

A dielectric relaxation study of precipitation and curing of Furrial crude oil

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Received 21 March 2006; accepted 31 March 2006

Available online 6 May 2006

Abstract

Low frequency dielectric spectroscopy was applied to investigate the properties of Furrial crude oil that is infamous for asphaltene precipitation during production. An experiment was conducted at ambient temperature by mixing Furrial crude oil with hexane to induce flocculation and subsequent precipitation. A drastic change in dielectric response was observed near the critical point when flocculation occurred. Evolution of the dielectric loss spectra as a function of time was observed and found to closely mimic epoxy-curing process. The curing process lasted for approximately 44 h with an induction period of at least 26 h. During the induction period, the conductivity contribution to the dielectric response remains dominant. Following the induction period a structural arrest occurs signaling the onset of deposition.

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Keywords: Asphaltene; Curing; Dielectric relaxation

1. Introduction

Heavy oil deposition on to production pipes in down-hole operations, transportation and even in the process of refining has been a threat to economic loss. Many researchers had reported in the past about the important role that asphaltene plays in the deposition processes. A wealth of literature evidence on this topic has prompted an interest in understanding the underlying physics of the deposition process [1–5].

Asphaltene is the most refractory fraction in petroleum liquids and often shows its prominent polarity, even in a complex mixture containing over one million components [6,7]. Whether asphaltene plays an essential role in the deposition kinetics or has a catalytic role is an open question. Its engagement in the deposition process, in terms of the molecular interplay with other components, is not clear. What had been demonstrated in recent years was

the relative low molecular weight of asphaltene [8,9]. This means the relative high molecular weight observed using VPO measurements are likely aggregates. In this regard, the deposition can be a result of a continuous aggregation process with a kinetic scale dictated by asphaltene properties and the induction process.

Prevention of deposits during production has been a challenge. Manipulation of well pressure and injecting solvents are achievable options, but not necessarily an economical one. The accurate control of the deposition kinetics is essential for preventing deposit-induced clogging. Even so, asphaltene can still pose a post-production threat, such as during transportation and storage. A common scheme to prevent precipitation during transportation, storage or prior to processing often involves solvent precipitation to remove heavy components, such as asphaltene. Heptane, hexane and pentane are common solvents used for this purpose. The use of solvent separation appears to avoid deposition and/or precipitation and provides flow assurance. However, as the production of sweet crude oils wanes, heavy oil comprises a significant

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percentage of the refining feedstock. These oils often contain an appreciable amount of asphaltene, which, though separable, would require substantial amount of solvents. Moreover, the separation produces a large amount of solid asphaltene that has a low market value. Some even pose an environmental threat and require proper treatment.

With so many potential pitfalls, there are several options to deal with oils of high asphaltene content: (1) avoid asphaltene precipitation or deposition by controlling the mixture in the one-phase region; (2) upgrade the heavy oils in situ to reduce the amount of the heavy components and (3) apply additives prior to production and to the pipeline. The most compelling option is to apply different strategies at different stages when its effect is optimized without economical compromise. For example, controlling the production kinetics to avoid deposition is the most economical option during the production stage, as long as the production rate and the amount of the injected solvent can be optimally coordinated. This is not an easy task and can only be achieved when the molecular kinetics of the deposition process is fully understood.

From the physics point of view, asphaltene deposition could arise from the dipole moments in asphaltene molecules (or aggregates) or from the induced dipole moments. When dipole moments interact with the pipeline surface, they could create a transient vacuum condition near the oil/pipe surface, generating a high enough potential at the local sites. These sites subsequently serve as nucleation centers to facilitate deposition. If this scenario is true, one might be able to correlate the dipole moment behavior to the deposition. A simple method to evaluate the dipole moment is to measure the dielectric response of an asphaltene system upon flocculation and precipitation. Once the dipole moment is characterized, a strategy can be set to control its values throughout the production process.

The correlation of the dipole moment to flocculation and precipitation might shed light on how to prevent the formation of nucleation sites that lead to precipitation and deposition. It is an important physical parameter to control, yet it is often overlooked. In fact, one can delay the deposition onset by quantitatively controlling the kinetic parameters. In this work, we investigated the dielectric response as a function of time near the flocculation condition. This allows us to study the dielectric response upon flocculation and its evolution through flocculation, precipitation and deposition processes. In particular, it is possible to estimate the critical onset time for precipitation and deposition. From the operation point of view, these are the kinetic parameters that matter in the fields.

2. Experimental

2.1. Sample

Furrial crude oil was used as the sample. This sample was not chemically treated after production, but was under vacuum treatment (crude b, see Table 1) prior to dielectric

Table 1
Elemental analysis of Furrial crude, maltenes and asphaltenes

Sample	Precipitant	C	H	N	H/C	N/C
Furrial	None (as received)	85.78	11.86	0.82	1.650	0.008
Furrial	None (under vacuum)	85.75	11.71	1.03	1.627	0.01
Asphaltene	<i>n</i> -C5	84.85	7.16	2.22	0.998	0.023
Asphaltene	<i>n</i> -C6	85.24	7.22	2.15	1.01	0.021
Asphaltene	<i>n</i> -C7	86.49	7.03	2.25	0.966	0.022
Asphaltene	<i>iso</i> -C8	84.81	7.66	1.91	1.075	0.019
Maltenes	<i>n</i> -C5	85.52	12.19	0.8	1.70	0.007
Maltene	<i>n</i> -C6	85.56	12.19	0.82	1.7	0.006
Maltene	<i>n</i> -C7	85.65	12.08	0.9	1.68	0.008
Maltene	<i>iso</i> -C8	85.55	12.07	0.98	1.681	0.008

All analyses were duplicated.

measurement. Table 1 shows its elemental analysis. No water was expected in the crude oil after vacuum treatment. Measurements were made for this “neat” sample, followed by the gradual addition of hexane (reagent grade, Sigma-Aldrich) to induce flocculation and precipitation. All experiments were performed at room temperature.

2.2. Dielectric measurement

A Hewlett Packard 4192A low frequency impedance analyzer was employed to measure the dielectric relaxation. The frequency range was from 1 kHz to 10 MHz. A customer-made electrode with four parallel platinum black plates was used as the electrode. The total electric area is 10 cm² and the distance between the electrodes is 1 mm leading to a cell constant of 0.001 cm⁻¹. This cell has the right range cell constant for a low conducting medium, such as toluene or toluene/hexane mixture. One needs to select the right cell constant to optimize the sensitivity, yet prevent charge deposition. The platinum black cell selected here has a rough surface, thus preventing charge deposition. In addition, the cell constant is low and the electrode area is large (10 cm²), which makes it more sensitive to a low current, or low charge movement.

Two series of measurements were performed. One series measures the dielectric response of the crude oil upon dilution of hexane. The purpose was to evaluate the sensitivity of the dielectric response to flocculation and precipitation. The second series was to measure the evolution of the dielectric relaxation at the flocculation point as a function of time to study the kinetics of flocculation–precipitation. This series was designed to evaluate the sensitivity and usefulness of the dielectric relaxation method for detecting the kinetics of flocculation, precipitation, and possibly deposition.

3. Theory of dielectric relaxation

Dielectric relaxation resembles the viscoelastic responses where the mechanical moduli represent the mechanical response of a system to an exerted oscillating force at a given frequency. The storage modulus represents the

energy stored upon the exertion of the force, thus characterizing the elasticity of the system. The loss modulus on the other hand dissipates the energy applied by the exerted force, thus representing the viscous properties of the system.

The dielectric response is analogous to the mechanical system. When an oscillating electric field is applied to the system, the polarity of the molecules, colloids, or polymers in the system responds to the exerted electric force by aligning themselves along the electric field. During the course of the alignment, some dipoles experience resistance from either the inter-molecular interaction (short range or long range interactions) or the molecular friction [10]. As a result, some energy given by the applied field is lost, similar to the resistor in an R–C circuit which dissipates energy, leading to the dielectric loss ε'' ; some energy is stored, similar to the capacitor in the R–C circuit, leading to the dielectric storage, ε' .

However, in a dielectric material, there are always free ions which respond to the applied electric field in a diffusive manner, resulting in conductivity contribution to the dielectric loss. This conductivity effect is normally more eminent and often dominant when the frequency is low. In light of the vast difference between dipole and conductivity mechanisms make it possible to monitor the transition from a conductivity dominating to dipole dominating kinetics. Mathematically, the overall dielectric loss can be expressed as

$$\varepsilon'' = \varepsilon''_{\text{ion}} + \varepsilon''_{\text{dipole}} \quad (1)$$

with the conductivity contribution

$$\varepsilon''_{\text{ion}} = \frac{\sigma}{2\pi\omega\varepsilon_0} \quad (2)$$

where σ is the ionic conductivity, independent of the applied field frequency ω . Since $\varepsilon''_{\text{ion}}$ is governed by ion diffusion, its contribution is dominant when the system viscosity and the applied frequency are both low [11]. From the time scale point of view, ion diffusion is often in the microsecond range if these ions are associated with colloidal particles. On the other hand, the structural kinetics of a molecule, when it is not caged, is generally much faster. As a result, their respective contributions may be distinguished by measuring the dielectric response of the whole system as a function of the applied frequency.

However, if the system is undergoing a structural change, such as molecular association via flocculation, the dipole kinetics can be substantially reduced when they are arrested or caged in the flocs. In this case, the reduced dipole kinetics can overlap with the usually much slower ion diffusion (conductivity) kinetics. Thus, it is feasible to reveal the structural change and its dynamics by evaluating the dielectric response of the system and its frequency dependence.

For asphaltene molecules, the molecular weight is of the order of hundreds [8,9], and their bond stretching is in the inferred red range. The dynamics of the aggregates can be

in the nanosecond, microsecond or even millisecond dynamics, depending on how big the aggregates are. In this case, a low frequency dielectric relaxation is suitable for investigation of the dynamics of the aggregates, either in the small isotropic steady aggregated state (some refer to this as the micellar state or the nanoaggregate state) or in the larger metastable flocculation state.

If a system is non-interacting and the object (in this case the asphaltene molecules or aggregates) has a zero size, then the Debye relaxation applies [10]. In the time domain, it reads

$$f(t) = \exp(-t/\tau) \quad (3)$$

where τ is the mean relaxation time. Since one measures the dielectric response by applying a wave of a certain frequency ω , it is convenient to express the response function in the frequency domain,

$$\varepsilon_r(u) = \frac{\chi(\omega) - \chi_\infty}{\chi_0 - \chi_\infty} = 1 - u\mathcal{L}\{f(t)\}(u) \quad (4)$$

where $u = -i\omega$ is the frequency, χ is a dynamic susceptibility normalized by the corresponding isothermal susceptibility, χ_0 is the static susceptibility and χ_∞ gives the ‘instantaneous’ response, and $\mathcal{L}\{f(t)\}(u)$ is the Laplace transform of the relaxation function $f(t)$. For the exponential relaxation function, this leads to

$$\varepsilon_r(\omega) = \frac{1}{1 + i\omega\tau} \quad (5)$$

This is the well-known Debye susceptibility.

Most of the real systems do not follow the Debye relaxation behavior; either there are appreciable interparticle interactions or the particle sizes are simply not negligible. As a result, there are many dynamic modes that will respond to the applied oscillating electric field in their respective ways, depending on their vibrational frequencies and translational diffusion rate. As these modes couple together, they end up with a fractional exponent function known as the ‘stretched exponential’ or the Kohlrausch relaxation function given as

$$f(t) = \exp[-(t/\tau)^\beta] \quad (6)$$

Taking the Laplace transformation of this function leads to the Cole–Cole susceptibility [12]

$$\varepsilon(\omega) = \frac{1}{1 + (i\omega\tau)^\alpha} \quad (7)$$

If one takes into account the normalization coefficient, then Eq. (7) becomes

$$\varepsilon(\omega) = \varepsilon_\infty + \frac{\Delta\varepsilon}{1 + (i\omega\tau)^{1-\beta}} \quad (8)$$

where ε_∞ is the dielectric constant at infinite frequency and $\Delta\varepsilon$ is the difference between the static dielectric constant and the high frequency dielectric constant ε_∞ . In addition to the Cole–Cole susceptibility, two other empirical formulas, namely, the Cole–Davison [13] and

the Havriliak–Negami [14] susceptibilities, have been used for interpreting the dielectric relaxation spectra. These two formulas were used empirically until recently when Hilfer [15] derived them using the H-function. In fact, his derivation led to the discovery that there had been a sign error in the real part of the Havriliak–Negami formula, which has been widely used in the past.

In order to minimize the number of adjustable parameters, the Cole–Cole (Eq. (8)) susceptibility will be used in this work. The fitting involves two parameters (stretch exponent β and the relaxation time τ) while Havriliak–Negami involves three adjustable parameters that may jeopardize the rigor of the data analysis.

4. Results

Table 1 shows the elemental analysis data of the Furrial crude oil and the maltenes and asphaltenes derived from it. All measurements were made in duplicate. Obviously, the vacuum treatment does not produce significant changes. This is important since the maltenes are obtained after removing the precipitant under vacuum. A notable condition is the H and H/C of *n*-C6 derived asphaltene. The hydrogen, H, is slightly higher than the *n*-C5 extracted asphaltene. It is also reflected in the H/C ratio. Other than the H number, the rest of the values do not show anomaly. Table 2 shows the SARA analysis of the crude oil, Furrial. The asphaltene concentration is high, 9.9 wt%. Since the vacuum treated sample was used in the experiment, no significant water molecules were expected to perturb the dielectric results, particularly in the conductivity part.

The calibration of the dielectric analysis is shown in Fig. 1, using toluene as the standard. The measurement

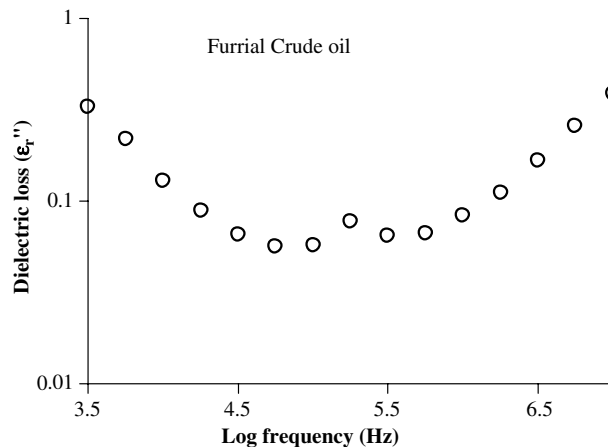


Fig. 2. Dielectric spectra of Furrial crude oil.

was performed at 25 °C. The dielectric constant obtained was consistent with the published value of 2.4. It remained constant until the frequency reached approximately 10 MHz. Fig. 2 shows the dielectric loss spectrum of the original Furrial crude oil at room temperature. The spectrum clearly shows two regions. The low frequency region appears to be conductivity dominant, while the dipole relaxation starts to appear at approximately 5.5 MHz. Taking the first three points at the low frequency and making a log-plot, the slope was found to be 0.81, not close enough to claim a Debye system. It may be attributed to the lack of enough data points.

As hexane is gradually added, the dielectric loss starts to change. Fig. 3 illustrates this evolution. When the C6 concentration approached 57.5%, the dielectric experienced a sudden increase. Beyond that the dielectric loss decreases again, as depicted in Fig. 4, at 65% hexane. This is an interesting phenomenon. To further reveal the detail, Fig. 5 shows the dielectric storage as a function of hexane concentrations at various frequencies. It clearly shows that the

Table 2
SARA analysis for Furrial

Saturates (%)	Aromatics (%)	Resins (%)	Asphaltenes (%)
37.9	31.9	20.3	9.9

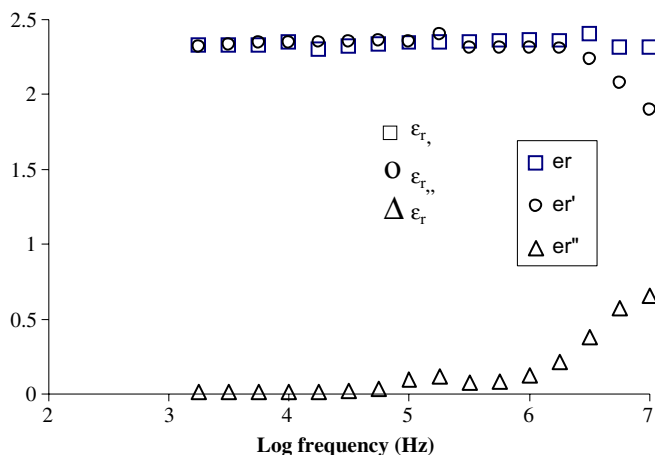


Fig. 1. Dielectric spectra of toluene at 25 °C.

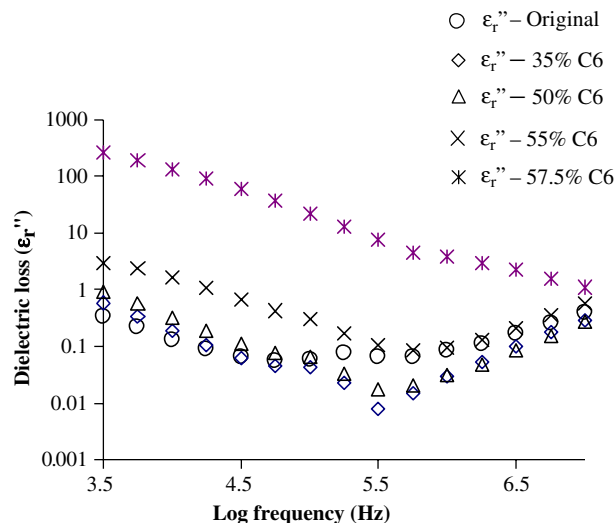


Fig. 3. Dielectric loss spectra at various C6 concentrations.

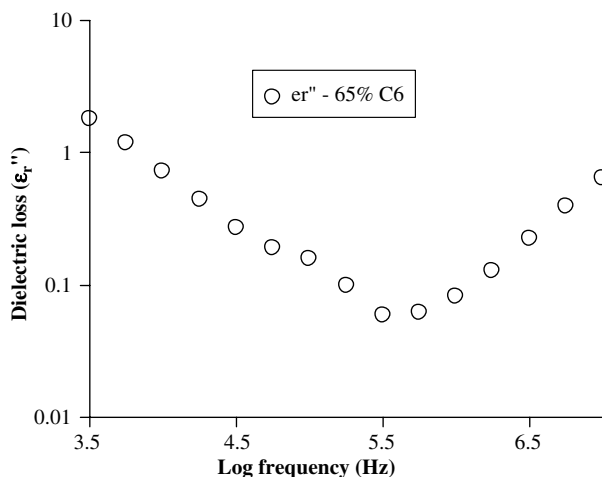


Fig. 4. Dielectric loss spectra at 65% C6 concentration, similar to the original crude oil in Fig. 2.

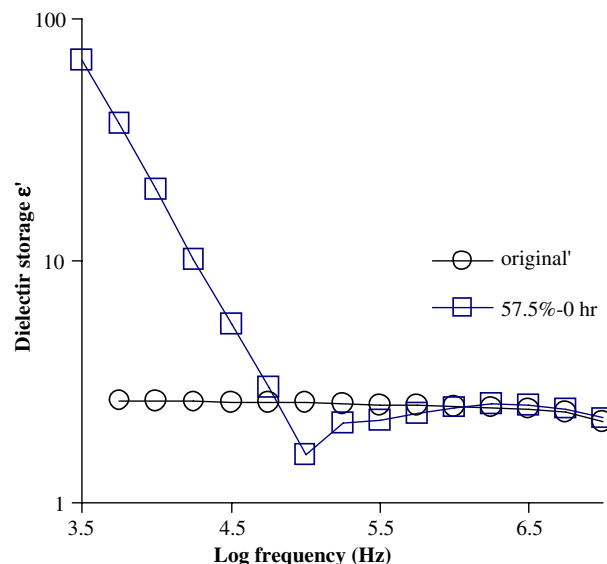


Fig. 6. Dielectric storage at the initial stage.

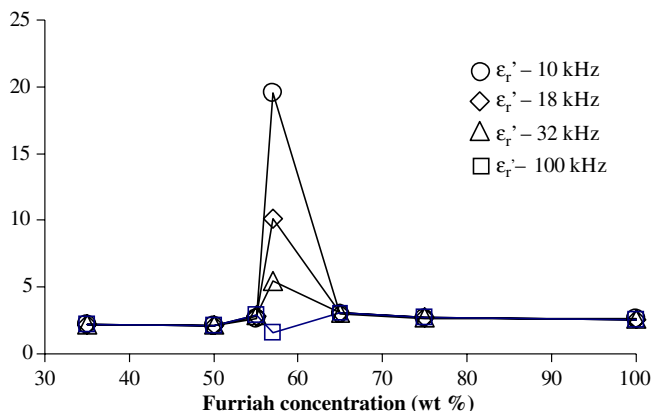


Fig. 5. Dielectric storage as a function of Furrial concentration (wt%) in hexane at various frequencies. Drastic change was observed at ~57.5%.

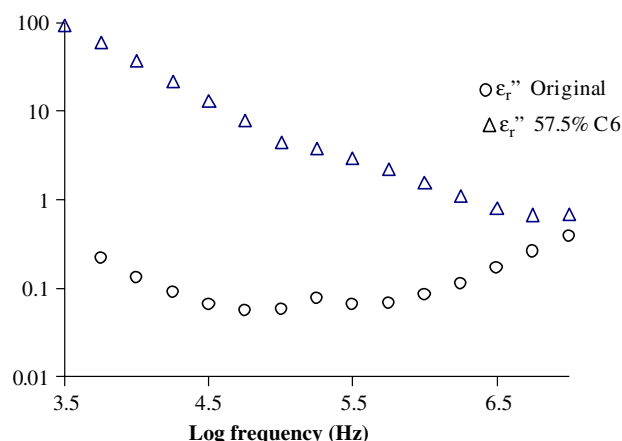


Fig. 7. Dielectric loss of 57.5 wt% Furrial crude oil in hexane at room temperature right after hexane dilution.

anomalous increase of ϵ_r'' occurs only at low frequency, indicating a conductivity driven process. Apparently, there is a phase transition near 57.5% hexane concentration. It represents a sudden “shutoff” of the resistor component and the capacitor rapidly increases (The storage component ϵ_r' suddenly increases.), indicating an onset of flocculation where a large structure cages the charge movement. This concentration was thus taken as the flocculation onset concentration at which a series of kinetic measurements were performed. The dielectric storage spectrum ϵ_r' as a function of frequency also indicates drastic change, as shown in Fig. 6.

As the Furrial/57.7% hexane mixture was first prepared (at time = 0 h), one clearly sees a Debye-like relaxation at a low frequency with the dielectric loss slope equal to approximately 1.0 (see Fig. 7). However, as the sample ages, the dielectric loss spectrum starts to shift toward a lower frequency range with the dipole contribution becoming more and more obvious. This is expected if the system is undergoing a structural growth with increasing correlation lengths. This is to say that it takes a long time for a

charge object to move the same distance because of the structural caging effect. A similar phenomenon was observed in a polymer curing process [11]. Fig. 8 depicts the evolution of the dielectric loss peak in a period of 44 h.

This is an interesting trend. First, the conductivity contribution was fairly dominant at the beginning, while little contribution from dipole relaxation was observed in the high frequency region. This status persists for at least 26 h. At about 31 h, the contribution from the dipole moment started to show. Between 30 h and 35 h, the dipole contribution quickly took over and the process seems to get complete at about 35 h because the 44 h spectrum was nearly identical to the one at 35 h.

This suggests that during the structural growth the average structure becomes larger and the ion movement more and more restricted. In the mean time, the dipole relaxation slows down. This can be interpreted as a process of flocculation or precipitation-like behavior.

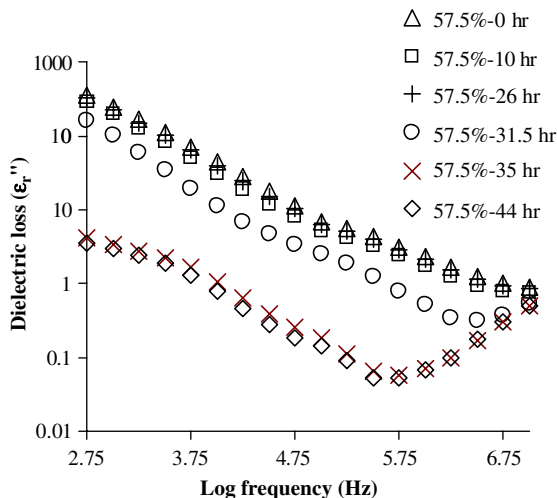


Fig. 8. Evolution of the dielectric loss spectra as a function of time at room temperature.

Figs. 9 and 10 pertain to the analyses of the relaxation slope at the low frequency range assuming Debye relaxation (taking $\beta = 0$ in Eq. (8)). If the Debye susceptibility is applicable, then one should obtain a slope of 1.0. As indicated, the slopes at $t = 0$ h (Fig. 9) and at 44 h (Fig. 10) are nearly 1. This means that the conductivity contribution remains present even as the dipole contribution starts to slow down to low the frequency range.

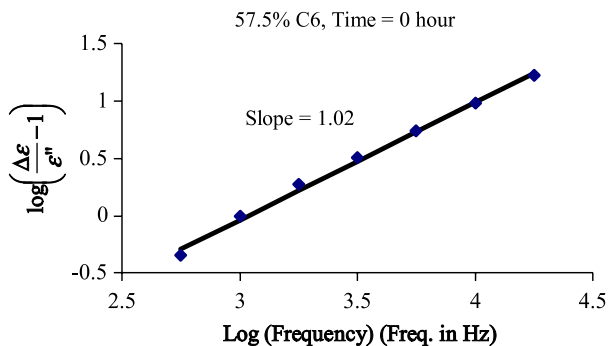


Fig. 9. The relaxation is Debye susceptibility like at the initial stage ($t = 0$ h).

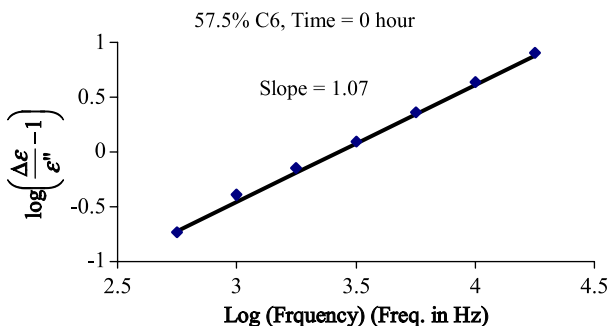


Fig. 10. The relaxation is Debye susceptibility like at the final stage ($t = 44$ h).

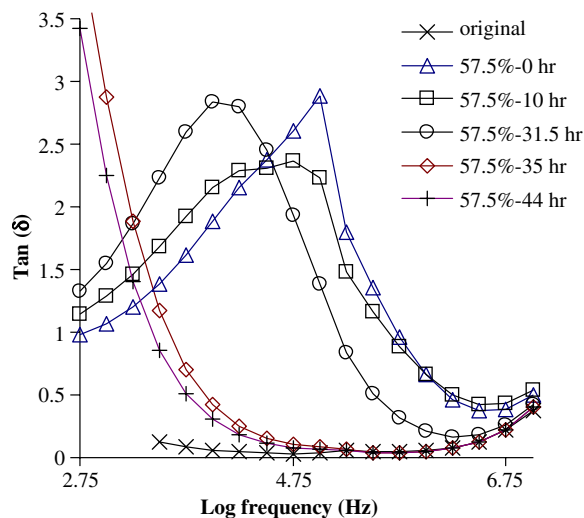


Fig. 11. Evolution of the loss tangent as a function of frequency. It behaved similar to an epoxy curing process.

Fig. 11 illustrates the original Furrial crude oil, at 57.5% hexane and the evolution of this 57.5% hexane solution. As one can see, the crude oil shows a very low loss tangent across the measured frequency range. It is definitely a conductivity governed dielectric relaxation. The loss tangent, however, exhibits a peak as 57.5% of hexane is added, indicating a dipole moment dominating relaxation. The loss tangent peak is initially at a higher frequency but gradually shifts to a low frequency range and eventually, after 35 h, moves out of the measured range. This again demonstrates a structural increase in the system.

Finally, the dielectric loss response (or the energy dissipating conductivity component) was examined at 10 kHz as a function of time after mixing 57.5% C6 (see Fig. 12). Within approximately 30 h, the dielectric loss remains more or less constant. This means that the charge movement is unaffected by the structural buildup, likely due to the relative small charge particle. However, at about 31 h, the dielectric loss starts to decrease rapidly and eventually levels off until the end of the measurement at 44 h. This is a direct indication that the charged particles are suddenly “arrested” (or caged) in a structure. Given the fact that the dipole moment response (Fig. 8) resembles an epoxy

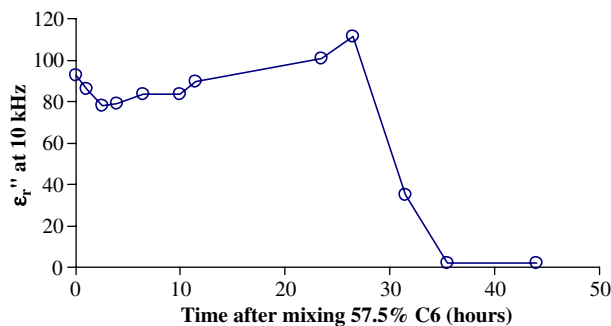


Fig. 12. The dielectric loss at 10 kHz exhibits a sudden drop at approximately 31 h and maintains at the similar level thereafter. This behavior is likely a consequence of surface deposit.

curing process, Fig. 12 may be an indication of deposition where the structure is “locked”, and the contribution from the ion movement drastically reduced and leveled off.

5. Discussion

The first question to be discussed is undoubtedly the peculiar behavior found in the dielectric loss spectra as hexane was gradually added to the Furril crude oil. The question to ask is “why does the dielectric storage undergo such a drastic change”? At this point, we do not fully understand the real physics underlying this fact. It however indicates that 57.5% of hexane likely induces the flocculation of asphaltene.

The second issue is related to the low frequency slope in the dielectric loss at 57.5 wt%, both at the initial stage and the late stage. The slope suggests that the conductivity component of the system behaves like a Debye system with a clear ω dependence. This is a strong evidence that the conductivity contribution is dominant within the low frequency regime of the measurement range. It exists through the measurement period of 44 h. However, its contribution is gradually taken over by the dipole moment contribution. This is indicative of a structure buildup, which gradually restricts the ion movement. Again, it is consistent with a flocculation picture.

However, the fact that the slope remains nearly constant throughout the flocculation and precipitation (or deposit) processes is an interesting phenomenon. This suggests that the conductivity contribution exists throughout the flocculation and precipitation course (clear precipitation can be observed visually), even though its contribution decreases (Fig. 12) eventually. This is an important point because it suggests that there are elementary objects (or spatial domain) responding to the applied oscillating electric field via a conduction mechanism, even after they are structurally restricted due to flocculation and precipitation. These objects apparently retain their charge conducting behavior, even after deposition occurs. If asphaltene is the major component that drives the flocculation and precipitation, then there is a fundamental unit within the asphaltene cluster that remains unchanged. These units flocculate to form large objects, but the conducting behavior contribution from each individual unit under the oscillating electric field does not change. This picture was in fact proposed long ago by Yen [16].

The other interesting point is the dielectric loss spectrum. As 57.5% hexane is added, the system appears to undergo a drastic change and the conductivity contribution appears to increase drastically. This is due to a viscosity reduction, allowing ion movement to increase. The dielectric loss spectrum captures this phenomenon well. However, as the system ages, the dipole moment contribution starts to increase. This is similar to a polymer curing process as shown in the previous reports [11]. This curing-like phenomenon was never demonstrated before in such a complex system like asphaltene.

Lastly, the phenomena observed in Figs. 11 and 12 require some explanation. First of all, Fig. 11 indicates the shift of the loss tangent peak from a higher to a lower frequency. It is an indication that the dielectric response becomes slower and slower, due to structural growth, as discussed earlier using the dielectric loss spectra. This is typical for the flocculation and precipitation process. However, if it is a typical structural growth phenomenon, then the process should be fractal-like. Otherwise, the elementary unit argument given above would not sustain. However, Fig. 12, at 10 kHz, shows a rapid decrease of the dielectric loss at approximately 31 h. At this same time point the loss tangent peak shifts much rapidly toward a lower frequency, much lower than the measurable range (see Fig. 11 where the peak was too low to be measured). We believe that this rapid change is an indication of the deposit where the structure is suddenly frozen.

In conclusion, we applied the dielectric relaxation method to investigate the flocculation and precipitation processes of asphaltene/hexane mixture and at the flocculation onset concentration to study the flocculation kinetics. The process is similar to a polymer curing process. However, the kinetics is not as gradual as in a curing process. A rapid growth of the structure (or deposit) leads to structure arrest, as indicated by the sudden decrease of the dielectric storage spectrum. We also demonstrated that the dielectric loss phenomenon is analogous to an epoxy curing process, suggesting a deposition of asphaltene approximately 31 h after the flocculation onset.

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