB) of polymers at different amount of AA.

Weight/g			mole/mol			w(HLB)/1
AA	MMA	EA	AA	MMA	EA	
0.6	8	0.5	0.0083	0.08	0.005	1.78
1.0	8	0.5	0.0139	0.08	0.005	2.81
1.4	8	0.5	0.0194	0.08	0.005	3.72
1.8	8	0.5	0.0250	0.08	0.005	4.55

The solubility of the polymer in an oily solvent is also adjusted while improving the attractiveness of the polymer to the aqueous phase of the W/O emulsion droplets.

When HLB is low, the system is difficult to form the sharp interface separation. Similarly, when HLB is too high, too much of demulsifier is dissolved in the water phase leading to the reduction of oil/water separation ability. Therefore, the two different trends will inevitably result in the best suitable HLB.

3.5.2. The Effect of Cross-Linkers on Demulsifying Performance of the Polymer

The effect of different amount of cross-linkers on the demulsifying performance of polymer in W/O emulsion is investigated at 70°C. Four kinds of polymers with different amount of cross-linker are obtained by using 0 g, 0.1 g, 0.2 g and 0.3 g cross-linkers respectively. The demulsification performance of polymers is shown in Figure 9. A small amount of cross-linker used in the polymer will enlarge emulsification efficiency. It is known that the molecular weight of the polymer is increased by cross-linker. A higher molecular weight of the polymer is more effective in replacing natural emulsifiers of water/oil interface. But the polymer with high molecular weight is hard to be dissolved in a solvent and W/O emulsion. Therefore, it is less effective when the amount of cross-linker is 0.2 g and 0.3 g. The synthetice mulsion strength of polymer is optimized and its solubility is reduced extremely.
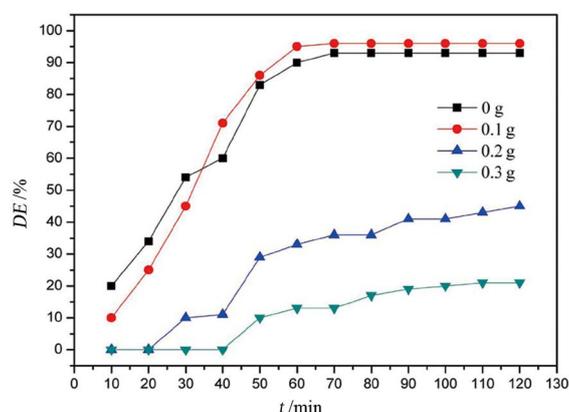

Figure 9. The effect of cross-linker on demulsifying performance of the polymer.

3.6. The Process of Demulsification under Microscope

Polymers of 300 ppm are added into W/O emulsion at 70°C for 10 minutes. A drop of the emulsion is magnified 100 times under the microscope. The bright spot in the picture is the water phase. Pictures of the emulsion are taken every two minutes three times. It is shown in **Figure 10** that water droplets are aggregated and merged into larger ones. The little water droplets are "eaten" by larger ones [22]. Furthermore, two large water droplets are gathered into a huge one marked with red arrows in **Figure 10**. The results elucidate that the interface of the emulsion is destroyed by the demulsifier during the initial stage of emulsification. It means that the droplet has a process of aggregation and the water is accumulated in large quantities under the action of demulsifier. At the later stage of the demulsification process, the water droplets are accumulated in large droplets and then settled under the action of gravity, and the nearly and completely oil-water phase separation could be achieved.
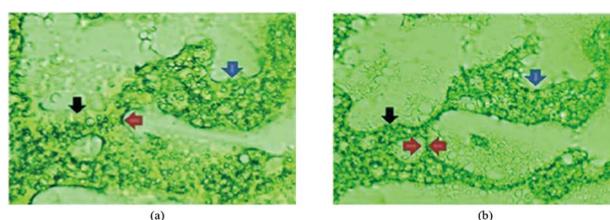

(a)   (b)

Figure 10. The microscopic view of demulsification heated at 70°C for 10 minutes.

A drop of emulsion with demulsifier of 300 ppm is magnified 100 times under the microscope. It is heated at 70°C for 5, 10, 15 and 20 min, respectively. As it is shown in **Figure 11**, the size of water droplets is increased obviously at different moments. Kang *et al.* pointed out that the action of the flocculation between water droplets overcame the inhibition of the W/O film to coalesced [23]. And then the water droplets which were separated from W/O emulsion were well-distributed in the emulsion. After that the water droplets were coalesced completely and the transparent water phase could appear on the bottom. On the other hand, the coalescence of the water droplets in the remaining emulsion could promote the quick sedimentation.
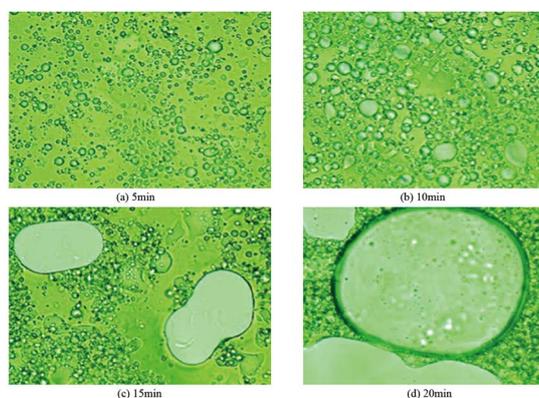

(a) 5min   (b) 10min

(c) 15min   (d) 20min

Figure 11. The microscopic view of demulsification heated at 70°C for different times ((a) 5 min; (b) 10 min; (c) 15 min; (d) 20 min).

4. Conclusions

1) In summary, a fast and efficient way is reported to separate water from W/O emulsion by using nano-P (MMA-AA-EA) as a demulsifier. It is found that 96% water is removed from the W/O emulsion within 60 min under the optimal conditions. The optimal reaction conditions are as follows: the amount of AA is 1.4 g; the amount of cross-linker is 0.1 g. And the demulsification conditions are as follows: the temperature is 70˚C; the amount of demulsifier is 400 ppm.

2) The surface tension reduction is 10.66 mN/m at 20˚C when the concentration of copolymer is 1000 ppm and the average size is 76.99 nm.

3) The process of demulsification is observed under a microscope. It is believed that a coalescence process of water droplets is taken place when the polymer is added into the W/O emulsion.

Acknowledgements

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

References

[1] Nikkhah, M., Tohidian, T., Rahimpour, M.R., *et al.* (2015) Efficient Demulsification of a Water-in-Oil Emulsion by a Novel Nano-Titania Modified Chemical Demulsifier. *Chemical Engineering Research and Design*, **94**, 164-172.
https://doi.org/10.1016/j.cherd.2014.07.021

[2] Razi, M., Rahimpour, M.R., Jahanmiri, A., *et al.* (2011) Effect of a Different Formulation of Demulsifiers on the Efficiency of Chemical Demulsification of Heavy Crude Oil. *Journal of Chemical & Engineering Data*, **56**, 2936-2945.
https://doi.org/10.1021/je2001733

[3] Pensini, E., Harbottle, D., Fan, Y., *et al.* (2014) Demulsification Mechanism of Asphaltene-Stabilized Water-in-Oil Emulsions by a Polymeric Ethylene Oxide-Propylene Oxide Demulsifier. *Energy & Fuels*, **28**, 6760-6771.
https://doi.org/10.1021/ef501387k

[4] Hao, L., Jiang, B., Zhang, L., *et al.* (2016) Efficient Demulsification of Diesel-in-Water Emulsions by Different Structural Dendrimer-Based Demulsifiers. *Industrial & Engineering Chemistry Research*, **55**, 1748-1759.
https://doi.org/10.1021/acs.iecr.5b04401

[5] Fang, S., Chen, T., Wang, R., *et al.* (2016) Assembly of Graphene Oxide at the Crude Oil/Water Interface: A New Approach to Efficient Demulsification. *Energy & Fuels*, **30**, 3355-3364. https://doi.org/10.1021/acs.energyfuels.6b00195

[6] Huang, X., Xiong, Y., Yin, W., *et al.* (2016) Demulsification of a New Magnetically Responsive Bacterial Demulsifier for Water-in-Oil Emulsions. *Energy & Fuels*, **30**, 5190-5197. https://doi.org/10.1021/acs.energyfuels.6b00687

[7] Almarouf, H.S., Nasser, M.S., Al-Marri, M.J., *et al.* (2015) Demulsification of Stable

Emulsions from Produced Water Using A Phase Separator with Inclined Parallel Arc Coalescing Plates. *Journal of Petroleum Science & Engineering*, **135**, 16-21. https://doi.org/10.1016/j.petrol.2015.08.005

[8] Chen, Z., Peng, J., Ge, L., *et al.* (2015) Demulsifying Water-in-Oil Emulsions by Ethyl Cellulose Demulsifiers Studied Using Focused Beam Reflectance Measurement. *Chemical Engineering Science*, **130**, 254-263. https://doi.org/10.1016/j.ces.2015.03.014

[9] Akbari, S., Nour, A.H., Jamari, S.S., *et al.* (2016) Demulsification of Water-in-Crude Oil Emulsion via Conventional Heating and Microwave Heating Technology in Their Optimum Conditions. *Social Science Electronic Publishing*, **10**, 66-74.

[10] Liang, J., Du, N., Song, S., *et al.* (2015) Magnetic Demulsification of Diluted Crude Oil-in-Water Nanoemulsions Using Oleic Acid-Coated Magnetite Nanoparticles. *Colloids & Surfaces: A Physicochemical & Engineering Aspects*, **466**, 197-202. https://doi.org/10.1016/j.colsurfa.2014.11.050

[11] Abullah, M.M.S., *et al.* (2016) Synthesis and Application of Amphiphilic Ionic Liquid-Based on Acrylate Copolymers as Demulsifier and Oil Spill Dispersant. *Journal of Molecular Liquids*, **219**, 54-62. https://doi.org/10.1016/j.molliq.2016.03.011

[12] Rajak, V.K., Singh, I., Kumar, A., *et al.* (2016) Optimization of Separation of Oil from the Oil-in-Water Emulsion by Demulsification Using Different Demulsifiers. *Liquid Fuels Technology*, **34**, 1026-1032. https://doi.org/10.1080/10916466.2016.1181654

[13] Fang, S., Chen, T., Chen, B., *et al.* (2016) Graphene Oxide at Oil-Water Interfaces: Adsorption, Assembly & Demulsification. *Colloids & Surfaces: A Physicochemical & Engineering Aspects*, **511**, 47-54. https://doi.org/10.1016/j.colsurfa.2016.09.058

[14] Shehzad, F., Hussein, I.A., Kamal, M.S., *et al.* (2017) Polymeric Surfactants and Emerging Alternatives Used in the Demulsification of Produced Water: A Review. *Polymer Reviews*, **58**, 63-101. https://doi.org/10.1080/15583724.2017.1340308

[15] Abdel-Raouf, E.S., Abdul-Raheim, A.R.M. and Abdel-Azim, A.A.A. (2011) Surface Properties and Thermodynamic Parameters of Some Sugar-Based Ethoxylated Amine Surfactants: 1-Synthesis, Characterization, and Demulsification Efficiency. *Journal of Surfactants & Detergents*, **14**, 113-121. https://doi.org/10.1007/s11743-010-1200-0

[16] Zolfaghari, R., Fakhru'L-Razi, A., Abdullah, L.C., *et al.* (2016) Demulsification Techniques of Water-in-Oil and Oil-in-Water Emulsions in Petroleum Industry. *Separation & Purification Technology*, **170**, 377-407. https://doi.org/10.1016/j.seppur.2016.06.026

[17] Alsabagh, A.M., Hassan, M.E., Desouky, S.E.M., *et al.* (2016) Demulsification of W/O Emulsion at Petroleum Field and Reservoir Conditions Using Some Demulsifiers Based on Polyethene and Propylene Oxides. *Egyptian Journal of Petroleum*, **25**, 585-595. https://doi.org/10.1016/j.ejpe.2016.05.008

[18] Sabagh, A.M.A., Kandil, N.G., Badawi, A.M., *et al.* (2000) Surface Activity and Thermodynamic of Micellization and Adsorption for Isooctylphenolethoxylates, Phosphate Esters and Their Mixtures with n-Diethoxylatedperfluorooctanamide. *Colloids & Surfaces: A Physicochemical & Engineering Aspects*, **170**, 127-136. https://doi.org/10.1016/S0927-7757(00)00475-1

[19] Al-Sabagh, A.M., Nasser, N.M. and Khamis, E.A. (2014) Demulsification of Crude Oil Emulsions Using Ethoxylated Aliphatic Amine Polyesters as Novel Demulsifiers. *International Journal of Science and Research*, **3**, 1171-1183.

[20] Ojinnaka, C.M., Ajienka, J.A., Abayeh, O.J., *et al.* (2016) Formulation of Best-Fit Hydrophile/Lipophile Balance-Dielectric Permittivity Demulsifiers for Treatment of Crude Oil Emulsions. *Egyptian Journal of Petroleum*, **25**, 565-574.

https://doi.org/10.1016/j.ejpe.2015.12.005

[21] Feng, X., Mussone, P., Gao, S., *et al.* (2010) Mechanistic Study on Demulsification of Water-in-Diluted Bitumen Emulsions by Ethylcellulose. *Langmuir*, **26**, 3050-3057. https://doi.org/10.1021/la9029563

[22] Li, Z., Yin, S., Tan, G., *et al.* (2016) Synthesis and Properties of Novel Branched Polyether as Demulsifiers for Polymer Flooding. *Colloid & Polymer Science*, **294**, 1943-1958. https://doi.org/10.1007/s00396-016-3956-x

[23] Kang, W., Guo, L., Fan, H., *et al.* (2012) Flocculation, Coalescence and Migration of Dispersed Phase Droplets and Oil-Water Separation in Heavy Oil Emulsion. *Journal of Petroleum Science & Engineering*, **81**, 177-181. https://doi.org/10.1016/j.petrol.2011.12.011