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Study of the effects of ionic liquid on microwave demulsification of polymer flooding wastewater

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ABSTRACT

The demulsification of polymer flooding wastewater emulsion is important for petroleum industry. In this study, the promoting effect of anion and cation types and concentrations of ionic liquids on microwave demulsification was analyzed. Firstly, the best radiation parameters of microwave demulsification polymer flooding wastewater: power 400 W, time 40 s. Secondly, the demulsification regularity of ionic liquids alone only and microwave synergistic ionic liquids were compared, and the mechanism of synergistic demulsification was analyzed according to the changes of zeta potential and interfacial tension before and after demulsification. By analyzing the influence of anion and cation types on demulsification, it is determined that [C16MIM]Br is the best ionic liquid. The changes of oil–water interfacial tension and zeta potential after demulsification show that long-chain ionic liquids have strong interfacial activity and can significantly reduce oil–water interfacial tension. The results of orthogonal experiments show that when the microwave radiation parameters are 600 W, 45 s and the concentration of [C16MIM]Br is 1.224 mmol/L, the oil removal rate is 92.42%, which is 1.3% higher than that of ionic liquids of the same concentration alone, indicating that microwave and ionic liquids have a synergistic demulsification effect.

Keywords: Microwave demulsification; Ionic liquids; Zeta potential; Interfacial tension; Polymer flooding wastewater

1. Introduction

Since oil fields are entering late stages of production, the water content of produced fluid is becoming increasingly high in oil wells [1]. In order to improve crude oil production, polymer flooding is widely used. However, some major questions remain. The polymer flooding wastewater emulsion contains specific crude oil, which will lead to severe environmental pollution if it is directly discharged or reinjected without treatment. Therefore, it is necessary to treat polymer flooding wastewater emulsion. Because the polymer flooding wastewater emulsion has the characteristics of complex treatment and high cost [2]. Therefore, the efficient and environmentally friendly treatment of polymer flooding wastewater emulsion has become a major problem. Common used demulsification methods are physical and chemical demulsification [3]. The physical demulsification method cannot achieve the ideal demulsification effect. The use of chemical methods may be loss to economic, and can pollute the environment. Thus, the development of new, fast, low-cost and demulsification methods is needed.

Microwave (MW) refers to the electromagnetic waves of 300 MHz–300 GHz, wavelength between 1 mm and 1 m [4]. Saifuddin and Chua [5] showed that the effect

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of microwave-assisted demulsifier is better than that of microwave demulsifier and demulsifier alone. Sun et al. [6] applied the microwave chemical method to the demulsification of crude oil. The use of microwave chemical method has many advantages compared to a single demulsification method, such as less demulsifier dosage, short heating time, high demulsification efficiency, and clear colour of dehydrated water. Cui et al. [7] used microwave to treat oilfield wastewater and found that the dominant roles of microwave demulsification are "thermal effect" and catalysis. Abdurahman et al. [8] studied the demulsification effect of microwave on 50%–50% and 20%–80% W/O emulsion. The results show that microwave demulsification is mainly "thermal effect", and its average heating rate is 0.473 and 0.527, respectively, but the heating rate decreases with the increase of temperature. The heating volume rate is related to the radiation time, and the heating volume rate decreases with microwave radiation time. Santos et al. [9] studied the demulsification effect of single-mode and multi-mode microwave on emulsion. Single-mode heating can reach a specific temperature and emulsified water content with less energy, and multimode microwave heating reflects better reproducibility. However, microwave demulsification alone cannot meet the relevant demulsification standards and sewage discharge standards.

Both the chemical and microwave methods have their own limitations, microwave and chemical methods can be combined for demulsification research. Sun et al. [10] studied the demulsification effect of inorganic salt Na_2SO_4 on oily sewage emulsion under microwave radiation. The results of experiment and theoretical model show that the demulsification effect of emulsion increases with the increase of inorganic salt concentration. Xia et al. [11] studied that after inorganic salt ions are added to O/W emulsion, inorganic ions can not only enhance the dielectric loss of emulsion but also have a coupling effect with microwave and produce much heat; in addition, inorganic salts can compress the electric double layer of emulsion droplets, reduce the repulsive force between droplets and facilitate demulsification.

Ionic liquids, or green solvents, are a group of salts with various anion–cation compositions, which are liquids at a temperature below 100°C [12]. Flores et al. [13] synthesized several ionic liquids: tri octyl methyl ammonium, octadecyl ammonium bisulfite, octadecyl ammonium methanesulfonate, and octadecyl ammonium toluenesulfonate. They used the synthesized ionic liquid for demulsification. The research results show that the prepared ionic liquid can demulsify the emulsion quickly. Atta et al. [14] prepared and studied polyionic liquid as demulsifier of crude oil emulsion and proved that polyionic liquid could break the oil film of the prepared heavy oil emulsion. Santos et al. [15] used ionic liquid to demulsify the prepared W/O emulsion. It was found that when ionic liquid was added, the viscosity of crude oil increased, indicating that there is a strong interaction between ionic liquid and crude oil components, which is the reason for studying the strong interaction between ionic liquid and crude oil. Jabbari et al. [16] used to synthesize ionic liquids and use them in emulsion, it was observed that there was a clear boundary between the oil phase and the water phase, and the particle size distribution of the emulsion was measured by dynamic light. It was found that when the ionic liquid was added, the particle size of the emulsion droplet increased noticeably so that the emulsion droplet could collide and gather more quickly and lose stability. Demulsify the emulsion. Adewunmi and Kamal [17] studied the demulsification of W/O emulsion prepared by ionic liquid on distilled water and self-made seawater in the laboratory and found that ionic liquid containing chloride ion, tetrahydropyridine (containing decanoate ion), and tetrahydropyridine (containing dicyanamide ion) had an excellent demulsification effect. By measuring the viscosity and elasticity of emulsion after adding different ionic liquids, it is revealed that ionic liquids can destroy oil–water interfacial film.

To date, a myriad of researches and studies have focused on ionic liquids demulsification. Few works were published to report the synergistic demulsification of ionic liquid and microwave, especially the mechanism of microwave-ionic liquid demulsification are unclear. Therefore, this paper will study whether microwave and ionic liquids have synergistic demulsification effect on polymer flooding wastewater emulsion, and explore its demulsification regularity and mechanism, to provide a theoretical basis for developing demulsification technology using microwave and ionic liquids for more types of emulsion.

2. Experiments and methods

2.1. Materials

The heavy oil was collected from Xinjiang Kelamayi Oil Field, China. Its moisture content was less than 0.1%. The viscosity of the heavy oil was 39,213.4 mPa·s at a shear rate of 150/s, and its density was 973.5 kg/m^3 at 30°C. The ionic liquids and polymer used are summarized in Table 1. Ionic liquids are purchased from Shanghai Macklin Biochemical Co., Ltd., (China).

2.2. Preparation of polymer flooding wastewater emulsion

Firstly, CAB-35 with 0.50% concentration and AmPAM with 0.02% concentration were dissolved in distilled water to prepare binary active water. Then the heavy oil with oil–water ratio of 0.001 and binary active water were stirred for 3 min at 1,000 rpm. The instrument used was JJ-1A digital electric mixer. The study polymer flooding wastewater emulsion used are shown in Fig. 1.

2.3. Stability test

The zeta potential of the polymer flooding wastewater emulsion was measured in order to confirm its stability. It was found that the emulsion is highly stable. The specific experimental results are presented in Table 2. The zeta potential value of the polymer flooding wastewater emulsion changes barely after standing for 3 h, indicating that it is stable and can be used to simulate the produced water at the oilfield.

2.4. Create a standard curve

To verify the demulsification effect, it is necessary to make a standard curve concerning the SYT0530-2011

Table 1
Ionic liquids and polymer

Abbreviation	Compound	Purities
CAB-35	Cocamidopropyl betaine	35%
AmPAM	Amphoteric polyacrylamide	≥90%
PE	Petroleum ether	99%
Na_2SO_4	Anhydrous sodium sulfate	99%
$[EMIM]BF_4$	1-ethyl-3-methylimidazolium tetrafluoroborate	98%
$[EMIM]PF_6$	1-ethyl-3-methylimidazolium hexafluorophosphate	98%
[EMIM]Ac	1-ethyl-3-methylimidazolium acetate	97%
[EMIM]Cl	1-ethyl-3-methylimidazolium chloride	98%
[EMIM]Br	1-ethyl-3-methylimidazolium bromide	98%
[EMIM]I	1-ethyl-3-methylimidazolium iodide	98%
[BMIM]Br	1-butyl-3-methylimidazolium bromide	97%
[HMIM]Br	1-hexyl-3-methylimidazolium bromide	98%
[DEMIM]Br	1-decyl-3-methylimidazolium bromide	98%
[C14MIM]Br	1-tetradecyl-3-methylimidazolium bromide	98%
[C16MIM]Br	1-hexadecyl-3-methylimidazolium bromide	99%

Fig. 1. An polymer flooding wastewater emulsion prepared.

standard for the determination of oil content in oilfield-produced water spectrophotometry. The principle of using this standard is that the oil in the oilfield produced water is extracted by solvent gasoline or petroleum ether, and the color depth of the extraction solution has a certain linear relationship with the oil content. The extraction solution is

Table 2
Zeta potential values of polymer flooding wastewater emulsion at different time points

Time (min)	Zeta potential (mV)
0	–55.2
10	–55.1
20	–54.9
60	–55.0
120	–54.8
180	–54.3

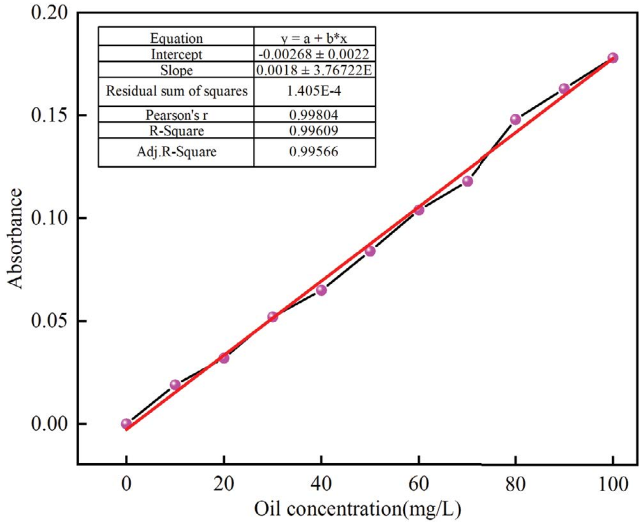

Fig. 2. Standard oil sample curve.

injected into the quartz colorimetric dish, and the absorbance is measured by a spectrophotometer. The oil content in the oilfield produced water is obtained by calculation, so as to draw the standard curve. The standard curve of the oil sample is shown in Fig. 2. The linearity of the regression curve R^2 = 0.99566 meets the regression accuracy requirements, and then the absorbance coefficient K is calculated to be 0.0018.

2.5. Demulsification experiment

In this study, the microwave equipment used is MAS-II, the system operates at 2,450 MHz frequency and works at 0–1,000 W power.

- The ionic liquid solution with 20 mmol/L concentration was prepared based on distilled water.
- 60 mL polymer flooding wastewater emulsion was poured into the colorimetric tube, and the corresponding volume ionic liquid was added to shake for 2 min.
- Start the MAS-II microwave synthesis workstation, preheat for 30 min, demulsification with microwave radiation, and record the temperature with the infrared probe of the machine.
- After microwave treatment, 50 mL polymer flooding wastewater emulsion was poured into the colorimetric

tube, 60°C water bath for 1 h, and 5 mL was extracted for zeta potential measurement.

- After water bath for 1 h, dip a little petroleum ether with absorbent cotton to absorb the oil on the upper layer of the colorimetric tube, and then use a syringe to extract 20 mL of polymer flooding wastewater emulsion water samples from the upper, middle, and lower positions of the colorimetric tube. Then evenly pack the extracted water samples into two centrifugal tubes, centrifuge at the speed of 4,000 rpm for 5 min, use a syringe to extract water samples from the bottom of the centrifugal tube, wash the centrifugal tube with petroleum ether, record the use volume of petroleum ether, and then use a particular beaker to contain the petroleum ether scrubber. Repeat the centrifugation operation many times until the extracted water is clear and transparent.
- Pour the petroleum ether washing product into the separating funnel, add 20 mL of 1% ammonium persulfate ($(NH_4)_2S_2O_8$) solution, shake the sample thoroughly for 20 s, turn on the piston for exhaust, and then place it on the iron stand for 5 min, discharge the bottom water, suck out the upper petroleum ether with a long needle tube, and place it in a special conical bottle; if the oil in the lower water sample is not entirely extracted, continue centrifugation until the lower oil is extracted by petroleum ether.
- Add an appropriate amount of Na_2SO_4 into the conical flask to absorb the water in petroleum ether. After 24 h, take 3 mL of dried extract and measure its absorbance with a spectrophotometer; if the absorbance value is too large, measure the sample after dilution. The formula for calculating the remaining oil content in the polymer flooding wastewater emulsion after demulsification treatment is shown in Eq. (1). The formula for calculating the oil removal rate is shown in Eq. (2).

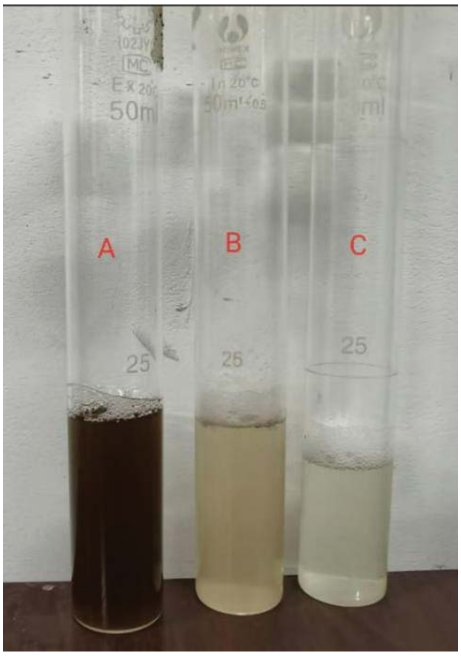

Fig. 3. Results after demulsification experiment.

$$C = \frac{\left(E - E_0 - a\right)V_0}{bV_W} \times n \tag{1}$$

where C is oil content of measured water samples (in mg/L), E is the absorbance of the measured water sample, E_0 is the absorbance of blank sample, a is standard curve intercept, V_0 is total volume of extract (in mL), b is standard curve slope, V_W is volume of measured water sample (in mL), n is dilution multiple.

$$R = \frac{C_0 - C}{C_0} \times 100\% \tag{2}$$

where R is oil removal rate after demulsification (in %), C_0 (in mg/L) is oil content of standard emulsion water samples containing polymer [6].

The comparison of polymer flooding wastewater emulsion after demulsification experiment is shown in Fig. 3. Fig. 3A shows the sewage emulsion, 3B shows the dispersed sewage after demulsification, and 3C shows the sewage following centrifugal separation and oil extraction in the dispersed sewage.

2.6. Interfacial tension test

To investigate the surface activity of ILs, the interfacial tension between crude oil and aqueous phase was measured using a JJ2000B2 (Shanghai Zhongchen Digital Technology Equipment Co.) rotary drop interfacial tension measuring instrument.

2.7. Zeta potential test

The zeta potential of the emulsion is one of the essential indicators to characterize its stability. Zeta potentials were measured using a Nano ZS90 instrument (Malvern Instruments, UK). In this paper, zeta potential analysis is based on absolute value. The dispersed phase droplets tend to agglomerate, and oil–water separation occurs. In this way, the advantages and disadvantages of demulsification and oil removal can be assessed by measuring the zeta potential before and after demulsification.

3. Results and discussion

3.1. Microwave demulsification tests

3.1.1. Effects of microwave radiation power

Microwave radiation time is 30 s, 40 s, and microwave radiation power is 100~800 W for demulsification of polymer flooding wastewater emulsion. The demulsification effect of microwave radiation was measured by the amount of oil removed following the experiment. Fig. 4 shows the demulsification results of microwave radiation applied to polymer flooding wastewater emulsion.

We can see from Fig. 4a that when power is 400 W, time is 30 or 40 s, the oil removal rate is 31.90% and 34.35%. Fig. 4b shows that at the same power, with the increase in the radiation time, the temperature and oil removal rate

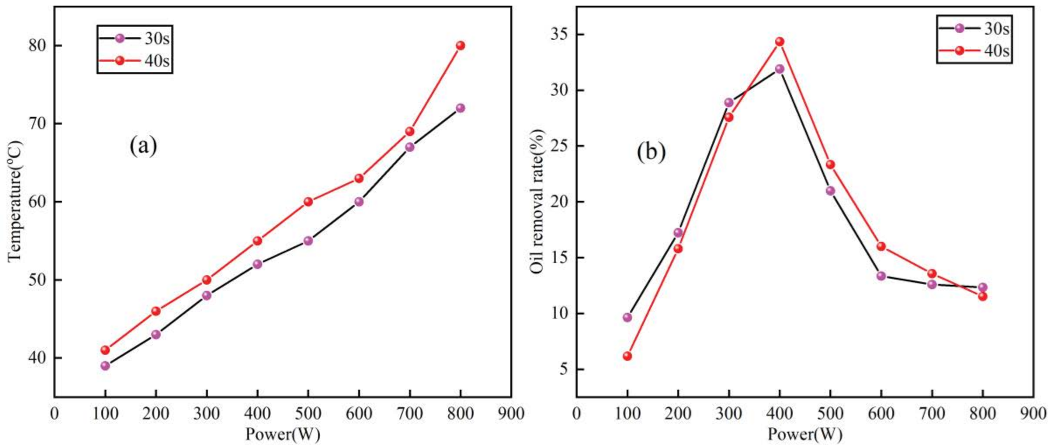

Fig. 4. Oil removal efficiency and temperature under radiation time 30 s, 40 s, 100 W–800 W power: (a) oil removal efficiency and (b) temperature.

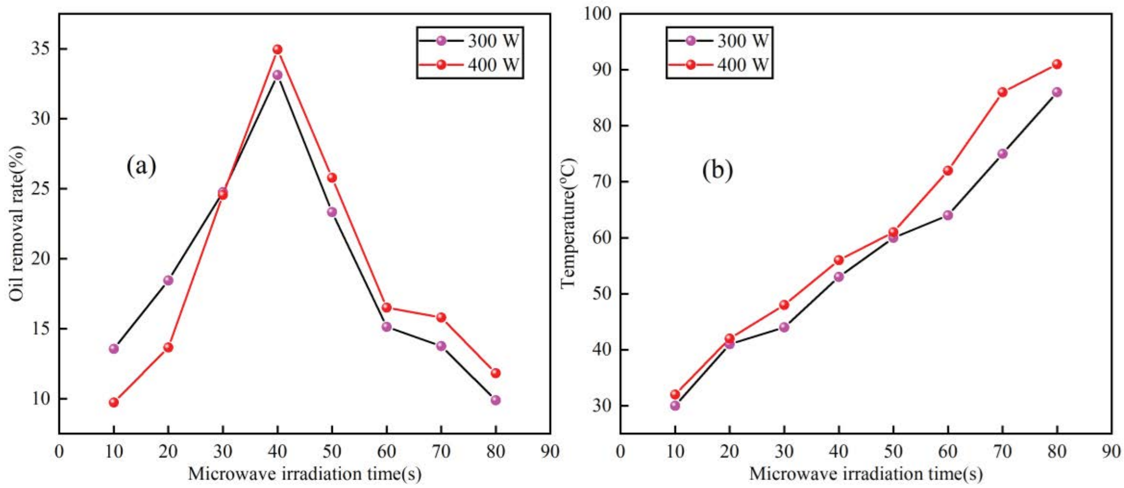

Fig. 5. Radiation power 300 W, 400 W, 10 s–80 s: (a) oil removal efficiency and (b) temperature.

increased, the collision coalescence of emulsion droplets is gradually intensified. At the highest oil removal rate, the microwave power is 400 W, the temperature is about 55°C, and the temperature reaches the most suitable temperature for demulsification. As the temperature higher than 60°C, the oil removal rate decreases. The reason is because Brownian motion of emulsion droplets flooding polymer wastewater is more intense, and the emulsion droplets are dispersed due to the intensification of collision. Therefore, the demulsification and oil removal rate decreases with increasing temperature.

3.1.2. Effect of microwave radiation time

The irradiation power was 300 and 400 W, respectively, and the irradiation time was 10 to 80 s in order to analyze the effect of microwave irradiation time on oil removal from polymer flooding wastewater emulsion. The results are shown in Fig. 5.

In Fig. 5a, when the microwave power is constant, the oil removal rate of the O/W polymer flooding wastewater emulsion increases initially, and then decreases. When the microwave radiation time is 40 s and the power is 400 W, the oil removal rate of polymer flooding wastewater emulsion reaches a maximum of 34.95%. In Fig. 5b, we can see that the best oil removal is achieved at the temperature of about 55°C, indicating that this is the best demulsification temperature under these conditions. High or low temperatures are not conducive to demulsification.

There are several reasons contribute to above results: (1) due to the "thermal effect" of microwave, the high-speed movement of polymer molecules and water molecules in polymer flooding wastewater emulsion in microwave electromagnetic field generates heat [18], the temperature of the emulsion increases, resulting in intensified collision and coalescence of emulsion droplets; on the other hand, due to the increase of temperature, the distance between molecules increases, and the attraction between molecules decreases significantly, which reduces the viscosity of polymer flooding wastewater emulsion, promotes the aggregation between polymer flooding wastewater emulsion droplets, and separates oil and water [19]. (2) As the emulsion of polymer containing wastewater forms a relatively stable adsorption layer, the "thermal effect" of microwave increases the temperature of the emulsion of polymer containing wastewater, thins the adsorption layer [20], reduces the osmotic pressure, makes the emulsion more unstable and promotes demulsification. (3) When the microwave power is too high or too low, the oil removal rate is low. The reason for the analysis is that when the microwave power is small, the heat generated is less, the Brownian motion of the droplets is not strong, the distance between the polymer molecules is very small, and the connection is tight, which is not enough to destroy the adsorption layer formed by the polymer molecules. When the microwave power is large, it produces too much heat, and the emulsion droplets move at high speed and disperse after collision. The strong microwave electromagnetic field will lead to the electrical dispersion of polymer flooding wastewater emulsion [21], hinder the aggregation of polymer flooding sewage emulsion droplets and inhibit demulsification.

3.2. Effect of anions of ionic liquids on demulsification

3.2.1. Effect of the Anion Type on oil removal rate

In order to study the demulsification effect of anionic types of different ionic liquids on polymer-containing wastewater emulsion, six ionic liquids ([EMIM]BF_4, [EMIM]PF_6, [EMIM]Ac, [EMIM]Cl, [EMIM]Br, [EMIM]I) were first selected. They were used to study the demulsification of single ionic and microwave-ionic liquids, respectively. The oil removal rate is shown in Fig. 6.

Fig. 6 shows that the demulsification and oil removal rate of the synergistic demulsification experiment with microwaves and ionic liquids was higher than that of the ionic liquid alone. When the ionic liquid is [EMIM]Br, the concentration is 0.50 mmol/L; the microwave parameters are 400 W, 40 s, the maximum oil removal rate is 46.58%; when the cationic alkyl chain is the same, from the perspective of anion, the order of demulsification and oil removal rate of ionic liquids is: imidazole bromide > imidazole iodide > imidazole hexafluorophosphate > imidazole chloride > imidazole tetrafluoroborate > imidazole acetate. As a result of the experimental results, the ionic liquid with bromide anion was chosen as the research object for the subsequent demulsification of emulsions containing polymer wastewater.

The reason may be due to the following respects. (1) When the cationic alkyl chain of ionic liquid is 1-ethyl-3-methyl, anions play a leading role in demulsification of O/W polymer flooding wastewater emulsion, mainly in that anions promote the combination of asphaltene and ionic liquid [15], destabilize the emulsion and promote demulsification. (2) When anions are halogen ions, the smaller their hydration radius is, the easier they are adsorbed on the surface of oil droplets [22]. The size of the three halogen ion hydrated radius is $Cl^- > I^- > Br^-$, because the minimum hydration radius of Br^- is the strongest [23], and the highest demulsification and oil removal rate is 50.05%.

3.2.2. Effect of anion types on oil/water IFT

In order to explore the effect of interfacial activity of anions on oil removal rate, the effects of different anionic liquids on oil / water interfacial tension of crude oil were compared. The experimental results are shown in Fig. 7.

From Fig. 7, it can be seen that after adding [EMIM]Br, the oil–water interfacial tension decreases the most, and the interfacial tension decreases from 0.1713 to 0.1441 mN/m. When the anion is a halogen element, chloride ions have the lowest ability to reduce the oil–water interfacial tension. In contrast, bromine ions and iodide ions can significantly reduce oil–water interfacial tension. The experimental results also reveal that bromine ions have the highest oil removal efficiency; hexafluorophosphate is a highly hydrophobic ion [23], which has a

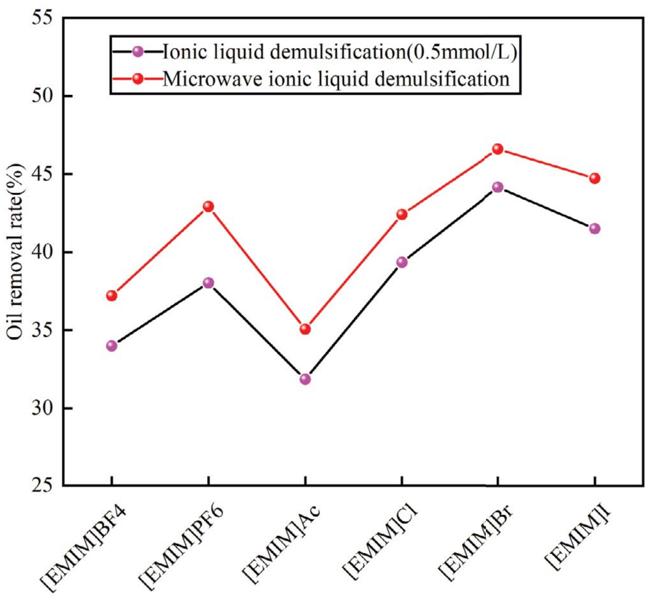

Fig. 6. Oil removal rate of ionic liquids with or without microwave radiation.

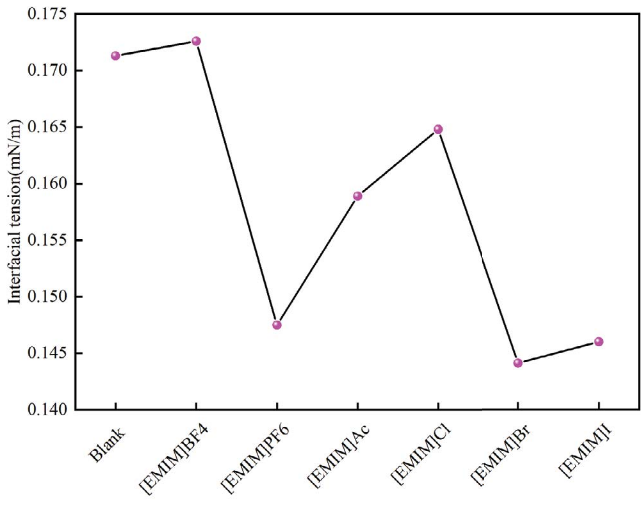

Fig. 7. Interfacial tension values of ionic liquids with six different types of anions and crude oil.

significant ability to reduce the interfacial tension between oil and water. Therefore, it also has a certain demulsification and oil removal rate at low concentrations, while acetate and tetrafluoroborate ions belong to hydrophilic ions, which are not conducive to demulsification [24].

3.2.3. Effect of anion types on zeta potential

In order to explore the mechanism of the effect of different charged potentials of anionic liquids on the oil removal rate, the zeta potentials of binary active water and different anionic liquids are compared. It is considered that the charged properties of oil droplets are directly related to emulsifiers and ionic liquids. The experimental results are shown in Fig. 8.

According to Fig. 8, the zeta potential value of the standard emulsion is –55.2 mV. zeta potential is a measure of the stability of an emulsion. When the ionic liquid is [EMIM]BF_4, the zeta potential of polymer flooding wastewater emulsion is reduced, but the demulsification and oil removal rate is not high. With or without microwave radiation, the tendency of ionic liquid to reduce the zeta potential of polymer flooding wastewater emulsion is the same, and the zeta potential value of polymer flooding wastewater emulsion treated by five ionic liquids is similar to that of standard emulsion, indicating that ionic liquid under this condition does not reduce the zeta potential value of polymer flooding wastewater emulsion and cannot destabilize the emulsion, That is, it has no significant promoting effect on demulsification, which is consistent with the experimental results.

3.3. Effect of cation of ionic liquids on demulsification

3.3.1. Effect of the cation type on oil removal rate

The best ionic liquid anion has been selected as the bromine ion. On this basis, the demulsification and oil removal experiments of ionic liquids with different alkyl chain lengths on polymer flooding wastewater emulsion have been studied. Six ionic liquids [EMIM]Br, [BMIM]Br, [HMIM]Br, [DEMIM]Br, [C14MIM]Br, and [C16MIM]Br have been selected, and the concentration is set to 0.5 mmol/L; set the microwave parameters to 400 W and 40 s, and the experimental results are shown in Fig. 9.

It can be seen from Fig. 9 that with or without microwave radiation, the oil removal rate of ionic liquids with bromine ions as anions decreases first and then increases with the increase of alkyl chain length. In the presence of a short alkyl chain, bromine ions play a prominent role; however, when the cationic alkyl chain is [C14MIM], the oil-removal rate of ionic liquid increases rapidly. When the alkyl chain is [C16MIM], the oil removal rate reaches a maximum of 91.72%.

3.3.2. Effect of anion types on oil/water IFT

In order to explore the effect of cationic alkyl chain length on the interfacial activity of ionic liquids, the interfacial tension of different types of cations was studied. The experimental results are shown in Fig. 10.

It can be seen from Fig. 10 that when the ionic liquid is [C16MIM]Br and the concentration is 0.5 mmol/L, the oil–water interfacial tension value is 0.0463 mN/m. Compared with the oil–water interfacial tension value without any ionic liquid, the value decreases by order of magnitude. The interfacial tension value reduces by 72.97%, indicating that the longer the alkyl chain length, the greater the interfacial activity between oil and water, the stronger the ability to reduce the interfacial tension is, and the stronger, the more substantial the demulsification ability is.

Analysis of the reasons: the oil–water interfacial tension value decreases rapidly with the increase of alkyl chain length of ionic liquids [25], indicating that the ionic liquids with alkyl chain length have vigorous interfacial activity,

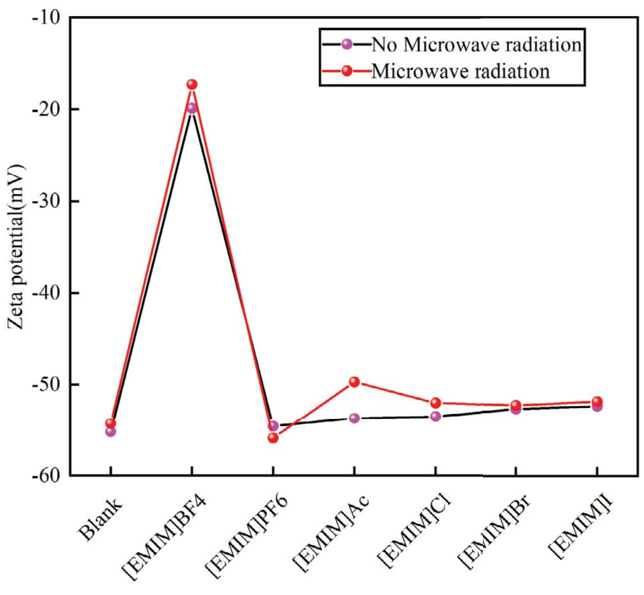

Fig. 8. Zeta potential values of demulsified wastewater emulsions containing polymer in six ionic liquids with or without microwave radiation.

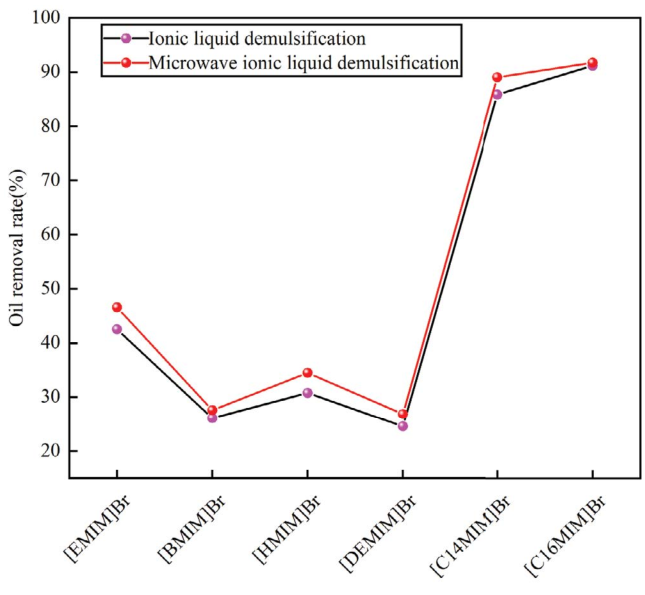

Fig. 9. Oil removal rates of different alkyl cations with/without microwave irradiation.

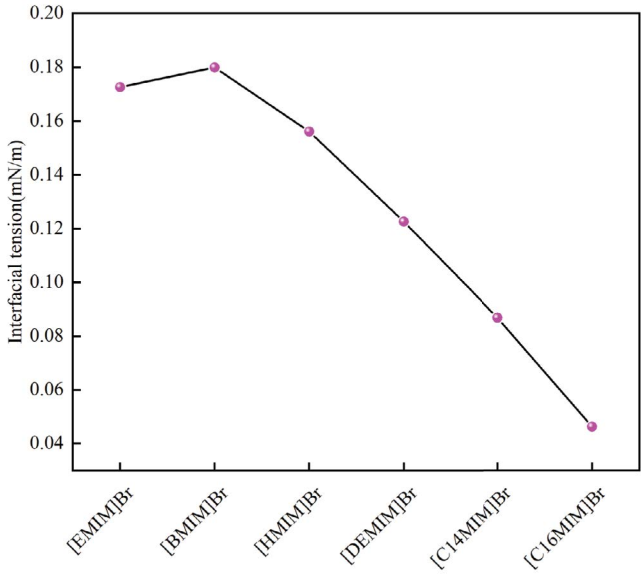

Fig. 10. Ionic liquids with concentration of 0.5 mmol/L and different alkyl chain lengths, oil–water interfacial tension value.

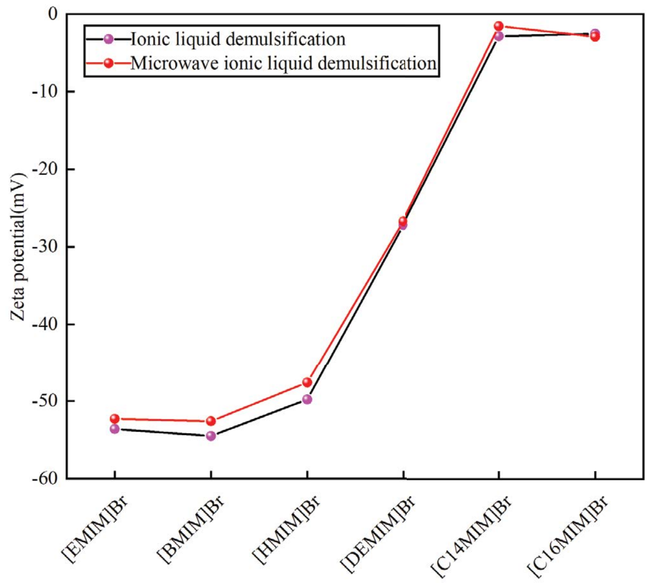

Fig. 11. Zeta potential of poly-sewage emulsion containing polymer after demulsification of ionic liquids with different alkyl chain lengths with or without microwave.

thus replacing the natural active molecules between emulsion droplets, breaking the interfacial film of emulsion, losing the stability of the emulsion, and promoting demulsification of emulsion containing polymer wastewater.

3.3.3. Effect of cation types on zeta potential

The zeta potential of demulsified emulsions and the interfacial tension between crude oil and active water were measured after different ionic liquids were added. Fig. 11 shows the results.

It can be seen from Fig. 11 that the minimum zeta potential was –2.53 mV without microwave irradiation, and the ionic liquid was [C16MIM]Br. Under microwave irradiation, the lowest zeta potential was –1.54 mV, and the ionic liquid was [C14MIM]Br. Therefore, it can be considered that the two salts have a similar ability to reduce the zeta potential of polymer-containing wastewater emulsion.

3.4. Effect of ionic liquid concentration on demulsification

3.4.1. Effect of the ionic liquid concentration on oil removal rate

The results show that [C16MIM]Br has good oil removal effect. For this reason, the experiments of different concentrations of [C16MIM]Br under microwave radiation and without radiation were carried out. The microwave radiation parameters are 400 W, 40 s, and the concentration range is 0.25–1.5 mmol/L. The experimental results are shown in Fig. 12.

It can be seen from Fig. 12 that with or without microwave radiation, the oil removal rate increases at first and then remains stable with the increase of concentration. In the absence of microwave radiation, the maximum oil removal rate is 88.30% when the ionic liquid concentration is 1.25 mmol/L; under microwave radiation, when the

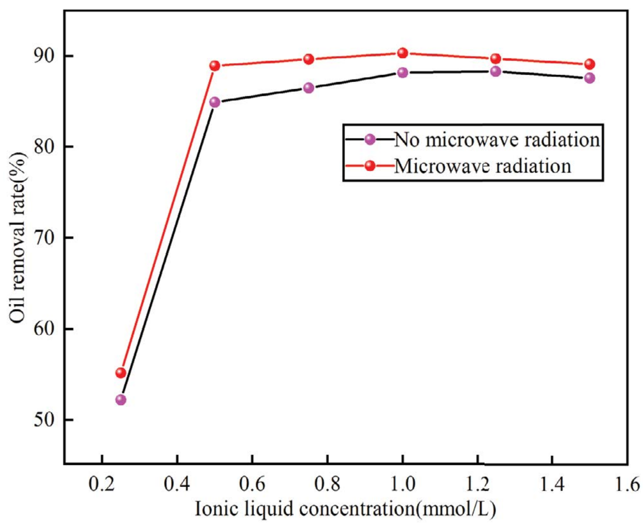

Fig. 12. Oil removal rate at total concentration of [C16MIM]Br with/without microwave radiation.

ionic liquid concentration is 1 mmol/L, the maximum oil removal rate is 90.31%.

3.4.2. Effect of concentration on oil/water IFT

In order to explore the demulsification and oil removal mechanism of ionic liquid [C16MIM]Br on emulsion containing polymer wastewater, the interfacial tension between different concentrations of [C16MIM]Br and crude oil was studied. The result is shown in Fig. 13. However, when the concentration of ionic liquid [C16MIM]Br is 1.25 and 1.5 mol/L, the crude oil is dispersed in the eyedropper and attached to the inner wall of the eyedropper, so it cannot form stable oil droplets, so the interfacial tension cannot be measured.

As can be seen from Fig. 13, when the concentration of ionic liquids increases to 0.5 mmol/L, the interfacial tension of the emulsion is significantly reduced to 0.0664 mN/m. When the concentration of ionic liquids is 1 mmol/L, the interfacial tension is 0.0288 mN/m, and the corresponding oil removal rate is 90.31%.

Analysis reason: (1) With the increase of ionic liquid concentration, the oil–water interfacial tension decreases, indicating that ionic liquids are adsorbed to the oil–water interface to replace natural active molecules, thus reducing interfacial tension and promoting demulsification. And with the increase of ionic liquid concentration, the oil removal rate does not increase, which indicates that the ionic liquid has reached the critical micelle concentration [26], increasing the concentration cannot continue to improve the oil removal rate. (2) When the concentration of the ionic liquid reaches the critical micelle concentration, the cationic alkyl chains of the ionic liquid and the polyacrylamide cations in the polyacrylamide-containing sewage emulsion repel each other due to the mutual repulsion between the same charges [27], and the oil droplets are wrapped in In the interface film formed by the polymer, the emulsion droplets are not easy to aggregate, which increases the difficulty of demulsification and does not improve the demulsification and oil removal rate.

3.4.3. Effect of concentration on zeta potential

In order to explore the oil removal mechanism of [C16MIM]Br on the demulsification of polymer-containing wastewater emulsion, the zeta potential of the ionic liquid after demulsification of polymer-containing wastewater emulsion at different concentration with/without microwave radiation was also tested. The results are shown in Fig. 14.

Fig. 14 shows that [C16MIM]Br can significantly reduce the zeta potential of polymer-containing wastewater emulsion at a lower concentration, indicating that long alkyl chain ionic liquids have the effect of significantly reducing the zeta potential of polymer-containing wastewater emulsion, reaching the potential instability range of emulsion below 5 mV. The zeta potential of emulsion with/without microwave radiation was compared and analyzed. The ability of the microwave-ionic liquid to reduce the zeta potential of emulsion containing polymer wastewater was slightly more substantial than that of ionic liquid. However, the effects of microwave were not noticeable. In connection with the experimental results, the zeta potential value is low under the different concentration experiment, and the ionic liquid has a good demulsification and oil removal effect.

3.5. Microwaves and ionic liquids parameter optimization

3.5.1. Orthogonal experiment

To explore whether there is an optimal microwave parameter and ionic liquid concentration, an orthogonal experimental table is made according to the required factors. This experiment includes microwave power, microwave radiation time, and ionic liquid concentration. The values of parameters in each trial are shown in Table 3.

According to the results presented in Fig. 15, when the concentration of ionic liquids was at the minimum of 0.25 mmol/L, the changes in microwave power and microwave radiation time had low demulsification and oil removal rate s for the emulsion containing polymer wastewater. In the following experiments, when the concentration of ionic liquids increased, the oil removal rate increased rapidly and reached a relatively stable level. When the trial number is 8, the highest oil removal rate is 90.95%. The relationship between oil removal rate and microwave radiation time and radiation power is not apparent, mainly related to the concentration of ionic liquids.

Taking the oil removal rate as the experimental index of regression analysis, the microwave radiation time and

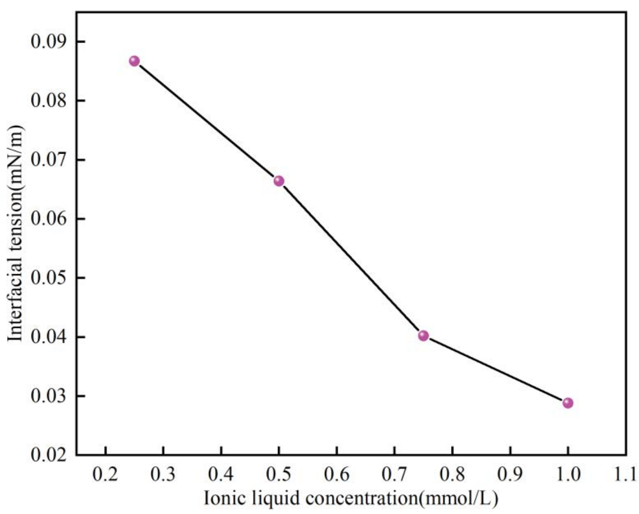

Fig. 13. Interfacial tension between [C16MIM]Br and crude oil at different concentration.

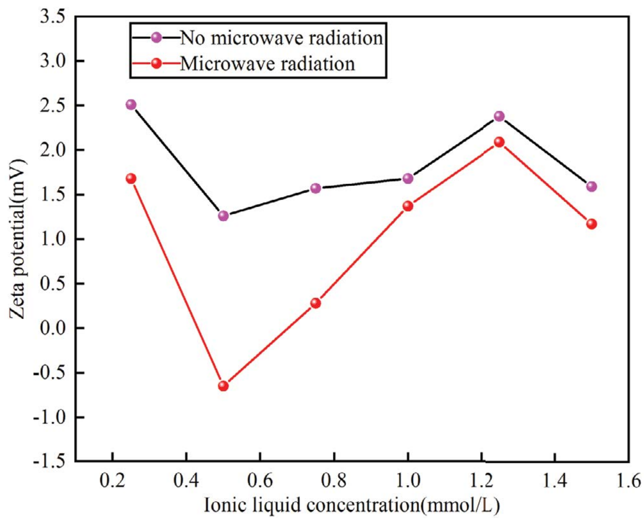

Fig. 14. Effects of different concentrations of [C16MIM]Br on zeta potential of emulsion containing polymer wastewater after demulsification with or without microwave radiation.

Table 3
Test factors and levels

Level	Factor 1	Factor 2	Factor 3
	Power (W)	Time (s)	Concentration (mmol/L)
1	100	10	0.25
2	400	40	0.875
3	800	80	1.5

The orthogonal experimental design of three factors and three levels was adopted, as shown in Table 4.

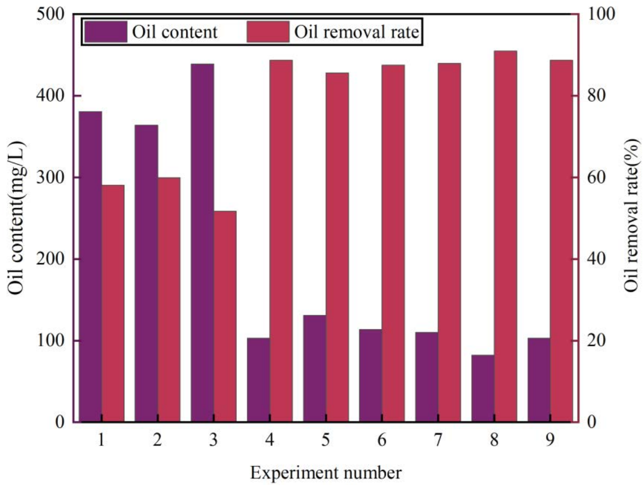

Fig. 15. Orthogonal test results of [C16MIM]Br.

power parameters and the concentration of ionic liquid [C16MIM]Br were normalized. The analysis results are shown in Tables 5–7. R^2 refers to the correlation coefficient, and the larger the ratio, the higher the correlation with the curve. The F-value represents the significance of the entire fitting equation, and the larger the value, the better the fitting of the equation. When the significance is less than 0.05, it means that this factor has the greatest influence on the dependent variable.

Multiple linear regression analysis with a stepwise approach was performed to predict oil removal rate using SPSS software. The fitting formula is shown in Eq. (3):

$$Y = e^{\left(4.073+1.136c-0.729c^2+0.372(ab)^2-0.501(ab)^3\right)} \quad (3)$$

where Y is oil removal rate, e is natural constant, a is normalized value of microwave radiation power, b is normalized value of microwave radiation time, c is normalized value of ionic liquid concentration.

Through the analysis of the fitting formula, when the ionic liquid and microwave cooperate with demulsification, the influence of various factors on the demulsification experiment is basically consistent with the actual results. There is a linear relationship between the concentration of ionic liquids and the oil removal rate of emulsion containing polymer, indicating that the concentration of ionic liquids plays a leading role. Microwave radiation power and radiation time do not play a leading role in the demulsification of emulsion containing polymer wastewater. The influence of microwave radiation power and radiation time is mainly reflected in the temperature. When the energy obtained by the emulsion increases and the temperature reaches a certain value, the droplet moves strongly, the collision intensifies and coalescence occurs. However, from the experimental results, due to the increase of temperature, the demulsification rate and oil removal rate of the emulsion containing polymer wastewater did not increase.

Table 4
Table of three factors and three levels

Trial number	Factor 1	Factor 2	Factor 3
1	1	1	1
2	2	2	1
3	3	3	1
4	3	2	2
5	2	1	2
6	1	3	2
7	1	2	3
8	2	3	3
9	3	1	3

Results of the orthogonal experiment have been displayed in Fig. 15.

Table 5
Model summary

Model	R	R^2	Adjusted R^2	Errors in standard estimation
4	0.999	0.999	0.997	0.01153498
Prognosis variate: (constant), c, c^2, $(ab)^2$, $(ab)^3$				

Table 6
F-test results

Model calibration					
Model	Sum of squares	Freedom	Mean square	F-value	Significance
Regression	0.412	4	0.103	773.413	0.1E-4
Residual	0.001	4	0.000	/	/
Total	0.412	8	/	/	/
Prognosis variate: (constant), c, c^2, $(ab)^2$, $(ab)^3$					

3.5.2. Regression equation verification

The best-fitted formula according to regression analysis was shown, and a = 0.75, b = 0.66, c = 0.78, that is, microwave radiation power = 600 W, radiation time = 45 s, ionic liquid concentration = 1.224 mmol/L, the theoretical oil removal rate reached 94.25%. Table 8 compares the theoretical and experimental results to validate the accuracy of the theoretical model.

Table 7
T-test and model collinearity diagnosis

Model	Non-standardized coefficient		Standardization coefficient	*T*	Significance
	B	Standard error	Beta		
(constant)	4.073	0.008	/	496.739	0.000
c	1.136	0.037	2.168	30.588	0.000
c^2	–0.729	0.034	–1.447	–21.345	0.000
$(ab)^2$	0.372	0.093	0.535	3.995	0.016
$(ab)^3$	–0.501	0.095	–0.724	–5.293	0.006

Table 8
Experimental verification of the optimal solution

Power (W)	Time (s)	Ionic liquid concentration (mmol/L)	Remaining oil content (mg/L)	Standard oil content (mg/L)	Actual oil removal rate (%)	Theoretical oil removal rate (%)	Absolute value of error (%)
600	45	1.224	68.92	908.50	92.42	94.25	1.9

4. Conclusions

Aiming at the O/W type polymer-containing wastewater emulsion, the experimental research was carried out on optimizing microwave radiation parameters, the effects of individual ionic liquid, and the synergistic demulsification of microwave-ionic liquid. The synergic effect of combined microwave and ionic liquid was also exploited. The main conclusions were as follows.

- Too high microwave radiation power and long microwave radiation time are not conducive to demulsification. Too much energy input will make the emulsion temperature too high, the oil droplet movement too intense, and oil–water separation is difficult. The optimal microwave parameters are radiation power 400 W and radiation time 40 s.
- Based on the optimal microwave radiation, the ionic liquid with the best oil removal effect was selected as [C16MIM]Br by comparing the demulsification of single ionic liquid and microwave ionic liquid. Reducing the interfacial tension is strongest when the anion is a bromide ion. At the same time, the long alkyl chain has a higher molar volume and polarizability, which is beneficial to demulsification.
- The oil removal rate of [C16MIM]Br was studied at different concentrations. When the concentration was 1 mmol/L, the oil removal rate reached the maximum, and the zeta potential value of the emulsion decreased from –55.2 to –2.91 mV. The oil–water interfacial tension decreased from 0.1713 to 0.0288 mN/m, which demonstrate the good performance of [C16MIM]Br.
- Both the experiment and regression show that microwave heating has an obvious promoting effect on the demulsification effect of ionic liquid.
- Under the optimal microwave radiation conditions, orthogonal experiments were conducted using the optimized ionic liquid, and it was concluded that when the microwave radiation power was 600 W, the radiation time was 40 s, and 1.224 mmol/L [C16MIM]Br would reach 92.42% of the oil removal rate.

References

[1] C. Li, J. Li, N. Wang, Q. Zhao, P. Wang, Status of the treatment of produced water containing polymer in oilfields: a review, J. Environ. Chem. Eng., 9 (2021) 105303, doi: 10.1016/j.jece.2021.105303
[2] J. Li, Y. Xiong, X. Wang, F. Wang, S. Fang, M. Duan, Synthesis and flocculation of a novel flocculant for treating wastewater produced from polymer flooding, Environ. Technol., 42 (2021) 1715–1722.
[3] R.C.B. Lemos, E.B. da Silva, A. dos Santos, R.C.L. Guimarães, B.M.S. Ferreira, R.A. Guarnieri, C. Dariva, E. Franceschi, A.F. Santos, M. Fortuny, Demulsification of water-in-crude oil emulsions using ionic liquids and microwave irradiation, Energy Fuels, 24 (2010) 4439–4444.
[4] A.L. Garcia-Costa, A. Luengo, J.A. Zazo, J.A. Casas, Cutting oil–water emulsion wastewater treatment by microwave assisted catalytic wet peroxide oxidation, Sep. Purif. Technol., 257 (2021) 117940, doi: 10.1016/j.seppur.2020.117940.
[5] N. Saifuddin, K.H. Chua, Treatment of oily waste water emulsions from metallurgical industries using microwave irradiation, Biotechnology, 5 (2006) 308–314.
[6] N.N. Sun, H.Y. Jiang, Y.L. Wang, A.J. Qi, A comparative research of microwave, conventional-heating, and microwave/chemical demulsification of Tahe heavy-oil-in-water emulsion, SPE Prod. Oper., 33 (2018) 371–381.
[7] H.M. Cui, L.F. Ke, H.B. Qi, L.Y. Chen, The study on experiments of oilfield wastewater treatment by microwave-assisted demulsification, Adv. Mater. Res., 599 (2012) 516–520.
[8] N.H. Abdurahman, R.M. Yunus, N.H. Azhari, N. Said, Z. Hassan, The potential of microwave heating in separating water-in-oil (W/O) emulsions, Energy Procedia, 138 (2017) 1023–1028.
[9] D. Santos, E.C.L. da Rocha, R.L.M. Santos, A.J. Cancelas, E. Franceschi, A.F. Santos, M. Fortuny, C. Dariva, Demulsification of water-in-crude oil emulsions using single mode and multimode microwave irradiation, Sep. Purif. Technol., 189 (2017) 347–356.
[10] S. NaNa, L.H. Peng, H.Y. Jiang, Effect of inorganic salt concentration on microwave demulsification mechanism, Oil-Gas Field Surf. Eng., 32 (2013) 32–33.
[11] L. Xia, G. Cao, S. Lu, Q. Liu, S. Tong, Demulsification of solids-stabilized emulsions under microwave radiation, J. Macromol. Sci. Part A Pure Appl. Chem., 43 (2006) 71–81.
[12] F. Shehzad, I.A. Hussein, M.S. Kamal, W. Ahmad, A.S. Sultan, M.S. Nasser, Polymeric surfactants and emerging alternatives used in the demulsification of produced water: a review, Polym. Rev., 58 (2018) 63–101.
[13] C.A. Flores, E.A. Flores, E. Hernández, L.V. Castro, A. García, F. Alvarez, F.S. Vázquez, Anion and cation effects of ionic

liquids and ammonium salts evaluated as dehydrating agents for super-heavy crude oil: experimental and theoretical points of view, J. Mol. Liq., 196 (2014) 249–257.
[14] A.M. Atta, H.A. Al-Lohedan, M.M.S. Abdullah, Dipoles poly(ionic liquids) based on 2-acrylamido-2-methylpropane sulfonic acid-co-hydroxyethyl methacrylate for demulsification of crude oil water emulsions, J. Mol. Liq., 222 (2016) 680–690.
[15] R.L.M. Santos, E.B.M. Filho, R.S. Dourado, A.F. Santos, G.R. Borges, C. Dariva, C.C. Santana, E. Franceschi, D. Santos, Study on the use of aprotic ionic liquids as potential additives for crude oil upgrading, emulsion inhibition, and demulsification, Fluid Phase Equilib., 489 (2019) 8–15.
[16] M. Jabbari, Y. Izadmanesh, H. Ghavidel, Synthesis of ionic liquids as novel emulsifier and demulsifiers, J. Mol. Liq., 293 (2019) 111512, doi: 10.1016/j.molliq.2019.111512.
[17] A.A. Adewunmi, M.S. Kamal, Demulsification of water-in-oil emulsions using ionic liquids: effects of counterion and water type, J. Mol. Liq., 279 (2019) 411–419.
[18] C. Eskicioglu, N. Terzian, K.J. Kennedy, R.L. Droste, M. Hamoda, A thermal microwave effects for enhancing digestibility of waste activated sludge, Water Res., 41 (2007) 2457–2466.
[19] H. Cui, L. Fang, Q. Zenglu, L. Hongyan, Y. Zhongchen, Research progress of microwave-assisted oil extraction wastewater treatment technology, Ind. Water Wastewater, 46 (2015) 1–5. Available at: https://kns.cnki.net/kcms/detail/34.1204.tq.20150925.1628.008.html
[20] S.-J. Zhang, M.-Y. Wang, B.-B. Liu, J.-S. Meng, D.-Y. Li, W. Tong, Preparation of macroporous magnetic particles for the treatment of wastewater containing emulsified oil, Sci. Adv. Mater., 11 (2019) 1299–1305.
[21] E. Vialkova, M. Zemlyanova, A. Pesheva, Effective sediment treatment of urban sewage by microwave radiation, Mater. Sci. Forum, 871 (2016) 223–232.
[22] J. Saien, S. Asadabadi, Alkyl chain length, counter anion and temperature effects on the interfacial activity of imidazolium ionic liquids: comparison with structurally related surfactants, Fluid Phase Equilib., 386 (2015) 134–139.
[23] A.G. Volkov, S. Paula, D.W. Deamer, Two mechanisms of permeation of small neutral molecules and hydrated ions across phospholipid bilayers, Bioelectrochem. Bioenerg., 42 (1997) 153–160.
[24] M.G. Freire, L.M.N.B.F. Santos, A.M. Fernandes, J.A.P. Coutinho, I.M. Marrucho, An overview of the mutual solubilities of water–imidazolium-based ionic liquids systems, Fluid Phase Equilib., 261 (2007) 449–454.
[25] N. Hazrati, A.A.M. Beigi, M. Abdouss, Demulsification of water in crude oil emulsion using long chain imidazolium ionic liquids and optimization of parameters, Fuel, 229 (2018) 126–134.
[26] F. Geng, J. Liu, L. Zheng, L. Yu, Z. Li, G. Li, C. Tung, Micelle formation of long-chain imidazolium ionic liquids in aqueous solution measured by isothermal titration microcalorimetry, J. Chem. Eng. Data, 55 (2009) 147–151.
[27] H. Sun, Q. Wang, X. Li, X. He, Novel polyether-polyquaternium copolymer as an effective reverse demulsifier for O/W emulsions: demulsification performance and mechanism, Fuel, 263 (2020) 116770, doi: 10.1016/j.fuel.2019.116770.