



Original Paper

A further investigation to mechanism of the electrorheological effect of waxy oils: Behaviors of charged particles under electric field



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ABSTRACT

Exposing waxy oils to an electric field may significantly improve their cold flowability. Our previous study has shown that interfacial polarization, i.e., charged particle accumulation on the wax particle surface, is the primary mechanism of the electrorheological behavior of waxy oils. However, the way that charged particles interact with wax particles under an electric field remains unknown. In this study, we found no viscosity and impedance change for two waxy crude oils after their exposure to a high-voltage electric field. However, the yield stresses were reduced obviously. We thus proposed that the collision of colloidal particles such as resins and asphaltenes with the wax particles could be an essential mechanism that the wax particle structure was weakened. To verify this hypothesis, a series of ad hoc experiments were carried out, i.e., by performing electrorheological tests on model waxy oils containing additives removable under an electric field, including electrically-neutral colloidal particles (Fe_3O_4), charged colloidal particles (resins), and oil-soluble electrolyte ($\text{C}_{22}\text{H}_{14}\text{CoO}_4$), respectively, and demonstrated that upon application of a high-voltage electric field, charged particles in a waxy oil may move and thus collide with wax particles, and consequently adhere to the wax particle surface. The particle collision results in damage to the wax particle network, and the electrostatic repulsion arising from the adhesion of the charged particle on the wax particle diminishes attraction between wax particles. This study clarifies the process of interfacial polarization.

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1. Introduction

Wax precipitation below the wax appearance temperature (WAT) deteriorates the cold flowability of waxy oils (Shailesh and Vikas, 2017; Guo et al., 2021), posing flow assurance challenges to crude oil production and transportation (Zhang et al., 2013; Zhen et al., 2018; Huang et al., 2020). Improving the cold flowability of crude oil is the fundamental solution to safe and economical transportation of crude oils (Zhang, 2022).

Previous studies have demonstrated that exposing a crude oil to a high-voltage electric field may improve the oil's cold flowability

due to the electrorheological effect of waxy oil, possibly with viscosity reduction of up to 90% (Zhang et al., 2021). This electrorheological effect can be obtained by applying an electric field along the oil's flow direction (Tao and Xu, 2006; Tao and Tang, 2014), or perpendicular to the oil's flow direction (Huang et al., 2021b), or even to a quiescent liquid oil (Ma et al., 2019), with more viscosity reduction at higher field strength and lower treatment temperature (Ma et al., 2017). Except for the liquid oil, electric treatment may result in weakened structural behaviors such as viscoelasticity, yield stress, and thixotropy both for cooled waxy oil gel (Li et al., 2019), which was previously electrically treated in its liquid state, and for gelled waxy oils with the yield stress, storage/loss modulus, and apparent viscosity reduced by more than 90% (Huang et al., 2021a). After the removal of the electric field, the flowability improvement disappears after about one day (Huang et al., 2021a; Li et al., 2021b).

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As for the mechanism of the electrorheological behaviors, earlier studies mainly focused on the changes in wax particle morphology caused by the electric field and contributed the viscosity reduction to the alignment of suspended particles along the streamline (Tao and Xu, 2006; Tao and Gu, 2015), and wax particles aggregation (Ma et al., 2017, 2019; Xie et al., 2020). Nevertheless, these hypotheses cannot properly explain the observed phenomena such as the electrorheological behaviors of gelled waxy oils (Huang et al., 2021a), and the latter is actually untenable quantitatively in consideration of the low fraction of wax particles according to the theory of the suspension rheology (Barnes, 1996). In the latest investigation, we demonstrated that interfacial polarization is an essential mechanism of the electrorheological behaviors of waxy oils (Chen et al., 2021). In that study, Chen et al. (2021) found that the impedance of waxy crude oils and model waxy oils containing resins and asphaltenes increased significantly after electric treatment at temperatures below the WAT. Moreover, the impedance increment was positively related to the viscosity reduction, indicating that some charged colloidal particles such as resins and asphaltenes had accumulated on the surface of wax particles upon the application of electric field, which results in a stronger electrostatic repulsion and consequently weakened van der Waals force between the wax particles, thus improving the cold flowability of waxy oils. After the removal of an electric field, the charged particles gradually diffuse back to the bulk fluid, and thus the viscosity and impedance gradually recover. Qualitatively, by interfacial polarization, the observed electrorheological behaviors of waxy oils can be well explained. However, the way that charged particles interact with wax particles under an electric field remains unknown.

In this study, we observed an interesting new phenomenon from two waxy crude oils that yield stress was reduced but viscosity remained unchanged upon the application of an electric field. Inspired by this observation, we made a hypothesis that the wax particle structure was collided by colloidal particles under the electric field. We thus performed a series of ad hoc experiments using model waxy oils, which contained additives removable under an electric field including electrically-neutral colloidal particles (Fe_3O_4), charged particles (resins), and oil-soluble electrolyte ($\text{C}_{22}\text{H}_{14}\text{CoO}_4$), respectively. Through these experiments, we demonstrate the occurrence of collision between colloidal particles and wax particles, which may result in damage to the wax particle structure, and moreover, as a result of this collision the charged particles, i.e., resins and asphaltenes may adhere to the wax particle surface, thus diminishing attractions between wax particles because of stronger electrostatic repulsion.

2. Phenomenon of no viscosity change but reduced yield stress after electric treatment

2.1. Experimental section

2.1.1. Crude oils

The properties of the two studied crude oils are listed in Table 1, and the wax precipitation curves determined by DSC are shown in Fig. 1. To eliminate the thermal and shear history, all oil samples were preheated to 80 °C and maintained at this temperature for 2 h, and then naturally cooled down to room temperature and maintained for 48 h before tests (Xie et al., 2020).

2.1.2. Rheological measurements

A stress-controlled rheometer HAAKE MARS III equipped with an electrorheological module was used to measure the rheological properties of oil samples (Huang et al., 2021a, b).

Firstly, loaded the oil sample (oil A at 70 °C, oil B at 50 °C) into

Table 1

Physical properties of the studied waxy crude oils.

Parameter	Test method	Value	
		Oil A	Oil B
Density at 20 °C, kg/m ³	ISO 3675-1998	895.6	884.0
Pour point, °C	ASTM D5853-17	43	19
WAT, °C	DSC	65	24
Wax content, wt%	DSC	23.36	9.60
Resins, wt%	ASTM D4124-09	14.56	19.19
Asphaltenes, wt%	ASTM D4124-09	0.89	0.39

the preheated rheometer, and then cooled the sample to the electric treatment temperatures at a rate of 0.5 °C/min and held for 10 min. An electric field (0–5 kV/mm) was then applied to the sample for 60 s. Five constant shear rates (10 s⁻¹, 20 s⁻¹, 50 s⁻¹, 100 s⁻¹, 150 s⁻¹) were sequentially applied for viscosity measurement, and the time under each shear rate was 10 min.

The structural characteristics of oil gels were tested as follows. After the oil samples were cooled to the electric treatment temperatures and maintained at that temperature for 60 min to ensure that the gel structure is fully developed (Liu et al., 2018), an electric field was imposed upon the oil for 60 s, of which an electric field exposure time is enough to improve the cold flowability of waxy oils (Huang et al., 2021a). Subsequently, the viscoelasticity, yielding behavior, and thixotropy of oil samples was measured in situ. The yield behaviors were investigated by dynamic stress sweep tests and constant stress shear tests. The thixotropy were assessed by stepwise shear rate tests (Teng and Zhang, 2013; Taraneh, 2016). Four constant shear rates (1 s⁻¹, 2 s⁻¹, 4 s⁻¹, 8 s⁻¹) were sequentially applied to the waxy gel, the shear rate was held at 1 s⁻¹ for 120 min and held at the other values for 30 min.

2.1.3. Impedance measurement

The impedance was measured by a frequency response analyzer (PSM3750) with Impedance Analysis Interface (IAI) equipment, which was connected to the rheometer HAAKE Mars III. The impedance properties of oil samples in the coaxial cylinder systems can thus be tested in situ before and after electric treatment. The frequency range was 0.02–2000 Hz. All experiments were repeated three times, and the relative uncertainty is less than 5%.

2.2. Electrorheological behaviors and impedance of waxy crudes

Fig. 2 shows the apparent viscosity of oil A and oil B before and after electric treatment at 3 kV/mm for 60 s at the temperature of 3 °C below their pour point. It can be seen that the viscosities of both oils do not change after electric treatment, which is quite different from our previous studies and other published works (Ma et al., 2017; Xie et al., 2020).

However, both the storage moduli and loss moduli under the same stress amplitude reduce significantly after electric treatment, and meanwhile, the yield stress (τ_y) and the critical linear stress (τ_1) are also decreased dramatically. For example, for oil A the yield stress is reduced from 90.2 Pa to 56.2 Pa, showing a reduction of 37.7%, and the critical linear stress is reduced from 28.1 Pa to 11.1 Pa, meaning a reduction of 60.4%. In addition, under the same shear stress, the strain values of oil gel treated by the electric field are bigger, which means the deformation degree of the electrically-treated oil gel is larger. These results clearly demonstrate that the structural strength is reduced by the electric treatment (Fig. 3).

Moreover, the Nyquist plots, with its x-axis and the y-axis representing the real part and the negative imaginary part of the impedance (Chen et al., 2019; Li et al., 2021a; Xie et al., 2022), of both oils show no change after electric treatment, see Fig. 4,

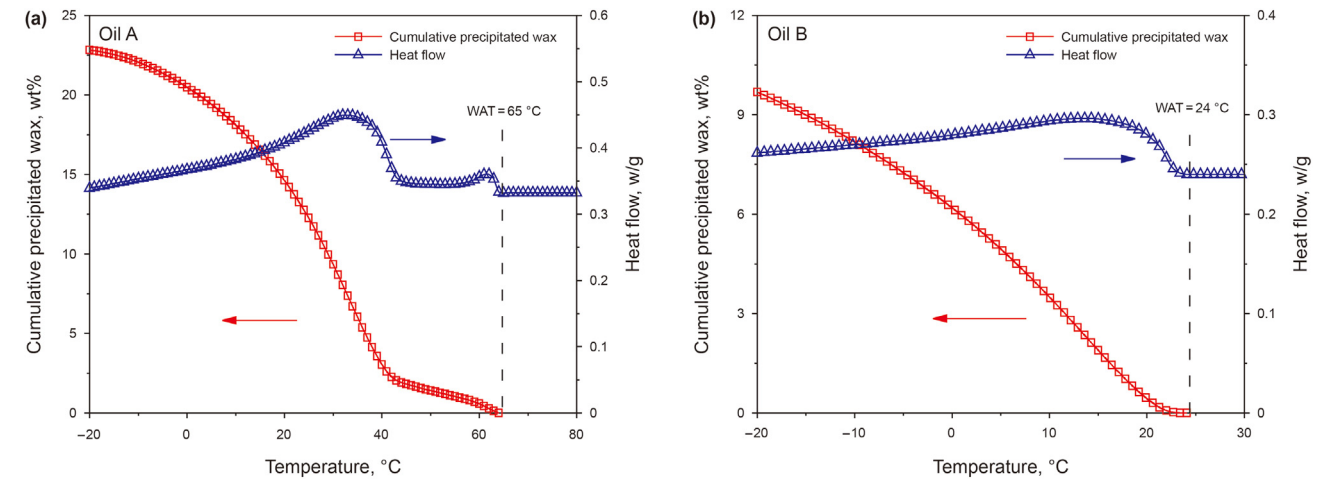


Fig. 1. Wax precipitation curve of oil samples, (a) oil A and (b) oil B.

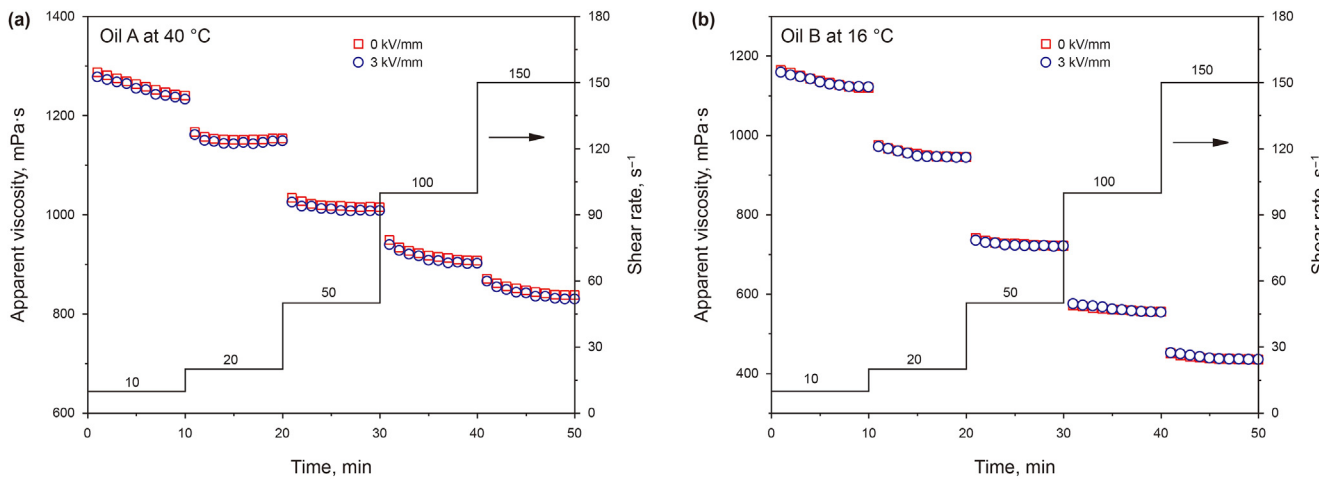


Fig. 2. Viscosities of crude oils before and after electric treatment.

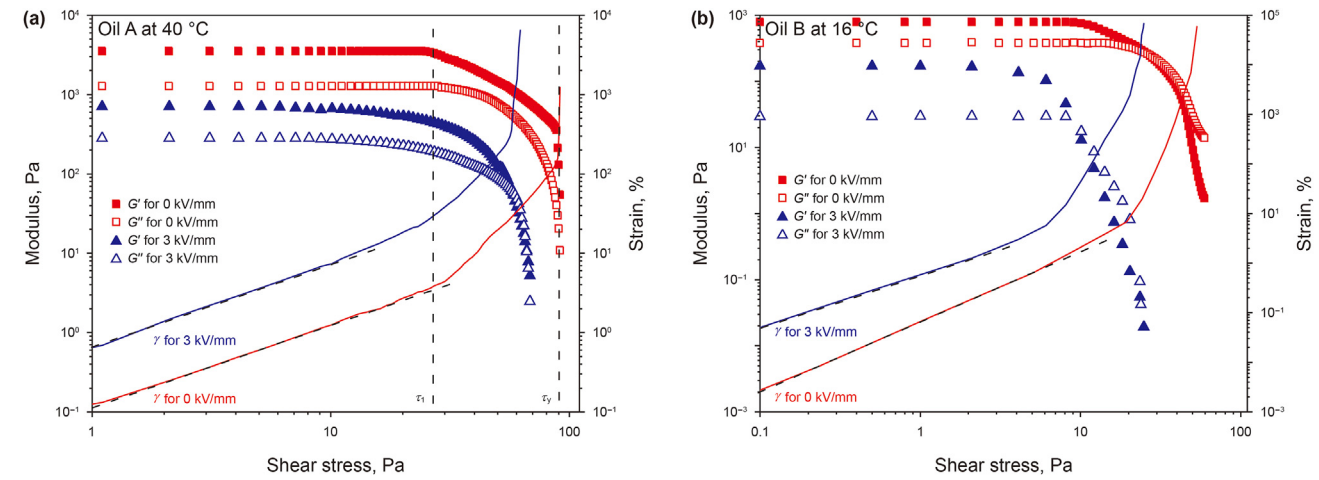


Fig. 3. Dynamic stress sweeps at 0.5 Hz for untreated and electrically-treated oil samples.

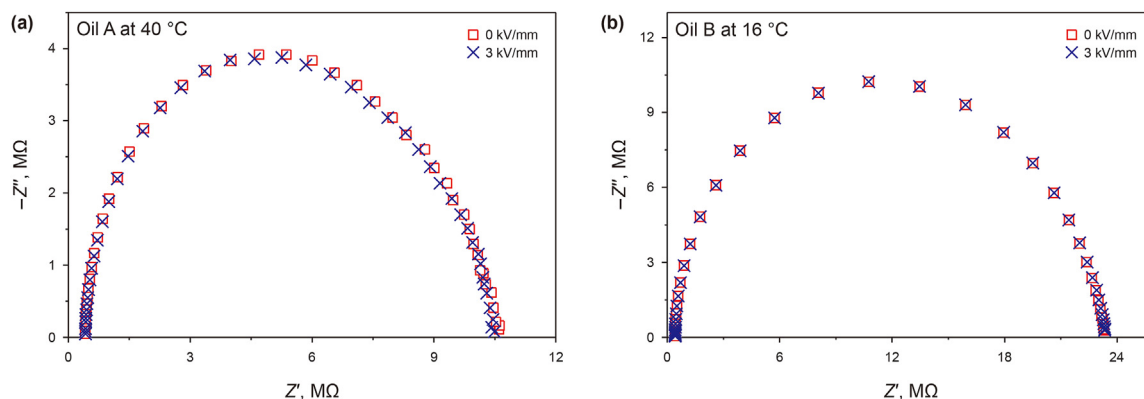


Fig. 4. Nyquist plot of untreated and electrically-treated oil samples.

implying that the amount of charged particles in the bulk of the oil changes little.

2.3. Discussion and hypothesis of particle collision

Since the rheological test temperatures are below the crude oils' WATs, both wax particles and charged particles (Sedghi and Goual, 2010) (asphaltenes and resins) coexist in the oils, which is the requirement for interfacial polarization (Chen et al., 2021). However, no impedance change after electric treatment means that no more asphaltene and resin accumulation occurs on the surface of wax particles after electric treatment. While strangely the yield stress significantly decreases after the treatment, indicating that the 3-D spongy-like structure formed by wax particles is partially destroyed.

From the observation of reduced yield stress but unchanged viscosity, we made a hypothesis that collision must have occurred between colloidal particles of resins and asphaltenes and the wax particles under the dielectrophoretic (DEP) force, leading to weakened gel strength. DEP refers to the phenomenon that in a nonuniform electric field, a net force will generate on particles in the direction of the maximum field strength, which drives particles to move in this direction (Liu et al., 2016). Specifically speaking for waxy oils, the application of an electric field makes the electric field strength around the wax particles nonuniform since the charges inside the wax particles partially gather at the solid-liquid interface. Meanwhile, asphaltenes and resins are charged particles in the oil because of ionization (Sedghi and Goual, 2010), so upon the application of an electric field, they can migrate directionally between the electrodes. When the charged particles pass right next to wax particles with a nonuniform electric field, the charged particles

would move in the direction of the maximum electric field strength, that is, toward wax particles as shown in Fig. 5, resulting in their collision with wax particles. Imaginably, this collision will partially damage the 3-D wax particle structure, resulting in reduced yield stress of the oil gels.

3. Verification of the collision hypothesis

To verify this hypothesis, model oil with controlled composition is used to rule out the multiple factors' effects in the crude oil. Colloidal particles removable in oil with wax particles under an electric field are carefully selected and added to the model oil. Because the most common charged particles in crude oil, i.e., resins, may act to diminish the van der Waals attraction between wax particles due to the electrostatic repulsion when they accumulate on the wax particle surface, it is crucial to find another kind of colloidal particles which does not generate electrostatic repulsion. If our hypothesis is true, we should see yield stress reduction in this system as a result of the collision of colloidal particles with wax particles under an electric field, but no reduction of the equilibrium shear viscosity would occur due to the absence of the electrostatic repulsion.

3.1. Model oils and additives

The model waxy oil system which consisted of 80% mineral oil, 10% o-xylene, and 10% commercial waxes was used in the study. Methods of formulating the model oil system can be found in our previous work (Ma et al., 2019).

Electrically neutral colloidal particles of Fe_3O_4 would be polarized and migrated in oil with wax particles under dielectrophoretic forces upon the application of an electric field. The Fe_3O_4 particles were purchased from Aladdin Industrial with an average particle size of 10 μm . Fe_3O_4 particles were added to model oils at the required concentrations and the mixture was sonicated at 50 °C for 30 min to fully disperse the particles into the oil.

Resins were used as an additive to compare the system with Fe_3O_4 . The resins were extracted from the crude oil and added at the concentration of 100 ppm using the published methods (Dai et al., 2019).

The oil-soluble electrolyte ($\text{C}_{22}\text{H}_{14}\text{CoO}_4$) was selected as another reference additive. $\text{C}_{22}\text{H}_{14}\text{CoO}_4$ exists in the form of ions and will migrate under an electric field in the form of ions (Kilpatrick, 2012), so its migration should not damage the wax particle structure. The used solution consisted of 8% $\text{C}_{22}\text{H}_{14}\text{CoO}_4$ and 92% mineral oil. After the addition of electrolyte at a dosage of 100 ppm, the model oil was heated to 50 °C and stirred for 30 min.

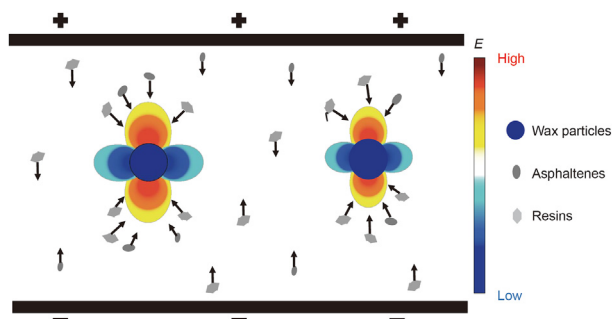


Fig. 5. Schematic diagram of dielectrophoresis of colloidal particles under the electric field.

Table 2
Compositions and pour point of the studied model oils.

Oil sample	Concentration, wt%			Additives	Pour point, °C
	Wax	Mineral oil	O-xylene		
Model oil 1	10	80	10	None	28
Model oil 2	10	80	10	C ₂₂ H ₁₄ CoO ₄	28
Model oil 3	10	80	10	Fe ₃ O ₄	28
Model oil 4	10	80	10	Resins	28

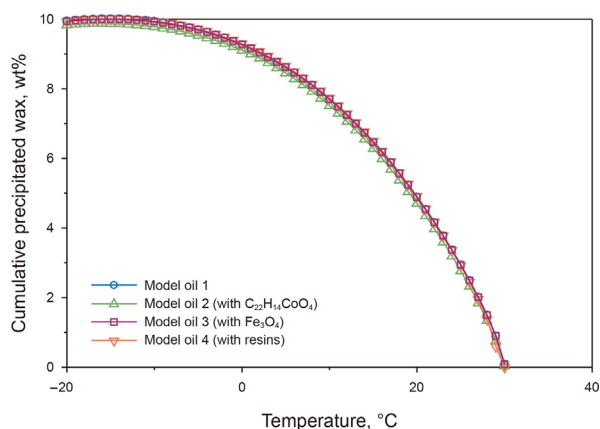


Fig. 6. Wax precipitation curves of model oils with additives.

The compositions and corresponding mass fraction of specific model waxy oils are shown in Table 2. As shown in Fig. 6, the three additives at the concentration of 100 ppm have almost no impact on the wax precipitation of the model oils.

3.2. Yield stresses of the model oils with Fe₃O₄ and C₂₂H₁₄CoO₄

The yield stress was determined using dynamic stress sweep tests before and after electric treatment of 5 kV/mm for 60 s at 24 °C, and the results are shown in Table 3. Obviously, the electric field has no influence on the yield stress of model oil 1 without removable additives under the electric field, which is consistent with our previous study (Chen et al., 2021). As is expected the electric treatment has virtually no influence on the yield stress of model oil 2 (with C₂₂H₁₄CoO₄), while the yield stress of model oil 3 (with Fe₃O₄) decreases from 110.7 Pa to 79.7 Pa, showing a reduction of 28%.

In addition, Fig. 7 shows the strain evolution of model oil 3 (with 100 ppm Fe₃O₄) before and after the application of an electric field of 5 kV/mm for 60 s at 24 °C. As can be seen in Fig. 7, for untreated gel, when the imposed stress is less than 60 Pa, the gel just exhibits viscoelastic creep, and the structural fracture cannot be observed in 600 s. When the imposed stress reaches 60 Pa, the strain increases rapidly after about 520 s, that is, gel structure fracture occurs. For the electrically-treated oil gel, the yield stress is just 40 Pa, corresponding to a yield stress reduction of 33%.

The above results preliminarily verify the occurrence of particle collision under an electric field. Considering that the amount of Fe₃O₄ may affect the effect of particle collision, we further investigated the yield stress of model oils with Fe₃O₄ concentrations from 20 to 1000 ppm after electric treatment of 5 kV/mm for 60 s at 24 °C, with the results shown in Fig. 8. As is expected, more yield stress reduction was observed with increased Fe₃O₄ concentration.

Table 3
Yield stress of three model oils before and after electric treatment.

Oil sample	Yield stress, Pa	
	Untreated	Electrically-treated
Model oil 1	104.6	104.2
Model oil 2 (with C ₂₂ H ₁₄ CoO ₄)	102.4	102.3
Model oil 3 (with Fe ₃ O ₄)	110.7	79.7

3.3. Yield stresses of the model oils with Fe₃O₄ and resins

To further demonstrate the occurrence of particle collision under the electric field, we measured yield stresses of model oil 3 (with Fe₃O₄) under the following two conditions.

Condition 1. The oil was electrically treated at 5 kV/mm for 60 s at 24 °C (4 °C below the pour point) and the yield stresses were measured at 24 °C by dynamic stress sweep tests. The detailed experiment procedures can be found in our previous work (Huang et al., 2021a).

Condition 2. The oil was electrically treated at 29 °C (1 °C above the pour point), and the yield stresses were measured at the same temperature as Condition 1, i.e., 24 °C. The experiment steps are as follows. Cooled the oil from 50 °C to 29 °C and held it at 29 °C for 10 min before imposing an electric field. After the electric treatment (5 kV/mm for 60 s), the oil sample was cooled down to 24 °C and held at this temperature for 60 min. Finally, the yield stress of the oil was determined by dynamic stress sweep tests.

The latter test was designed by considering the following fact. The amount of precipitated wax of the studied oil is only 0.58 wt% at 29 °C, and thus the 3-dimensional wax particle structure should have not been formed yet. However, when the oil further cools down to 24 °C, the precipitated wax reaches 3.35 wt% and therefore the 3-D spongy-like structure should have been built. By comparing the yield stresses of these two condition tests, we should be able to further understand the effect of particle collision.

In addition, as an important part of this effort, we also measured the yield stresses of model oil 4 (with resins) under the above two conditions. The difference between these two additives is that the resins have double effects of the collision and electrostatic repulsion arising from their adhesion on the wax particle surface after the collision, but the Fe₃O₄ particles have only the former.

As can be seen from Table 4, the yield stress of model oil 3 treated at 29 °C is 108.7 Pa, representing little yield stress reduction compared with that of the untreated oil. This can be attributed to the increased precipitated wax when the oil cools down from 29 °C to 24 °C after the treatment. Obviously, the newly precipitated wax particles make a great contribution to the formation of the 3-D network after the wax crystal aggregations were damaged at 29 °C under the electric field.

For the untreated model oil 4 (with resins), the yield stress is only 15.1 Pa at 24 °C, much lower than that of oil 3. This is the effect of resins, as is well known that resins are called “natural pour point depressants” (Dai et al., 2019). The yield stress of oil 4 is reduced by 99% to 0.1 Pa after being treated at 24 °C. This much better effect of yield stress reduction is attributed to resins’ double role of collision and electrostatic repulsion. Moreover, the yield stress at 24 °C of the same oil treated at 29 °C is 5.1 Pa, remarkably higher than that treated at 24 °C. This also suggests the contributions of the newly precipitated wax particles and the electrostatic repulsion of the resins.

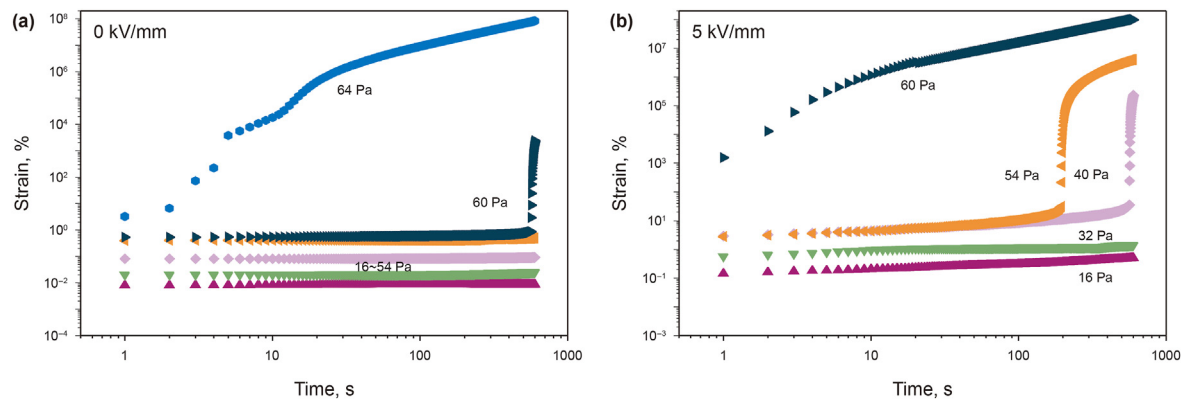


Fig. 7. Strain evolution of model oil 3 under different imposed stresses at 24 °C.

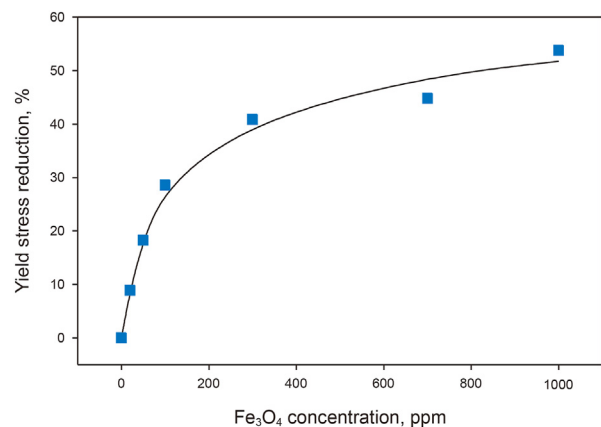


Fig. 8. Yield stress reduction vs. Fe₃O₄ concentration (5 kV/mm, 24 °C).

3.4. Viscosities of the model oils with Fe₃O₄ and resins

This section is intended to further investigate the effect of the particle collision from another perspective, i.e., viscosity. The electric treatment and rheological tests were performed at 28 °C (pour point of the model oils), at which wax particle aggregation should have occurred, and thus the oils are thixotropic, however, the 3-D spongy-like network should have not formed. That is to say, the wax crystal structure at this temperature is weak and thus could be more sensitive to disturbance. Viscosity and its variations should represent information about the structure of wax particles. Therefore, it was expected that the Fe₃O₄ particle collision might reduce the oil's viscosities in the thixotropic process, but the shear equilibrium viscosity should not change since no electrostatic repulsion occurs. While the model oil with resins should show lower viscosity in the whole process including lower equilibrium viscosity.

Fig. 9 presents the stress decay at the shear rate of 1, 2, 4, 8 s^{−1}

Table 4
Yield stress of model oils treated under different conditions.

Oil sample	Yield stress at 24 °C, Pa		Yield stress at 24 °C after electrically treated at 29 °C, Pa
	Untreated	Electrically treated	
Model oil 3 (with Fe ₃ O ₄)	110.7	79.7	108.7
Model oil 4 (with resins)	15.1	0.1	5.1

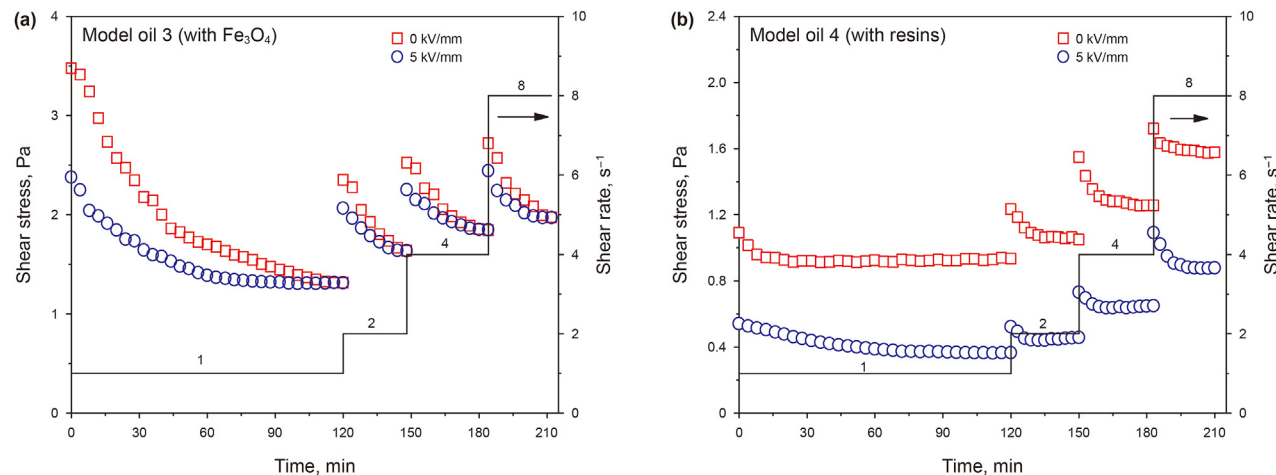


Fig. 9. Thixotropic behaviors of model oils before and after electric treatment at 28 °C.

for model oil 3 (with Fe_3O_4) and model oil 4 (with resins) before and after electric treatment at 5 kV/mm for 60 s. Both two oils show typical thixotropic viscosity decay at constant shear rates. Fig. 9(a) shows that the electrically-treated oil 3 has much lower thixotropic viscosities, but the equilibrium viscosities are just the same as that of the untreated oil, with the most typical case observed at the shear rate of 1 s^{-1} . The much lower thixotropic viscosities of the treated oil strongly suggest that the wax particle aggregations were damaged by Fe_3O_4 particle collision under the electric field, while the same equilibrium viscosities imply that Fe_3O_4 particle does not change microscopic interactions within the oil at shear equilibrium.

Nevertheless, from Fig. 9 (b), we can see a quite big difference in the whole shear process. This suggests the occurrence of resins' adhesion to the wax particle surface as a result of the collision, which results in stronger electrostatic repulsion between the wax particles, and thus much lower equilibrium viscosity. Because the electric treatment and subsequent rheological test were performed at the same temperature, the co-crystallization of wax and resins should have not occurred.

3.5. Discussion on crude oil A and B's unchanged viscosity after the treatment

Previous studies reported both yield stress and viscosity reduction arising from the electric treatment of crude oil gels (Huang et al., 2021a). This can be well explained by the presently proposed mechanism of particle collision and consequent adhesion of charged particles on the surface of wax particles. The phenomenon of unchanged viscosity but reduced yield stress found in this work is strange. Currently, we cannot give a perfect explanation with direct evidence. It can be found that the two waxy crude oils used in this study contain high contents of resins and asphaltenes. Therefore, we speculate that there might have several possible reasons for this phenomenon. One could be that the wax particles have been fully wrapped by the charged particles before electric treatment due to the high content of resins, which provides sufficient electrostatic repulsion to prevent further adhesion of more charged particles under an electric field. The unchanged impedance after the application of an electric field, which means the amount of charged particles changes little, could be evidence supporting the conjecture. The other would be that the colloidal particles at high concentration are self-associated to form aggregates (Alvarez-Ramirez et al., 2006; Li et al., 2018), and thus lose the ability of adhesion. Further investigations will be made to clarify the mechanism of this phenomenon.

4. Conclusions

No viscosity and impedance change but reduced yield stress was found for two waxy crude oils after their exposure to a high-voltage electric field. Inspired by this surprising phenomenon, it is hypothesized that upon application of the electric field charged particles in the crude oil, i.e., resins and asphaltenes, would collide with wax particles and adhere to them due to the viscous nature of resins and asphaltenes. To verify this hypothesis, a series of ad hoc experiments were performed by using model waxy oil with carefully selected colloidal particles of Fe_3O_4 , as well as resins and oil-soluble electrolyte ($\text{C}_{22}\text{H}_{14}\text{CoO}_4$), respectively. For the model oil with Fe_3O_4 particles, it is found that the electric treatment makes the yield stress and the thixotropic viscosities at the treatment temperature reduced remarkably, but the shear equilibrium viscosity is unchanged. While for the model oil with resins, yield stress as well as thixotropic and equilibrium viscosities are reduced as a result of the treatment. Therefore, it is demonstrated that upon application of a high-voltage electric field, colloidal particles such

as charged particles and Fe_3O_4 in a waxy oil may move and thus collide with wax particles, and as a result the charged particles further adhere to the wax particle surface. The particle collision partially damages the 3-dimensional wax particle structure, thus weakening the structural strength of the wax particle network. And in addition, the charged particle adhesion diminishes the mutual attraction of wax particles, thereby improving the cold flowability of waxy oils. The unchanged equilibrium viscosity of the oil system with Fe_3O_4 is attributed to the lack of electrostatic repulsion of Fe_3O_4 particles. For the system of $\text{C}_{22}\text{H}_{14}\text{CoO}_4$, no particle collision occurs since the electrolyte exists as ions in the oil. It is speculated that the lack of viscosity reduction for the two crude oils could be related to their high contents of resins and asphaltenes. This study further supports the presence of interfacial polarization and makes its process clarified.

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