Synthesis and Evaluation of Hydroxymethyl Tetramides as Flow Improvers for Crude Oil

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Summary: In this work, a series of hydroxymethyl tetramide (HMTEA) was synthesized from vegetable oil, triacetylenetetramine and hexamethylenetetramine, which was evaluated as viscosity reducer and pour point depressor for crude oil. The results showed that HMTE has a good viscosity reduction effect on the crude oil from Yanchang Oilfield, with the highest viscosity reduction rate of 93%. The highest pour point reduction depression was achieved as 6.5℃. Differential scanning calorimetry and paraffin crystal morphology characterization were conducted on the crude oil to elucidate the mechanism of viscosity reduction and pour point depression.

Key words: Vegetable oil; Hydroxymethyl tetramide; Crude oil; Viscosity reducer; Pour point depressor.

Introduction

Heavy oil extraction and transportation has been one of the topic interests in the world and different methods has been used to reduce the viscosity of the heavy crude for easier production and transportation in recent years [1,2]. Several options are available in practice, which include blending with lighter oil, stream heating, mechanical scraping and use of chemical additives [3]. At present, the possible mechanism of pour point depressant to improve the fluidity of crude oil is by reducing the irregularity of the wax shape, or reducing the degree of aggregation of wax crystals. In addition, the non-crystalline hydrocarbon chain in the molecule of the pour point depressant linked to the polar group is soluble in the crude oil, and has a spatial barrier to the wax crystals, which can overcome the vander Waals force between the wax crystals, so as to improve the dispersion of wax in crude oil. Resins and asphaltenes are the components with the highest molecular weight and the highest polarity in crude oil. Resins and asphaltenes are not isolated in crude oil, the two unit structure is similar to that of asphaltenes is further aggregates of resins. They contain large amounts of polar groups such as carboxyl, amine and carbonyl groups, which can form hydrogen bonds to increase cohesion, resulting in increased viscosity of crude oil, so the research of the crude oil flow improver should based on the interaction of improver and the components in crude oil [4-6]. In this work, we used long chain fatty acyl polyamines of vegetable oil as reaction intermediates, by introducing the polar hydroxyl groups, to synthesis hydroxymethyl tetramine as crude oil flow improver. Furthermore, the inhibitive performance as well as probable mechanism of selected HMTEA were investigated by using differential scanning calorimetry (DSC) analysis and paraffin crystal morphology analysis.

Experimental

Materials

Castor oil, rapeseed oil and soybean oil were purchased from Shaanxi Janxing Agriculture Technology Co., Ltd. All chemicals were purchased from Sinopharm Chemical Agent Co., Ltd. The crude oil used for evaluations was obtained from Yanchang Oilfield with no suspended sand particles. The physical properties of the three crude oil samples from Yanchang Oil Field of China were summarized in Table 1

Table-1: The physical parameters of the crude oil.

Oil sample	H^{50} (mPa•s)	Pour point t/℃	ρ^{20} (g·cm^{-3})	Saturated hydrocarbon*w* /%	Aromatic hydrocarbons *w* /%	Asphaltene *w* /%	Resins *w* /%
Chang 6	188	20.2	0.892	46.64	28.80	6.40	18.16
Chang 2	37	19.4	0.881	50.90	29.17	6.28	13.65
Yanchang pipeline	100	20.0	0.887	49.1	29.00	6.88	15.02

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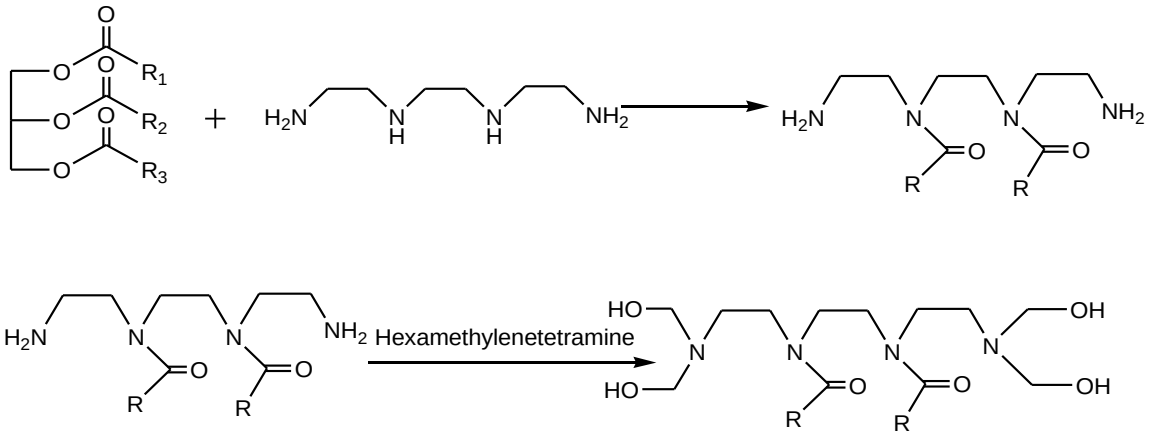

Fig. 1: Preparation of hydroxymethyl tetramide.

Table-2: Nomenclature of hydroxymethyl tetramide.

Vegetable oil	Amine	Hydroxylation reagent	Name
Rapeseed oil	Triethylenetetramine	Hexamethylenetetramine	HMTEA-1
Soybean oil			HMTEA-2
Castor oil			HMTEA-3

Preparation of hydroxymethyl tetramine (HMTEA)

Vegetable oil and triethylenetetramine were added in a beaker with the 1: 3 molar ratio, stirred uniformly and refluxed for 4h under 180℃ to prepare the intermediate product. And then hexamethylenetetramine was added with a certain proportion of triacetylenetetramine. After refluxing for another 4h at a constant temperature of 180℃, hydroxymethyl tetramide (HMTEA) was obtained. The synthetic route was shown in Fig 1, and hydroxymethyl tetramides were named in Table 2.

Characterization of HMTEA

The synthesized HMTEA was characterized by FTIR. The spectra were recorded in KBr pellets with a Bruker Tensor 37 spectrometer in the 400–4,000cm^{-1} region. The samples were also evaluated by thermogravimetric analysis (TGA). The instrument was preheated under nitrogen protection for 30 min, after the baseline was stabilized, the temperature was raised from 50℃ to 500℃ and the heating rate of 10℃/min. The quality of the sample is 3~6mg, the nitrogen flow rate of 20 mL/min. The instrument automatically records changes in the quality of the heating process.

Effect of HMTEA on crude oil's viscosity and pour point

The viscosity of the treated heavy oil was recorded by a BROOKFIELD DV-II + programmable Viscometer at different temperature according to Industrial Standard of China Petroleum SY/T0520-2008. The ratio of viscosity reduction Δη% was calculated as follows: $\Delta\eta\% = ((\eta_0 - \eta)/\eta_0)\times 100$, where Δη(%) is the rate of viscosity reduction, η0(mPa·s) the viscosity of the oil before the reaction, and η(mPa·s) the viscosity of the oil after the reaction. The crude oil was sealed and heated to 45℃ in a constant temperature bath, which was removed after 1h, the crude oil was weighed 30g and placed in the measuring cylinder, heated to 45℃, constant temperature 10min. 500 mg/kg *n*-butanol solution of HMTEAs was prepared, the solution was injected into the waxy crude oil, stirred uniformly and the cylinder into the thermostat, constant temperature 1.5h, and a control experiment was carried out at the same time. Then the viscosity of crude oil was measured with a rotational viscometer at different temperatures [7,8]. The pour point was tested according to Industrial Standard of China Petroleum SY/T0541-2009.

Paraffin inhibition and paraffin crystallization in simulated crude oil

Saturated hydrocarbons were separated by the column chromatography-based method according to Industrial Standard of China Petroleum SY/T 5119. The paraffin crystal in the saturated hydrocarbons of the heavy oil with and without 500 mg/kg HMTEA-2 was investigated

using an Olympus BH-2 polarizing microscope [9,10].

Differential scanning calorimetry (DSC) analysis

The DSC analysis of crud oil and with and without 500 mg/kg HMTEA-2 were performed using a rotary evaporator RE-52A DSC apparatus. The temperature profile follows two steps: (1) Previous step: Sample is heated at 11℃/min from room temperature to 50℃ to completely dissolve possible solid phase and to remove any thermal history; (2) Cooling step: Sample is cooled down from 50 to -20℃ at 8℃/min.

Results and Discussion

Characterization of HMTEA

The synthesized HMTEA1 was characterized by IR, and the spectrum was shown in Fig 2. It was easy to see from the results that the stretching vibration absorption peaks of hydroxyl and amide carbonyl appeared at 3304cm^{-1} and 1656 cm^{-1}, diffraction vibration absorption peak of carbon-hydrogen bond in the methyl, methylene of the long alkane chain appeared at 3030cm^{-1}, 2936cm^{-1} and 2852 cm^{-1} [11]. HMTEA has the characteristic absorption peak of hydroxyl and amide carbonyl, and the hydroxyl absorption peak is stronger and wider. Due to the different number of hydroxyl groups and the long chain alkyl chain, the characteristic peak has obvious had shifted.

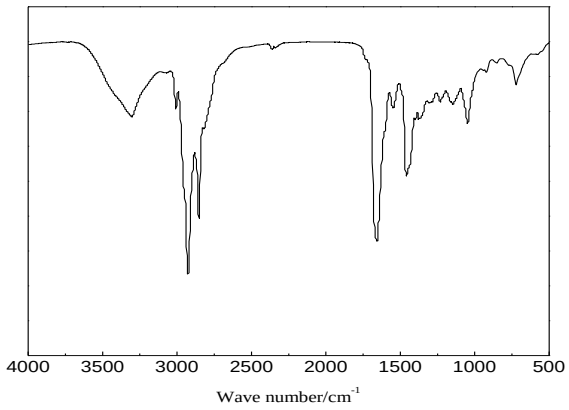

Fig. 2: Infrared absorption spectrum of HMTEA-1.

TGA of the synthesized HMTEA-1 is shown in Fig 3. The weight loss range of the products is 50-500℃, respectively. Under 100℃, the weight does not change obviously, when the temperature up to 100℃, the mass gradually decreases, and the weight loss rate of the products was higher than 90% within 500℃. The TGA shows that the thermo stability of HMTEA is relative low, but it is stable in common temperate as a crude oil additive.

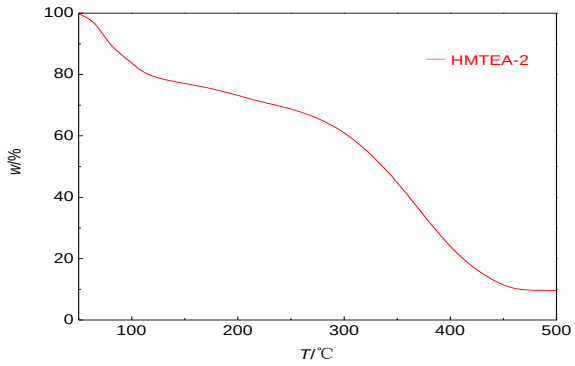

Fig. 3: Thermogravimetric analysis of HMTEA-1.

Effect of HMTEA on the viscosity of crude oil

The three HMTEAs were evaluated in crude oil sample from Yanchang Oilfield pipeline as viscosity reducer. The HMTEAs were added to the crude oil with the concentration of 500 mg/kg, the viscosity of the crude oil after the addition of the additive was measured under different temperatures, and the blank rest was conducted at the same time. The results were shown in Fig 4. It can be seen from the results that the viscosity increases along with decrease of temperature, and the three HMTEAs can reduce the viscosity obviously under low temperature. Compared to HMTEA-3, HMTEA-1 and HMTEA-2 showed better performance as viscosity reducer, and the viscosity reduction rate of them was 79% and 71% respectively at 20℃.

Then the three HMTEAs were evaluated in the crude oil from Chang 2 reservoir. From the results shown in Fig 5, three HMTEAs display quite different ability in viscosity reduction. Similarly, both HMTEA-1 and HMTEA-2 were more efficient on reducing the viscosity of crude oil from the Chang 2 than HMTEA-3. Especially, HMTEA-2 can reduced viscosity from 5780mPa•s to 403mPa•s at 20℃, with the viscosity reduction rate of 93%.

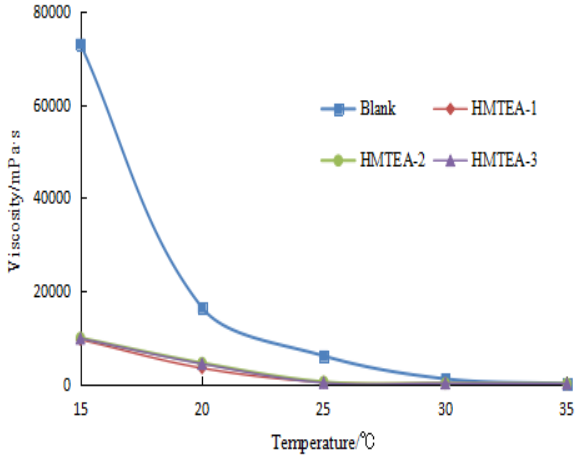

Fig. 4: The effect of HMTEAs on the viscosity of crude oil from Yanchang pipeline.

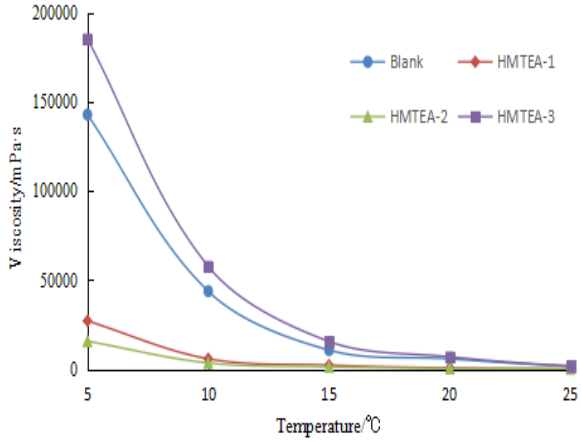

Fig. 5: The effect of HMTEAs on the viscosity of crude oil from Chang 2 reservoir.

In addition, the three HMTEAs were also evaluated in the crude oil from Chang 6 reservoir as shown in Fig 6. Compared with blank, all the three HMTEAs can reduce the viscosity of the crude oil, although HMTEA-2 and HMTEA-3 can only reduce the viscosity slightly. It was noticed that HMTEA-1 is more efficient on reducing the viscosity of crude oil from the Chang 6 reservoir. HMTEA-1 can reduced viscosity from 4520mPa•s to 2580mPa•s at 20℃, with the viscosity reduction rate of 43%.

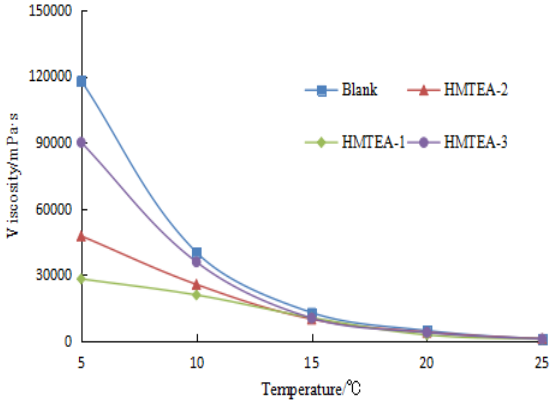

Fig. 6: The effect of HMTEAs on the viscosity of crude oil from Chang 6 reservoir.

Influence of HMTEA on the pour point of crude oil

The HMTEAs were added into crude oil with a concentration of 500 mg/kg. The crude oil was uniformly stirred and the pour points of the three crude oil samples were measured, and the results were summarized in Table 3

Table-3: The effect of HMTEAs on the pour point of crude oil.

Crude oil from Chang 2 reservoir		Crude oil from Chang 6 reservoir		Crude oil from Yanchang pipeline	
Additive	**Δ Pour point /℃**	**Additive**	**Δ Pour point /℃**	**Additive**	**Δ Pour point /℃**
HMTEA-1	**-1.8**	**HMTEA-1**	**-1.3**	**HMTEA-1**	**-0.5**
HMTEA-2	**6.4**	**HMTEA-2**	**-2.4**	**HMTEA-2**	**3.6**
HMTEA-3	**3.2**	**HMTEA-3**	**6.5**	**HMTEA-3**	**1.7**

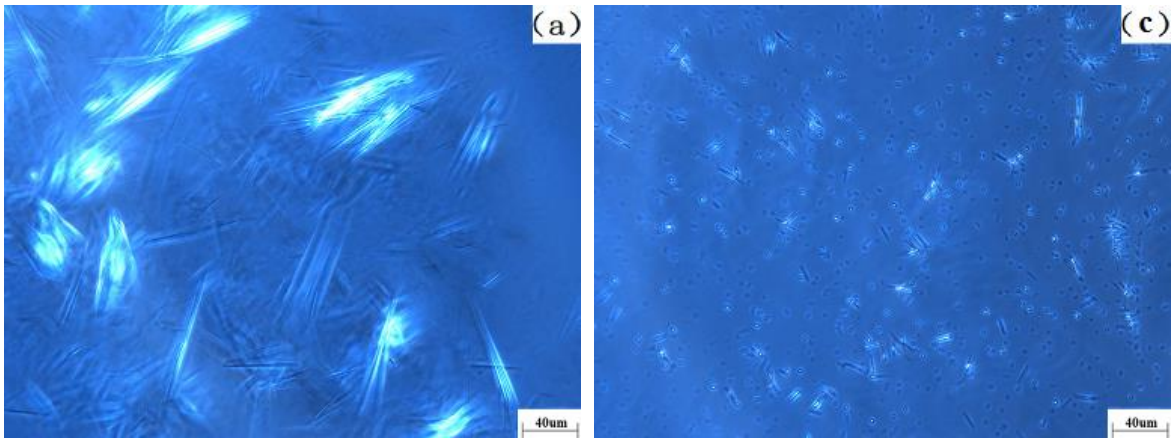

Fig. 7: The wax crystal morphology in saturated hydrocarbon of crude oil from Yanchang 6 reservoir without (left) and with (right) HMTEA-2.

As can be seen from Table 3, the effects of HMTEA on the three kinds of crude oil are significantly different. HMTEA-1 is noneffective for the pour point depression, but leads the pour point to increase. HMTEA-2 can depress the pour point of the crude oil from Chang 2 reservoir and Yanchang pipeline by 6.4 and 3.6°C, although noneffective for the crude oil from Chang 6 reservoir. HMTEA-3 is more efficient on reducing the pour point of crude oil from Chang 6 reservoir, and the maximal pour point depression was obtained by 6.5°C. The hydroxyl groups of HMTEA can act on resins and asphaltenes in the crude oil by hydrogen bonding, and the alkyl side chains interact with the non-polar parts (waxes) in the crude oil. As the types of vegetable oils are different, the alkyl side chains of the synthesized HMTEA changes, which will effect the interaction of HMTEA and crude oil during the precipitation and growth of wax crystals, so as to influence the pour point.

Paraffin crystal morphology analysis

In order to investigate probable mechanism, the morphology of paraffin crystal in HMTEA-3 treated saturated hydrocarbon of crude oil from Chang 6 reservoir, as well as control were investigated (Fig 7), combined with functional group characterization (Fig 2). We know that paraffin crystals will deposit from crude oil, grow in the solution and tend to plug lines and filters when the temperature goes below the pour point value. It can be seen that the untreated crude oil (Fig7a) has the obvious cotton-shaped wax crystals, which is easy to form a three-dimensional network and can confine the flow of the liquid so as to raise the viscosity and eventually lead to solidification. While HMTEA-2 or HMTEA-3 treated samples both exhibited decreased wax crystals with reduced length. which are hard to form a three-dimensional network. Theoretically, the paraffin inhibitors, alternatively known as wax crystal modifier, can modify the size and shape of paraffin crystals and inhibit the formation of large wax crystal lattices [11,12]. Owing to this formation of smaller crystals with a higher volume to surface ratio and reduce growth of the paraffin crystal, the viscosity and pour point of HMTEA-2 or HMTEA-3 treated samples was modified, especially the latter, which was consistent with their evaluation test as inhibitive performance (Table 3).

DSC analysis

Taking aforementioned Paraffin crystal morphology analysis and performance on reducing the pour point of crude oil from Chang 6 reservoir of HMTEA-3, the DSC analysis of HMTEA-3 treated crude oil from Chang 6 reservoir was further studied (Fig 8).

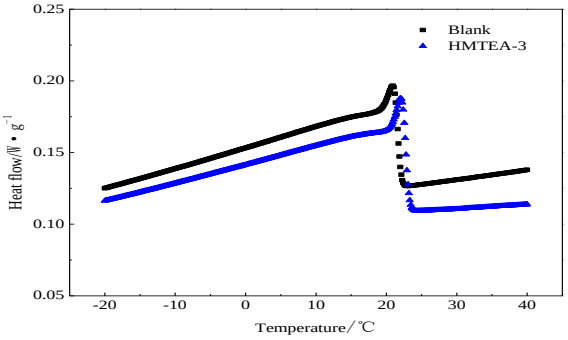

Fig. 8: Comparative analysis of DSC in crude oil and HMTEA-3 oil sample.

According to the literature [13], the final temperature integral calculation of wax precipitation temperature range is selected at -20℃, 210J/g was chosen as the average heat release during wax crystallization, and the wax content in crude oil was calculated by using formula (1), in other words, the ratio of the heat released by wax crystallization and the average heat of crystallization of crude oil samples from the wax precipitation point (T_0) to -20℃ is calculated:

$$\text{Wax precipitation} = \frac{\int_{t_0}^{-20} Q d_Q}{\overline{Q}}$$

In the formula, d_Q is the amount of heat released from the wax in the crude oil sample at the temperature t~ (t+dt), and its unit is J/g. $\overline{Q}$ is the average crystallization heat of crude oil, unit is J/g. Heat of the temperature range [t_0, t_s] of the wax point to the pour point on the DSC curve is integrated to obtain the amount of wax before the pour point, the results were shown in Table 4.

It can be seen from Table 4, the wax precipitation point, wax content and peak temperature of wax precipitation were increased after adding HMTEA-3. According to the nucleation theory, with the decrease of crude oil temperature, HMTEA-3 precipitates and forms nuclei, becoming the center of wax crystal development, so that the wax in the crude oil can precipitate earlier than the blank oil sample, and the wax peak temperature reaches preferentially. At the same time, because the hydroxyl group (-OH) of the polar group in the HMTEA-3 can interact with the resins and asphaltene in the crude oil, the long alkyl chain can interact with the wax crystals to increase the van derWaals force between the wax crystals in the crude oil, resulting in an increase in the amount of wax crystals in the crude oil [14].

Table-4: DSC analysis of crude oil from Chang 2 reservoir with and without HMTEA-3.

Pharmacy	Wax point/ ℃	Wax peak temperature/ ℃	Amount of wax/%	Average heat release/J·g^{-1}
Crude oil	23.07	21.04	4.19	8.80
Crude oil + HMTEA-3	23.73	22.10	5.17	10.85

Mechanism

HMTEA plays an important role in viscosity reduction and pour point depression. The steady conformations of SDB were expressed in Fig 9, which were simulated by a minimize energy of MM2 in Chem 3D. In the molecular structure, the two alkyl chains extend to different directions. There is certainly a combination of different mechanisms including nucleation, co-crystallization and adsorption involved in the crystallization of paraffin [11-14]. In this research, it is clear that HMTEA can modify the crystal morphology and limit the aggregation of wax crystals by packing and/or co-crystallizing to paraffin in the manner with its long alkyl chain and blocking the extensive growth of the paraffin matrices with the polar part (yellow part in Fig 9). HMTEA-3 acts as a paraffin crystal modifier and leads the paraffin to pack in different direction (blue and green parts in Fig 9) to change the nature of the paraffin crystals and also to destroy cohesive forces between the crystals, thereby reducing the risk to form three-dimensional networks which is the main cause of high viscosity and pour point [6,16-18].

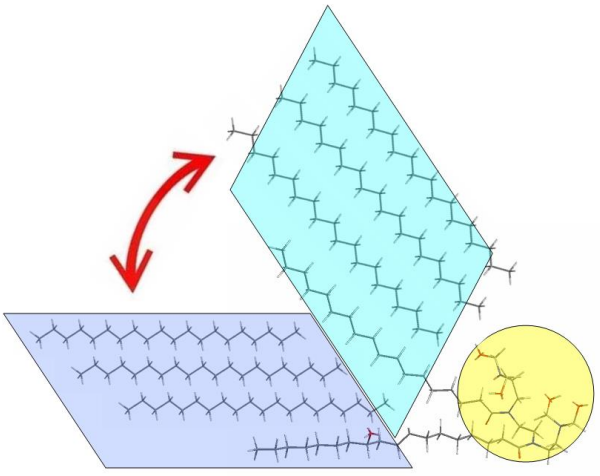

Fig. 9: SDB induced crystallization of paraffin in saturated hydrocarbon.

Conclusions

Hydroxymethyl tetramide (HMTEA) was synthesized from vegetable oil, triethylenetetramine and hexamethylenetetramine. HMTEAs were evaluated as flow improver from the crude oil from Yanchang Oilfield. The three HMTEAs display quite different ability in viscosity reduction in different crude oils. The maximum viscosity reduction rate, 93% (20℃), was achieved from

HMTEA-2 treated crude oil from the Chang 2. The effect of HMTEAs is general on the pour point of the three crude oils. HMTEA-3 is more efficient on reducing the pour point of crude oil from Chang 6 reservoir, and the maximal pour point depression was obtained by 6.5℃. Paraffin crystal morphology analysis and DSC analysis discover the mechanism of the interaction between HMTEA and crude oil. However, we can found that the efficiency of the HMTEAs is quite selective, which means HMTEA can only be used in certain crude oil. So the efficiency of HMTEAs should be enhanced before their wide application. Beside, the mechanism and the synergistic effect of other flow improvers also should be considered.

Acknowledgments

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References

1. M.R. Jorda. Paraffin deposition and prevention in oil wells, *J. Pet. Technol.*, **18**, 1605 (1966).
2. G. Chen, J Lin., W.M. Hu, *et al*. Characteristics of a crude oil composition and its in situ waxing inhibition behavior. *Fuel*, **218**, 213 (2018).
3. X.M. Wei, X.L. Liu, W.D. Wang, *et al*. Overview on viscosity reducing methods of heavy oil. *Specialty Petrochemicals*, **5**, 45 (2002).
4. G. Chen, X.L. Li, J. Zhang. Influence mechanism of crude oil component tnteraction on wax. *Acta Petrolei. Sinica (Petrol. Pro.)*, **29**, 845 (2013).
5. W.J. Yu, Y.F. Yin. Separation and detection of crude components. *J. Petrol. Sci. & Eng.*, **39**, 209 (2010).
6. X.F. Gu, Y.F. Li, J. Yan, *et al*. Synthesis and investigation of a spiro diborate as a clean viscosity-reducer and pour point depressor for crude oil. *Petrol. Chem.*, **59**(6): 570 (2019).
7. G. Chen, Y. Bai, J. Zhang, *et al*. Synthesis of new flow improvers from canola oil and application to waxy crude oil. *Petro. Sci. & Technol.*, **34**(14), 1285(2016).
8. M.K. Mishra. Poue point depressants via anionic polymerization of (meth) acrylicmonomers. P. US 5834408. (1998).
9. G. Chen, W.H. Yuan, F. Zhang, *et al*. Application of polymethacrylate from waste organic glass as a pour point depressor in heavy crude oil. *J. Petrol. Sci. Eng*., **165**, 1049 (2018).
10. G. Chen, Y. Tang, J. Zhang. Synthesis and application of polyaminoamide as paraffin inhibitor from vegetable oil. *Chem. Cent. J.*, **5**, 82 (2011).
11. J. Zhang, Z. Guo, W.C. Du, *et al*. Preparation and performance of vegetable oils fatty acids hydroxymethyl triamides as crude oil flow improvers, *Petrol. Chem*., **58**(12): 1070 (2018).
12. A.G. Holder, J. Winkler. Crystal-growth poisoning of *n*-paraffin wax by polymeric additives and its relevance to polymer crystallization mechanisms. *Nature*, **207**, 719 (1965).
13. C.R. Price. Flow improvers for waxy crudes. *J. Inst. Petrol*., **57**, 106 (1971).
14. G. Chen, J. Zhang, C Cheng, *et al*. Study on synergistic treatment of oily sludge with surfactant and alkali. *J. Petrol. Sci. Eng.*, **183**: 106420 (2019).
15. Q. Deng, Y. Bai, X.F. Gu, *et al*. Synthesis of poly-hydrazide from canola oil and use as flow improver for crude oil, *Adv. Engin. Res.*, **103**, 281(2016).
16. X.F. Gu, F. Zhang, Y.F. Li, *et al*. Investigation of cationic surfactants as clean flow improvers for crude oil and a mechanism study, *J. Petrol. Sci. Eng.*, **164**, 87 (2018).
17. G. Chen, Y.F. Li, W. Zhao, *et al*. Investigation of cyclohexanone pentaerythritol ketal as a clean flow improver for crude oil, *Fuel Process. Technol.*, **133**, 64 (2015).
18. S.J. Chen, K. Zhao, G. Chen, *et al*. Synthesis and application of a spirocompound as clean viscosity-reducer for crude oil. *J. Chem.*, **3827403**, 1 (2016).