



# Study on the dipole moment of asphaltene molecules through dielectric measuring



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## HIGHLIGHTS

- This method is capable of measuring multi dipoles in one solution simultaneously.
- This method can deduce dipole moment without measuring the refractive index.
- This method is potential to study the aggregation of asphaltenes.

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## ABSTRACT

The polarity of asphaltenes influences production, transportation, and refining of heavy oils. However, the dipole moment of asphaltene molecules is difficult to measure due to their complex composition and electromagnetic opaqueness. In this work, we present a convenient and efficient way to determine the dipole moment of asphaltene in solution by dielectric measurements alone without measurement of the refractive index. The dipole moment of n-heptane asphaltenes of Middle East atmospheric residue (MEAR) and Ta–He atmospheric residue (THAR) are measured within the temperature range of  $-60\text{ }^{\circ}\text{C}$  to  $20\text{ }^{\circ}\text{C}$ . There is one dielectric loss peak in the measured solutions of the two types of asphaltene at the temperatures of  $-60\text{ }^{\circ}\text{C}$  or  $-40\text{ }^{\circ}\text{C}$ , indicating there is one type of dipole in the solution. Furthermore, there are two dielectric loss peaks in the measured solutions of the two kinds of asphaltene when the temperature rises above  $-5\text{ }^{\circ}\text{C}$ , indicating there are two types of dipoles corresponding to the two peaks. This phenomenon indicates that as the temperature increases above  $-5\text{ }^{\circ}\text{C}$ , the asphaltene molecules aggregate and present larger dipole moment values. The dipole moments of MEAR  $C_7$ -asphaltene aggregates are up to 5 times larger than those before aggregation. On the other hand, the dipole moments of the THAR  $C_7$ -asphaltene aggregates are only 3 times larger than those before aggregation. It will be demonstrated that this method is capable of simultaneously measuring multi dipoles in one solution, instead of obtaining only the mean dipole moment. In addition, this method can be used with a wide range of concentrations and temperatures.

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## 1. Introduction

The solubility and stability of asphaltenes in heavy oils play an important role in heavy oil recovery, transport, or refining, which

are dependent on their polarity [1–3]. The most straightforward way to evaluate the polarity of asphaltenes is to measure their dipole moment. However, since asphaltenes are complex mixture defined as a solubility class, the complicated compositions of asphaltenes with various polar compounds increase the measurement difficulty of dipole moments. In the past, the polarity of asphaltenes was deduced by their dielectric permittivity as well as the refractive index of the asphaltene solution. For example, Goual et al. [4] inferred the dipole moment of asphaltenes and resins dissolved in toluene at the concentrations of 0.2–0.8% wt by

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### Nomenclature

$\tan \delta$	the ratio of the dielectric loss to the dielectric storage	$\tau_0$	relaxation time (s)
$\epsilon'$	the dielectric storage or the real part of dielectric permittivity	$\alpha$	the polydispersity parameter having the value between 0 and 1
$\epsilon''$	the dielectric loss or the imaginary part of dielectric permittivity	$\sigma'$	conductivity (S/m)
$\epsilon_\infty$	the dielectric constant at infinite high frequencies	$\sigma'_{ion}$	ionic conductivity (S/m)
$\epsilon_0$	the dielectric constant at very low frequencies	$\epsilon_v$	the dielectric constant of vacuum ( $8.854 \times 10^{-12}$ F/m)
$c$	concentration ( $\text{mol cm}^{-3}$ )	$f$	the applied frequency (Hz)
$w$	concentration ( $\text{g g}^{-1}$ )	$\epsilon'$	measured real part of dielectric permittivity = ratio of solution capacity to capacity of air
$M_W$	the molecular weight of solute, ( $\text{g mol}^{-1}$ )	$\omega_{peak}$	the angular frequency corresponding to the peak of dipolar dielectric loss
$N$	Avogadro number	$T$	temperature (K)
$k$	Boltzmann's constant	$k$	Boltzmann's constant
$\mu$	mean dipole moment (Debye)	$\eta$	the effective viscosity
$\omega$	the angular frequency in radians per second, $\omega = 2\pi f$	$R_d$	the dipole moment weighted particle radius
$\rho$	the density of the solution ( $\text{g cm}^{-3}$ )	$f_{peak}$	the frequency of the dipolar dielectric loss peak (Hz)
$\epsilon''_{ion}$	contribution to dielectric loss from ionic conductivity		
$\epsilon''_{dipole}$	contribution to dielectric loss from dipole relaxation		

measuring the refractive index, density, and the dielectric constant of the solutions at a frequency of 800 Hz and a voltage level of 1.0 V. Zhang et al. [5] measured the dipole moment of fractions of heavy oil dissolved in benzene with a simplified method [6–11], which measured the dielectric constant and refractive index of the solution, but not the density. Asphaltene molecules absorb and scatter light strongly. As a result, measurement of the asphaltene dipole moment based on measuring the refractive index is limited to low concentration solutions. This is a major limitation to study on the characteristics of asphaltene at high concentrations.

In this work, a new method that allows the dipole moment to be measured from dielectric measurements alone is reported. The dipole moment of asphaltenes at high concentrations can be determined as a function of temperature, which allows analysis of aggregation of asphaltenes at a wide range of temperatures or concentrations. An equation based on the Debye theory is used to calculate the dipole moment of asphaltene that can avoid atomic polarization approximations [12–16]. Most importantly, this method has the potential to simultaneously measure multi dipoles in one solution, instead of obtaining only the mean dipole moment.

## 2. Experimental section

Middle East atmospheric residue (MEAR) and Chinese Ta–He atmospheric residue (THAR) were used as samples in this study, which have different origins and possess different properties. Asphaltenes were separated by adding certain amount of n-heptane ( $40 \text{ cm}^3/\text{g}$  oil) into the heavy oil. Precipitates were filtrated and extracted using a Soxhlet Apparatus by boiling n-heptane until the filtrate was colorless. Therefore the asphaltenes are denoted as n-heptane asphaltenes ( $C_7$ -asphaltenes). Contents of carbon, hydrogen, sulfur and nitrogen were analyzed by a VARIO EL III CHNS/O elemental analyzer. The metal contents were analyzed by the ContraA-700 continuous light source high resolution flame and graphite furnace atomic absorption integration spectrometer. The oxygen content was calculated by subtraction method from the other elements. The properties of  $C_7$ -asphaltenes are shown in Table 1 [17].

The toluene used is HPLC grade by Sigma–Aldrich, and the molecular sieve was used to adsorb the impurities. The asphaltenes were then dissolved in toluene at 1.0 wt% concentration and their dielectric permittivity parameters were measured. The molecular

weight of the asphaltenes was measured by a Knauer vapor pressure osmometer at  $80.0^\circ\text{C}$  with toluene as the solvent. The previous study have demonstrated that asphaltenes had a strong tendency toward self-association in solution, and the single asphaltene molecules only can be observed at very low concentrations [18]. However, it is very difficult to measure the asphaltene molecular weight in solutions under such low concentrations, because of the sensitivity of the measurement methods [19]. So in this research, we deduced the mean structural module number obtained from the elemental analysis and  $^1\text{H}$  NMR data [17,20], which represented the average number of asphaltene in one aggregate. The molecular weight measured by vapor pressure osmometer at  $80.0^\circ\text{C}$  was assigned as the mean  $M_W$  of the aggregates, and the  $M_W$  of the single asphaltene was defined as the value of  $M_W$  measured by VPO divided by the mean structural module number. The  $M_W$  of aggregated asphaltenes or single asphaltenes were used to calculate the dipole moment of asphaltene aggregates or single asphaltenes separately.

The dielectric measurements are conducted with an Alpha-A high resolution dielectric, conductivity, impedance and gain phase modular measurement system (Novocontrol Technologies, German), equipped with a Quatro Cryosystem to control the measurement temperature. The Novocontrol liquid sample cell (BDS 1308) was used to avoid solution volatilization with quartz class spacer rather than polytetrafluoroethylene spacer to decrease the background signal of spacer, while the spacing between the

**Table 1**  
Elemental composition of  $C_7$ -asphaltenes.

Properties and elemental composition	MEAR $C_7$ -asp	THAR $C_7$ -asp
$M_W$ of aggregated asphaltene (g/mol)	$3.54 \times 10^3$	$6.89 \times 10^3$
Mean module number	2.90	6.14
$M_W$ of single asphaltene (g/mol)	$1.22 \times 10^3$	$1.12 \times 10^3$
C (wt%)	83.12	83.77
H (wt%)	7.38	7.31
S (wt%)	6.29	4.77
N (wt%)	0.91	1.43
O (wt%)	2.18	2.16
H/C	1.057	1.039
Ni ( $\mu\text{g/g}$ )	244	185
V ( $\mu\text{g/g}$ )	444	813
Fe ( $\mu\text{g/g}$ )	486	209
Ca ( $\mu\text{g/g}$ )	55.4	655
Mg ( $\mu\text{g/g}$ )	5.0	134

electrodes was designated as 0.7 mm. Measurements were performed at different temperatures ranging from  $-60\text{ }^{\circ}\text{C}$  to  $20\text{ }^{\circ}\text{C}$  with the temperature variation during single measurement  $<0.05\text{ }^{\circ}\text{C}$ . Since the melting point of toluene is  $-95\text{ }^{\circ}\text{C}$ , the solution of toluene with 1.0 wt% asphaltene is liquid within the entire temperature range in this study.

### 3. Results and discussion

#### 3.1. Dielectric loss as a function of frequency and temperature

The dipole moment of molecules can be measured by the dielectric properties of their solution in non-polar or low polarity solvents [12–16]:

$$\tan \delta = \frac{\epsilon''}{\epsilon'} = \frac{(\epsilon_0 + 2)(\epsilon_{\infty} + 2)}{\epsilon'} \frac{4\pi c N \mu^2}{27kT} \frac{\omega\tau}{1 + \omega^2\tau^2} \quad (1)$$

$$c = \frac{w\rho}{M_w} \quad (2)$$

The dielectric loss of 1 wt% MEAR  $C_7$ -asphaltenes solution in toluene as a function of frequency at different measurement temperatures is shown in Fig. 1. Based on this figure, it should be noted that the dielectric loss decreases sharply with the increase in the excitation frequency. The slope of the logarithm of dielectric loss versus the logarithm of frequency is about  $-1$ , indicating that this dielectric loss measurement mainly arises from the solution conductivity, as consistent with the previous report [21,22]. Therefore, it is necessary to remove the contribution from ionic conductivity to obtain the dielectric loss from the asphaltene dipoles. The method will be detailed below.

Considering the solvent of toluene has a negligible dipole moment of only 0.3 Debye, the dielectric loss in our experiments is mainly composed of two parts: ionic conductivity and dipole moment, as expressed in Eqs. (3) and (4):

$$\epsilon'' = \epsilon''_{ion} + \epsilon''_{dipole} \quad (3)$$

The ionic conductivity,  $\sigma_{ion}$ , is considered as the representation of the mobility of free ions and is independent on the frequency applied [23–27]. The contribution from ionic conductivity to the dielectric loss can be described as Eq. (4) [21,28–30]:

$$\epsilon''_{ion} = \frac{\sigma'_{ion}}{2\pi f \epsilon_v} \quad (4)$$

The contribution from dipole relaxation to the dielectric loss can be expressed with the Cole–Cole equation [31]:

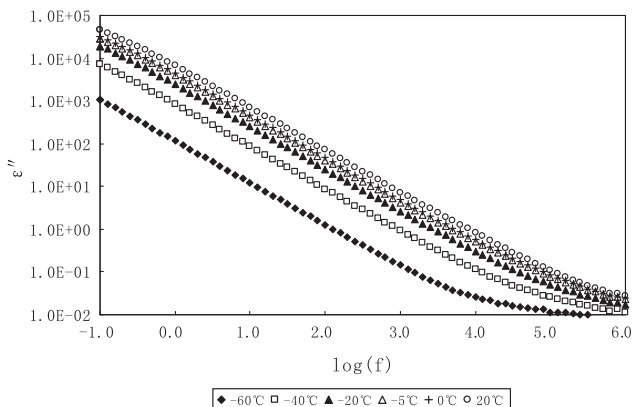


Fig. 1. The dielectric loss of  $C_7$ -asphaltenes of MEAR at different measuring temperatures.

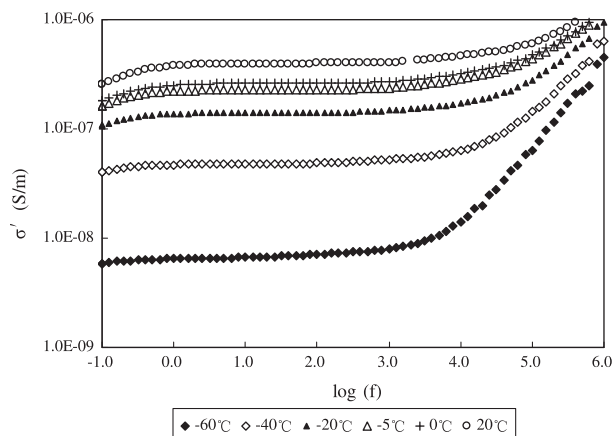


Fig. 2. The conductivity of  $C_7$ -asphaltenes of MEAR at different measuring temperatures.

$$\epsilon''_{dipole} = \frac{(\epsilon_0 - \epsilon_{\infty})\omega\tau_0}{1 + (\omega\tau_0)^{2(1-\alpha)}} \quad (5)$$

Fig. 2 shows the conductivity variation as a function of frequency at temperatures ranging from  $-60$  to  $20\text{ }^{\circ}\text{C}$ . All conductivity curves start with a plateau between  $\sim 1\text{ Hz}$  and  $\sim 1000\text{ Hz}$ , and then the conductivity increases sharply at frequencies greater than  $\sim 1000\text{ Hz}$ . When the frequency is higher than  $1000\text{ Hz}$ , the conductivity exhibits a power law dependence on the logarithm of applied field frequency and reflects charge-transport mechanisms [32]. The curves decrease with frequency at frequency less than  $1\text{ Hz}$  because of polarization effects, and the decrease becomes more apparent as the temperature increases. These changes are caused by an increase in polarization that mainly occurs below  $\sim 1\text{ Hz}$ . The plateau conductivity is the representative of the ionic conductivity (direct conductivity) of the solution. The plateau conductivities increase significantly with temperature increase. This can be explained by a decrease of solution viscosity and an increasing molecular thermal motion with temperature increase.

The method shown in the current paper is to measure the ionic conductivity of the solution, and subtract contribution from ionic conductivity to the dielectric loss from the total dielectric loss using Eqs. (3) and (4). The contribution from dipole relaxation was obtained, described by Eq. (5), and defined as dipolar dielectric loss. The intermediate steps are shown in Figs. 2 and 3, while the dipolar dielectric loss in solution is shown in Fig. 4. The inflection point of the plateau of each curve in Fig. 2 can be determined more accurately if the derivatives of the curves are taken into account, as

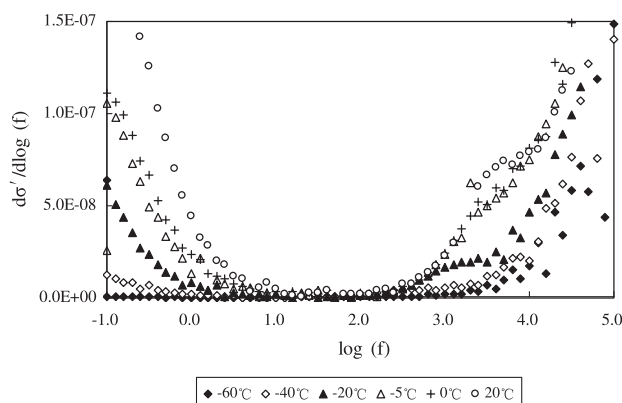


Fig. 3. The derivative of conductivity of  $C_7$ -asphaltenes of MEAR with respect to  $\log(f)$ .

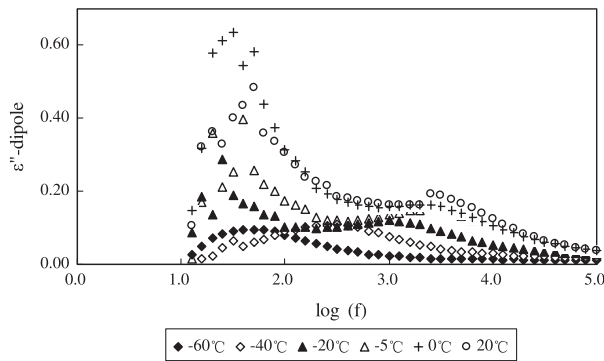


Fig. 4. The dielectric loss of C<sub>7</sub>-asp of MEAR from dipoles at different temperatures.

shown in Fig. 3. All derivative curves in Fig. 3 show a minimum value when the logarithm of frequency is between 0.8 and 2.5, and thus the ionic conductivities used in Eq. (3) are the conductivities at about 10 Hz where no distinctive polarization effects occur. Fig. 4 shows the dipolar dielectric loss when the dielectric loss related to solution conductivity, as calculated by Eq. (4), which is subtracted from the total measured dipole loss as indicated by Eq. (3).

The portions of the dipolar dielectric loss curves at frequencies below 1 Hz in Fig. 4 are disturbed by polarization effects. Nevertheless, Fig. 4 clearly shows that a single peak at low temperatures is divided into two peaks at temperatures above  $-20\text{ }^{\circ}\text{C}$ . In general, every peak corresponds to a kind of dipole. This phenomenon indicated that there was mainly one kind of dipole at low temperatures. When the temperatures were above  $-20\text{ }^{\circ}\text{C}$ , there were two kinds of dipoles in the solution, and the new one was possibly resulting from asphaltene aggregation. In addition, the peaks shift to higher frequencies with increase in temperature. The reason is that the viscosity decreases with increase in temperature, and the dipole molecules re-orient more freely under an altering dielectric field. Furthermore, it can be seen in Fig. 4 that as the measurement temperature increases, the ratio of the peak areas between the lower frequency and the higher frequency increased. This means more asphaltene aggregates with increase in the measurement temperature.

### 3.2. Deducing the dipole moment of asphaltene

The dipole moment of asphaltene can be calculated from the dipolar dielectric loss using Eq. (1).

The relaxation time corresponding to each peak in Fig. 4 can be calculated from Eq. (6) with results shown in columns 2 and 3 in Tables 2 and 3.

Table 2

The n-heptane asphaltenes of MEAR in toluene at the concentration of 1 wt%.

T (K)	$f^a$ (Hz)	$\tau$ (s)	$M_w$ (g/mol)	$\tan \delta_{\text{dipole}}$	$\epsilon'$	$\rho$ (g/cm <sup>3</sup> )	$\epsilon_0$	$\epsilon_{\infty}$	$\mu$ (Debye)
213	50	0.003172	$1.22 \times 10^3$	0.0396	2.393	0.940	2.50	2.20	11.7
233	317	0.000502	$1.22 \times 10^3$	0.0438	2.485	0.922	2.90	2.40	12.4
253(peak1)	1000	0.000159	$1.22 \times 10^3$	0.0483	2.468	0.904	4.80	2.20	11.9
253(peak2)	25	0.006344	$3.54 \times 10^3$	0.0884	3.239	0.904	4.80	2.20	31.3
268(peak1)	2510	6.34E-05	$1.22 \times 10^3$	0.0654	2.454	0.890	7.00	2.40	12.1
268(peak2)	20	0.007962	$3.54 \times 10^3$	0.0751	4.757	0.890	7.00	2.40	30.8
273(peak1)	2000	7.96E-05	$1.22 \times 10^3$	0.0656	2.483	0.885	8.00	2.40	11.7
273(peak2)	32	0.005023	$3.54 \times 10^3$	0.162	3.926	0.885	8.00	2.40	39.4
293(peak1)	2510	6.34E-05	$1.22 \times 10^3$	0.0799	2.421	0.867	11.00	2.40	11.7
293(peak2)	50	0.003172	$3.54 \times 10^3$	0.486	3.577	0.867	11.00	2.40	59.9

<sup>a</sup> The frequency at the peak of dipolar dielectric loss.

$$\tau_0 = \frac{1}{\omega_{\text{peak}}} = \frac{1}{2\pi f_{\text{peak}}} \quad (6)$$

In Eq. (6),  $\omega_{\text{peak}}$  is the angular frequency corresponding to the peaks shown in Fig. 4.  $\tan \delta_{\text{dipole}}$  is determined from the ratio of  $\epsilon''_{\text{dipole}}$  to  $\epsilon'$  as indicated in Eq. (1) and is shown in column 5 in Table 2.  $\epsilon'$  is the real permittivity, which is a measured quantity and equals to the ratio of the capacitance of the experimental apparatus filled with solution to that filled with air. Its values are shown in column 6.

Other parameters required are the static dielectric constant,  $\epsilon_0$ , and the infinite dielectric constant,  $\epsilon_{\infty}$ . Fig. 5 shows plots of dipolar dielectric loss against the dielectric storage (real part of the dielectric permittivity). Values of  $\epsilon_0$  and  $\epsilon_{\infty}$  can be obtained from a plot of  $\epsilon''_{\text{dipole}}$  to  $\epsilon'$  as shown in Fig. 5. The derivation from semicircle indicates polydispersity of the particles in the solution, that is, more than one kind of dipole moment exists. It can be seen from Fig. 5 that the curves of low temperatures were somewhat more similar to semicircle, indicating that the asphaltenes were closer to monodisperse at low temperatures. The infinite permittivity,  $\epsilon_{\infty}$ , is the left intercept of the arc, and the static permittivity,  $\epsilon_0$  is the right intercept. The values taken from Fig. 5 for the various temperature curves are shown in columns 8 and 9 in Table 2. It is clear that  $\epsilon_0$  has higher values when the temperature increases. The reason is that the relatively low viscosity of the solution at high temperatures allows the dipole molecules to re-orient more quickly under the altering dielectric field.

The parameters discussed above are used to calculate the dipole moment of the asphaltene populations in the solution with Eq. (1). The values are placed in the last column of Table 2. Assuming that the asphaltene aggregates are spherical, the mean radius of the asphaltene dipole,  $R_d$ , can be calculated from the peaks in the  $\epsilon''_{\text{dipole}}$ -frequency spectra with the following equation [29]:

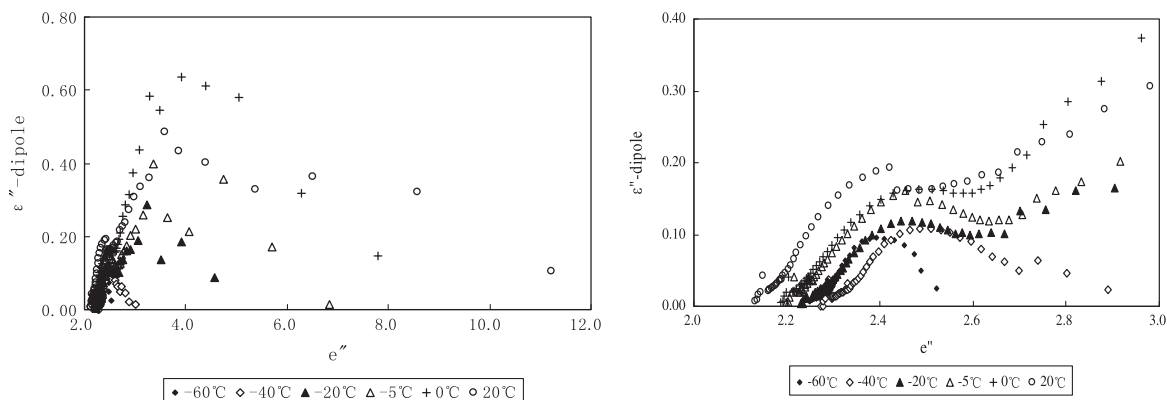
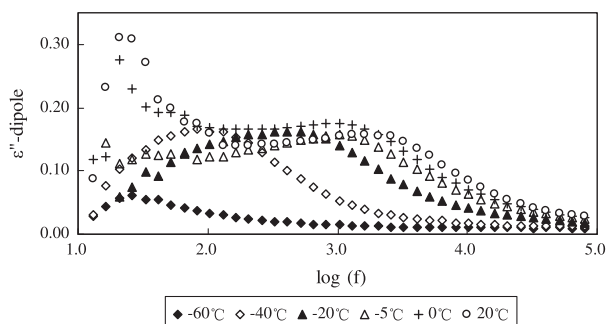
$$2\pi f = \frac{1}{\tau} = \frac{kT}{4\pi\eta R_d^3} \quad (7)$$

With the measuring temperatures above  $-20\text{ }^{\circ}\text{C}$ , a single peak at low temperatures was divided into two peaks, which corresponded to two types of asphaltene dipole. The dimension of radii of different asphaltene dipoles in one solution can be deduced from Eq. (7). The asphaltene dipole corresponding to higher frequency will have smaller radius.

Fig. 6 shows the dipolar dielectric loss of THAR C<sub>7</sub>-asp after subtracting the ionic conductivity contribution at different temperatures. As shown in Fig. 6, a single peak at low temperatures will transform into two peaks at temperatures equal to or higher than  $\sim -20\text{ }^{\circ}\text{C}$ , as similar to MEAR C<sub>7</sub>-asp solutions. This phenomenon indicates that two types of asphaltene dipoles co-exist in the solution when the temperature is higher than  $-20\text{ }^{\circ}\text{C}$ . Table 3 exhibited the THAR C<sub>7</sub>-asphaltenes data in a similar fashion as MEAR C<sub>7</sub>-asphaltenes.

**Table 3**The C<sub>7</sub>-asphaltenes of THAR in toluene at the concentration of 1 wt%.

T (K)	f <sup>a</sup> (Hz)	τ (s)	M <sub>W</sub> (g/mol)	tan δ <sub>dipole</sub>	ε'	d (g/cm <sup>3</sup> )	ε <sub>0</sub>	ε <sub>∞</sub>	μ (Debye)
213	26	0.006078	1.12 × 10 <sup>3</sup>	0.0237	2.615	0.940	2.70	2.50	6.5
233	83	0.00193	1.12 × 10 <sup>3</sup>	0.0615	2.691	0.922	3.10	2.40	10.9
253	411	0.000387	1.12 × 10 <sup>3</sup>	0.0623	2.602	0.904	3.40	2.30	11.2
268(peak1)	1030	0.000155	1.12 × 10 <sup>3</sup>	0.0625	2.507	0.890	4.50	2.30	10.4
268(peak2)	17	0.009651	6.89 × 10 <sup>3</sup>	0.0366	3.929	0.890	4.50	2.30	24.7
273(peak1)	819	0.000194	1.12 × 10 <sup>3</sup>	0.0685	2.547	0.885	5.50	2.20	10.5
273(peak2)	21	0.007656	6.89 × 10 <sup>3</sup>	0.0732	3.761	0.885	5.50	2.20	32.6
293(peak1)	1630	9.77E-05	1.12 × 10 <sup>3</sup>	0.0663	2.369	0.867	6.20	2.10	10.1
293(peak2)	21	0.007656	6.89 × 10 <sup>3</sup>	0.0772	4.019	0.867	6.20	2.10	35.0

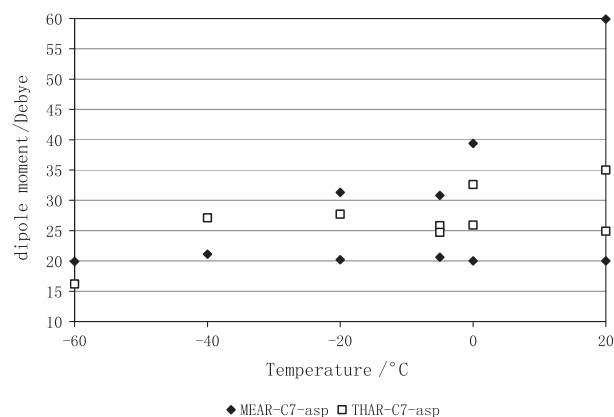
<sup>a</sup> The frequency at the peak of dipolar dielectric loss.**Fig. 5.** The dielectric loss from dipole to the dielectric storage. The right hand figure is a magnification of the left figure.**Fig. 6.** The dielectric loss from dipole of THAR C<sub>7</sub>-asp at different temperatures.

The Figures of THAR C<sub>7</sub>-asphaltenes in toluene at the concentration of 1 wt% were provided in the [supplementary file](#). The dipolar dielectric loss of C<sub>7</sub>-asphaltene of MEAR at 213 K was fitted by using Eq. (5) and provided in the [supplementary file](#) as Fig. 5. The fitted value of  $\alpha$  is 0.098, which states that the polydispersity is very low. This result indicates that single type particle or molecules exist in the solution at 213 K, which is consistent with the phenomenon that the curves of low temperatures were more similar to semicircle in Fig. 5 than the curves of high temperatures.

### 3.3. Discussion

According to Fig. 4 and Table 2 for the n-heptane asphaltenes of MEAR in toluene at the concentration of 1 wt%, the dipolar dielectric loss has only one peak when the temperature is -60 °C. This means there is only one type of dipole in the solution. The corresponding dipole moment is 11.7 Debye. As shown in Fig. 4, when the measurement temperature increases to -40 °C, the dielectric

loss curve still has only one peak with a slightly larger dipole of 12.4 Debye. At this stage, the aggregation of asphaltene has not occurred to a significant extent. However, when the temperature is higher than -20 °C, two dielectric loss peaks can be observed, showing the co-existence of two types of dipoles in the solution. The values of the smaller dipole moment population remain almost the same as those of the population at -60 °C for all higher temperatures. On the other hand, the larger dipole moment population increases with the measurement temperature increase, and reaches 59.9 Debye at 20 °C. The dipole moment values of n-heptane asphaltene of MEAR were 11.7 and 59.9 Debye at 20 °C, which is consistent with the mean dipole moment of 31.1 Debye for this kind of asphaltene measured by other methods in our laboratory [33]. The near 5 times larger of the dipole

**Fig. 7.** Dipole moments of asphaltene particles at different measurement temperatures.

moment as the particles aggregate shows that the particles are aggregating in a fashion that allows their dipole moments to add constructively and increase the dipole moment of the aggregation. The near-circularity of the arcs at the lowest temperature curves in Fig. 5 confirms that the asphaltene particles are almost a single size population at low temperatures.

Table 3, Figs. 6 and 7 show that the C<sub>7</sub>-asphaltenes of THAR presents a similar variation trend but different dipole moment values compared to C<sub>7</sub>-asphaltenes of MEAR as discussed above. When the measurement temperatures are –60 °C and –40 °C, the dipolar dielectric loss has only one peak. However, the dipole moment of the low-dipole moment population increases remarkably from –60 °C and –40 °C, and changes little at higher temperatures. This contrast in the change in dipole moment with temperature of the two asphaltenes is clearly shown in Fig. 7. The dipole moment values of THAR C<sub>7</sub>-asphaltenes are 10.1 and 35.0 Debye for the un-aggregated or aggregated populations at 20 °C in this study, which are consistent with the mean dipole moment value of 32.9 Debye measured via another approach method [17].

The peak moments for the two distinct dipole moment populations are shown in Table 2 and 3 for asphaltene from each oil. The method proposed in the current work can simultaneously present the multi dipoles in one solution, instead of the mean dipole moment.

The phenomenon that single and aggregated asphaltene co-exist in solution is consistent with the study by fluorescence probing. The fluorescence spectroscopy is capable of identifying the single and aggregated asphaltenes. The fluorescence signals at different wavelength can be attributed to different asphaltene aggregation state in toluene solution. Goncalves et al. [34] studied the tendency of asphaltene aggregation in toluene by absorption and fluorescence spectroscopy. They found that the changes of fluorescence signals could indicate the changes of the monomers and n-mers in the solution because of aggregation. Hoepfner and Fogler [35] studied asphaltenes behavior in various solvents (toluene, tetrahydrofuran, and 1-methylnaphthalene) at dilute concentrations by Small-angle X-ray and neutron scattering (SAXS/SANS). Both the breakup of clusters and the dissociation of nanoaggregates, induced by diluting asphaltene solutions with organic solvents, occurred gradually, indicating that single and aggregated asphaltenes will coexist. This phenomenon is consistent with the equilibrium between the monomers and n-mers in solution studied by ultra visible study [36].

#### 4. Conclusions

In the current work, the dipole moments of asphaltene molecules were measured from the dielectric measurements alone without measuring the refractive index of the asphaltene solution. Consequently asphaltene measurements can be made in solutions with a wide range of concentrations and temperatures. Furthermore, this method is capable of simultaneously measuring multi dipoles in one solution instead of obtaining only the mean dipole moment. Therefore, this method has the potential to study the influence of dipole–dipole interactions in asphaltenes aggregation.

The dipole moments of the asphaltene particles were summed and the dipole moments of the aggregated population are ~5 times that of un-aggregating particles. On the other hand, the THAR C<sub>7</sub>-asphaltenes aggregate with temperature in a similar fashion, but the dipole moments of the aggregated population are ~3 times that of un-aggregating particles. This illustrates the potential use of the new methods in dipole moment measurement and the aggregation of asphaltenes. Moreover, this method has the potential to be used to simultaneously measure multi dipoles in one solution, instead of obtaining the mean dipole moment.

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#### Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.fuel.2014.10.010>.

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