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Study on the dipole moment of asphaltene molecules through dielectric measuring

Long-li Zhang [a,b,c,*], Chao-he Yang [a], Ji-Qian Wang [a], Guo-hua Yang [b], Li Li [c,*], Yan Vivian Li [d], Lawrence Cathles [c]

[a] State Key Laboratory of Heavy Oil Processing, China University of Petroleum (East China), Qingdao, Shandong Province 266580, PR China
[b] College of Science, China University of Petroleum (East China), Qingdao, Shandong Province 266580, PR China
[c] KAUST-Cornell Center of Energy and Sustainability, Cornell University, Ithaca, NY 14853, USA
[d] Department of Design and Merchandising, Colorado State University, 326 Gifford, 1574 Campus Delivery, Fort Collins, CO 80523-1574, USA

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 °C to 20 °C. There is one dielectric loss peak in the measured solutions of the two types of asphaltene at the temperatures of −60 °C or −40 °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 °C, indicating there are two types of dipoles corresponding to the two peaks. This phenomenon indicates that as the temperature increases above −5 °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.

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

* Corresponding authors at: State Key Laboratory of Heavy Oil Processing, China University of Petroleum (East China), Qingdao, Shandong Province 266580, PR China. Tel.: +86 532 86983374; fax: +86 532 86983369 (L.-l. Zhang). KAUST-Cornell Center of Energy and Sustainability, Cornell University, Ithaca, NY 14853, USA. Tel.: +1 412 482 8712 (L. Li).
E-mail addresses: llzhang@upc.edu.cn (L.-l. Zhang), lilicmu@gmail.com (L. Li).

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Nomenclature

$\tan\delta$	the ratio of the dielectric loss to the dielectric storage
ε'	the dielectric storage or the real part of dielectric permittivity
ε''	the dielectric loss or the imaginary part of dielectric permittivity
ε_∞	the dielectric constant at infinite high frequencies
ε_0	the dielectric constant at very low frequencies
c	concentration (mol cm^{-3})
w	concentration (g g^{-1})
M_W	the molecular weight of solute, (g mol^{-1})
N	Avogadro number
k	Boltzmann's constant
μ	mean dipole moment (Debye)
ω	the angular frequency in radians per second, $\omega = 2\pi f$
ρ	the density of the solution (g cm^{-3})
ε''_{ion}	contribution to dielectric loss from ionic conductivity
ε''_{dipole}	contribution to dielectric loss from dipole relaxation
τ_0	relaxation time (s)
α	the polydispersity parameter having the value between 0 and 1
σ'	conductivity (S/m)
σ'_{ion}	ionic conductivity (S/m)
ε_v	the dielectric constant of vacuum (8.854×10^{-12} F/m)
f	the applied frequency (Hz)
ε'	measured real part of dielectric permittivity = ratio of solution capacity to capacity of air
ω_{peak}	the angular frequency corresponding to the peak of dipolar dielectric loss
T	temperature (K)
k	Boltzmann's constant
η	the effective viscosity
R_d	the dipole moment weighted particle radius
f_{peak}	the frequency of the dipolar dielectric loss peak (Hz)

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 cm^3/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 °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}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 °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)	3.54×10^3	6.89×10^3
Mean module number	2.90	6.14
M_W of single asphaltene (g/mol)	1.22×10^3	1.12×10^3
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 (μg/g)	244	185
V (μg/g)	444	813
Fe (μg/g)	486	209
Ca (μg/g)	55.4	655
Mg (μg/g)	5.0	134