



Rheological, dielectric and structural characterization of asphaltene suspensions under DC electric fields

L. Rejon^{a,c,*}, O. Manero^{b,c,1}, C. Lira-Galeana^{c,2}

^a*Instituto de Investigaciones Eléctricas, Calle Reforma No. 113, Colonia Palmira, 62490 Cuernavaca, Morelos, Mexico*

^b*Instituto de Investigaciones en Materiales, UNAM. A.P. 70-360, 04510 México, DF, Mexico*

^c*Instituto Mexicano del Petróleo, Programa de Ingeniería Molecular, Eje Central Lázaro Cárdenas 152, Col. San Bartolo Atepehuacan 07730 México, DF, Mexico*

Received 15 April 2003; revised 5 September 2003; accepted 12 September 2003; available online 14 October 2003

Abstract

The rheological, dielectric and structural behavior of suspensions composed of silicon oil and asphaltene particles under DC electric fields are investigated experimentally. In the absence of an electric field, the suspensions show a near Newtonian behavior. When the electric field (E) is applied, the suspensions behave as Bingham plastics with a yield stress that varies as a power of the electric field. The increase in the viscosity of the suspensions (electrorheological phenomenon, ER) is more accentuated at low shear rates and depends on the electric field intensity. The resulting rheological behavior can be attributed to the formation of structures induced by the electric field, and they brake when the shear rate is increased. The relation between the structural arrangements of the suspension under an electric field and the rheological behavior is analyzed in this study. Results show that the ER response of asphaltene suspensions is not as large as that observed in conventional ER fluids, but nevertheless they throw light on the contribution of electrorheological mechanisms upon asphaltene particle aggregation observed in the transport of the crude oil in the petroleum industry.

© 2004 Elsevier Ltd. All rights reserved.

Keywords: Asphaltene; Electrorheological effect; Viscosity

1. Introduction

Pipe blockage by deposition of heavy organics from petroleum fluids is an important problem in the oil industry. Heavy organics such as paraffin/waxes, resins, asphaltene, mercaptans, and organo-metallic compounds may exist in the crude oil in various concentrations and forms. Such compounds could precipitate out of the crude oil solution due to various forces causing blockage in the processing facilities [1].

Solid particles suspended in the crude oil may stick to the wall of the conduits and reservoirs. The toughness of the precipitate depends on the presence of minute quantities of asphaltene. Asphaltene is a highly polar compound, which

acts as glue or mortar in hardening the deposits, causing the formation of a barrier to the oil flow. The main factors that influence asphaltene deposition are temperature, pressure, composition, flow regime, and electro-kinetic effects. The asphaltene are hypothesized to be formed as a result of oxidation of natural resins. Heavy organics depositions in the North Sea and in the Gulf of Mexico oil fields have caused under-sea pipeline plugging resulting in substantial economic losses to the oil production operations [1]. These problems have motivated an important research effort aimed at understanding the colloidal, rheological and dielectric properties of asphaltene dispersions as a function of flow conditions.

An important factor that induces deposition on the pipe walls is the existence of an electric potential between the asphaltene particles or aggregates and the metallic wall. It has been observed in the past that when charged asphaltene suspensions flow through porous media or pipes, a streaming potential causes asphaltene clustering and subsequent precipitation [2,3]. The magnitude of the potential and deposition rates may not be large, but for

* Corresponding author. Address: Instituto de Investigaciones Eléctricas, Calle Reforma No. 113, Colonia Palmira, 62490 Cuernavaca, Morelos, Mexico. Tel.: +52-777-3623831; fax: +52-777-3623832.

E-mail addresses: lrejon@iie.org.mx (L. Rejon), manero@servidor.unam.mx (O. Manero), clira@imp.mx (C. Lira-Galeana).

¹ Tel.: +52-55-56224589; fax: +52-55-56161201.

² Tel.: +52-55-30036507; fax: +52-55-30036239.

long periods, accumulation of asphaltene on the walls due to this streaming potential may be important. Experiments performed by Evdokimov et al. [4] indicate that in some cases electrodeposition of asphaltene suspensions may be controlled by the polar nature of the asphaltene/resins suspensions [5]. Asphaltene suspensions may be regarded as strongly dipolar fluids, which even in the absence of electric fields may exhibit formation of aggregates [6,7]. Application of electric fields to asphaltene suspensions should naturally enhance the above dipolar effects. Nevertheless, a systematic investigation of the polarization mechanisms of asphaltene agglomerates and their behavior under electric fields in a flowing system is still lacking. In this regard, the objective of this work is the analysis of the rheological behavior of model suspensions made of silicon oil (a non-polar medium) and asphaltene, under external dc electric fields. Rheometric, dielectric and microscopic studies are presented with the aim to relate the flow behavior of the suspensions influenced by an electric field to the arrangement of the aggregated structures. The viscosity of the suspensions is studied as a function of electric field intensity and shear rate for a given asphaltene concentration.

2. Experimental

2.1. Preparation of suspensions

The suspensions employed in this study were prepared with asphaltene particles obtained by precipitation in heptane from a sample of KU-42 Mayan Mexican crude oil, kindly provided by PEMEX E & P. The asphaltene-aggregated particles of irregular shape (average size of 50 μm) were suspended in silicon oil (Spectrum), which had a viscosity of 0.95 Pa s. Fig. 1 shows a photograph of asphaltene particles, obtained from dried samples using scanning electron microscopy (SEM). The electrical and dielectric properties are summarized in Table 1.



Fig. 1. SEM micrograph of asphaltene particles.

Table 1

| Material | Permittivity 10 Hz | Conductivity S/cm |
|-------------|--------------------|-----------------------|
| Silicon oil | 2.40 | 7.7×10^{-15} |
| Asphaltene | 3.83 | 6.0×10^{-13} |

The concentration of asphaltene was 0.08-volume fraction (ϕ). The mixture was prepared in a Cowles mixer at 3000 rpm during 10 min at room temperature. The suspensions were placed in a vacuum chamber to extract the air bubbles prior to the rheological, dielectric and structural measurements.

2.2. Rheological characterization

Rheological measurements were made in a Rheometrics Controlled-Strain Rheometer ARES (2KFRN1) using parallel plates geometry with a diameter of 50 mm. A steady shear sweep at 25 °C was applied with DC voltages supplied by a Trek High Voltage Amplifier model 609E-6. The yield behavior exhibited by the asphaltene suspensions is characteristic of a Bingham viscoplastic fluid. Following the usual procedure, field-dependent yield stresses were obtained by extrapolating the curve to zero shear-rate.

2.3. Dielectric measurements

Dielectric measurements were performed in a Dupont (DEA 2970) dielectric analyzer. Experimental conditions covered a frequency range of 0.01–100 kHz, 1-volt amplitude at 25 °C. The permittivity of the asphaltene particle ϵ_p (3.83) was estimated from that of the suspension by a volume average calculation [8] given by the equation

$$\epsilon = \epsilon_p \phi + (1 - \phi)\epsilon_L \quad (1)$$

where ϵ and ϕ are the permittivity and volume fraction of the suspension and ϵ_L is the permittivity of the fluid (silicon oil).

2.4. Electrical measurements

The asphaltene particles were compacted under pressure (5 ton) to obtain a circular sample of 2 cm of diameter and 1.3 mm of thickness. Using a Megger High-Resistance Meter, we measure the resistance under 1 kV. The silicon oil (40 ml) was tested in the same equipment.

2.5. Spatial arrangements observations

The sample cell and procedure to observe the spatial arrangements of asphaltene particles at different intensities of the electric field, was reported previously [9]. The type of the cell used to keep the suspensions and to apply different intensities of electric field is shown schematically in Fig. 2a. The electrodes were 1 mm-thick cooper foils and were

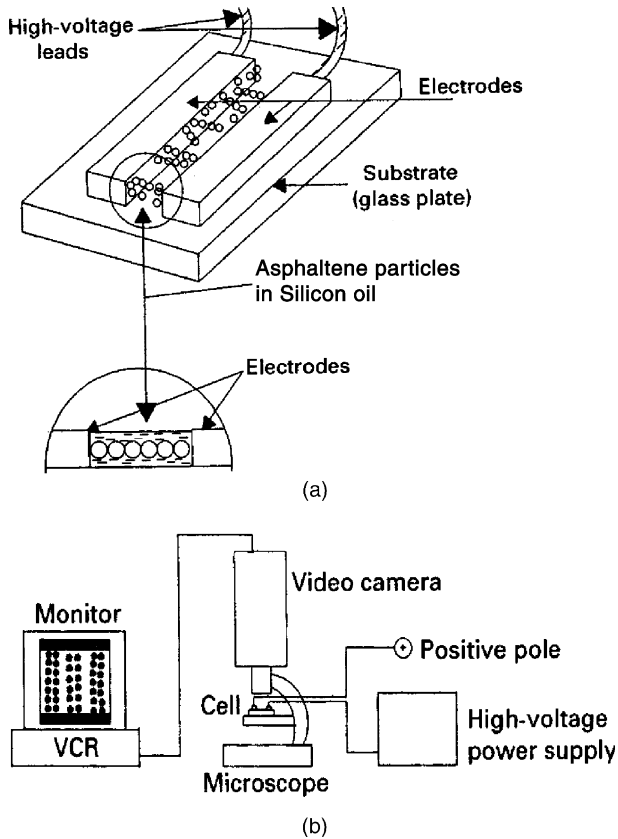


Fig. 2. Sample cell (a) and experimental arrangement (b).

glued to glass plates. The spacing of the electrodes was 1 mm gap. The sample cell was placed on the stage of a Nikon Microscope SMZ-2t equipped with a video camera (Fig. 2b). Before and after application of electric field, the images were stored on the PC. The suspension volume was of the order of 500 μl .

3. Results and discussion

3.1. Rheological properties

Fig. 3 shows the viscosity of suspensions (0.08 volume fraction) as a function of the shear rate for various electric fields. In the absence of the electric field, the suspensions show a near-Newtonian behavior with constant viscosity. Upon application of the electric field, a shear-dependent viscosity that increases as the shear rate lowers is observed. The increase of the viscosity with the electric field is more accentuated at high electric fields. Generally, this phenomenon is observed in electrorheological (ER) suspension and has been ascribed to the formation of fibrous structures due to polarization of the particles [10,11]. Asphaltene aggregates are polar compounds and it is likely that they may give rise to similar patterns of fibrous structures. When the electric field is higher than 2 kV mm^{-1} , the growth of the viscosity with the electric field becomes asymptotic. This

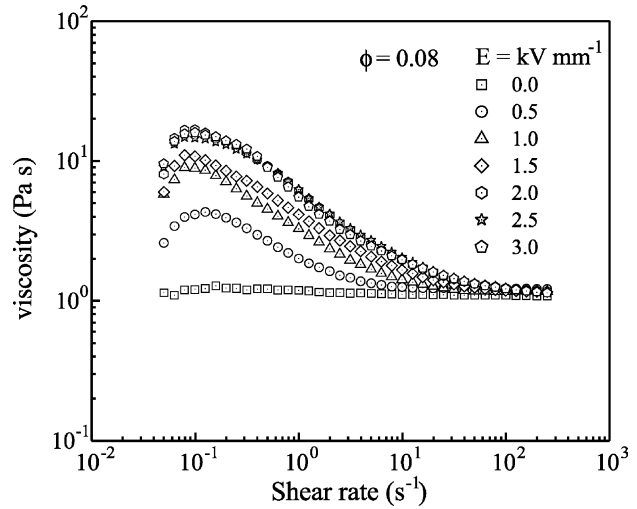


Fig. 3. Shear viscosity as a function of shear rate for a suspension of asphaltene in silicon oil (volume fraction, $\phi = 0.08$) for various electric fields.

observation has been reported in ER fluids [12], and represents a critical electric field related to a transition from the alignment of the aggregates at relatively moderate electric fields to disruption of the aligned structure under strong electric fields.

Another important feature of the viscosity behavior is the presence of a maximum at a given shear rate for most electric fields, such as for smaller shear rates the viscosity diminishes. For sufficiently weak flows, polarization of particles and electrophoretic-like forces overcome the flow forces, leading to particle migration towards the electrodes, and such effect weakens the structures. Evidently, two forces tend to weaken the structures formed under the electric field: the flow (at high shear rates) and the electrophoretic-like force that causes hydrodynamic instabilities (at low shear rates or high electric fields). On the other hand, polarization forces tend to reform the structures. Thus, the maximum in the viscosity represent the balance between the three forces.

An average relaxation time of the suspension under electric fields may be estimated from the region where the viscosity becomes constant at high shear rates in Fig. 3. This region represents the balance between the flow and polarization forces. Interestingly, the relaxation time increases linearly with the electric field. This characteristic time represents the time scale of the structure breakage process, such as for larger times (lower shear rates) the polarization forces dominate, meanwhile for shorter times (larger shear rates) the flow forces dominate.

Fig. 4 shows the variation of the shear stress versus shear rate for various electric fields. Upon application of the electric field, the suspension exhibits an apparent yield stress τ_y , representative of a Bingham viscoplastic behavior, which is described by the equation

$$\tau = \tau_y(E) + \eta\dot{\gamma} \quad (2)$$

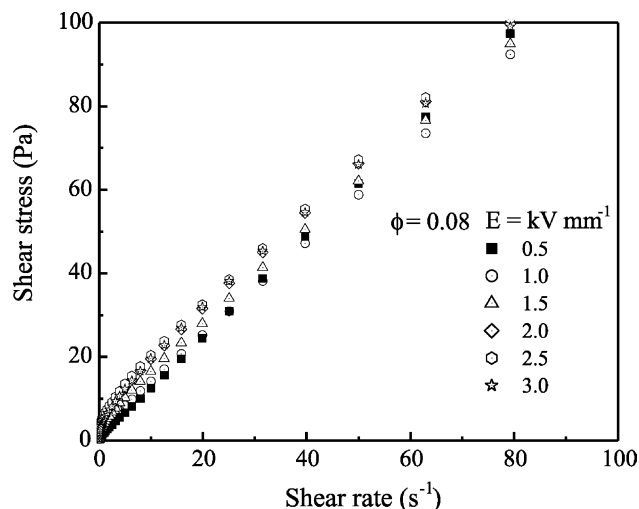


Fig. 4. Shear stress versus shear rate for a suspension of asphaltene in silicon oil ($\phi = 0.08$) for various electric fields.

where τ is the shear stress, η is the plastic viscosity of the suspension, γ is the shear rate and E is the applied electric field. A linear plot reveals that all curves depart from zero stress indicating that the yield stress measured is an apparent yield. In fact, the zero shear rate viscosity variation with the electric field is equal to the yield stress variation with the electric field.

In Fig. 5a a plot of $\log \tau_y$ versus $\log E$ is shown. τ_y was evaluated from extrapolation to zero γ of data shown in Fig. 4. The results indicate that τ_y is proportional to the 1.6 power of the electric field for the suspension with 0.08 volume fraction, up to a critical electric field (2 kV mm^{-1}). For higher field values, the power decreases near zero, indicating that the yield stress levels off, similarly to the behavior found in the viscosity. In Fig. 5b, an alternative evaluation of τ_y from the maxima of the viscosity in Fig. 3 is shown. In this case, the yield stress is proportional to the 0.6 power of the electric field, and levels off at the critical field. This value of the slope is similar to that of a dynamic yield stress, found at a given vanishing shear-rate. Otsubo et al. [13] found that a power of two corresponds to the formation of the single chains that cover the gap between the electrodes in ER fluids. In our case, a value of a power less than two indicates the formation of weak fibrous structures, which gives rise to the observed yield stress. This behavior is more accentuated at high field intensities. Rejon and collaborators [14], reported similar behavior for systems based on silica gel and tricresyl phosphate suspensions. In the following section, we discuss this issue with observations of the structural arrangements for different electric fields using optical microscopy.

3.2. Structural arrangements

Figs. 6–9 shows the structural arrangement of the asphaltene aggregates in silicon oil at 0, 1, 2 and 3 kV mm^{-1} , respectively, for the 0.08 volume fraction.

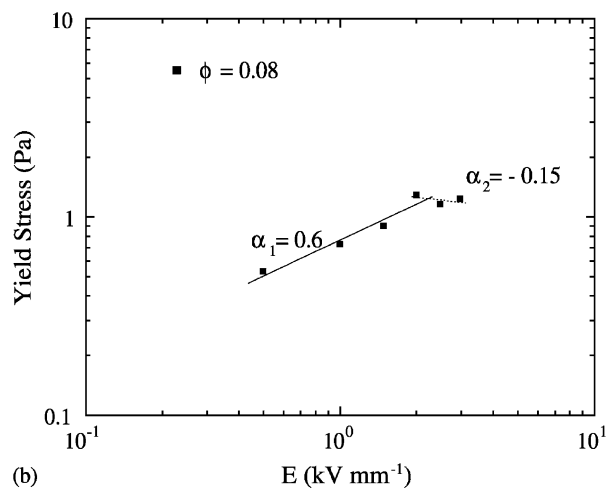
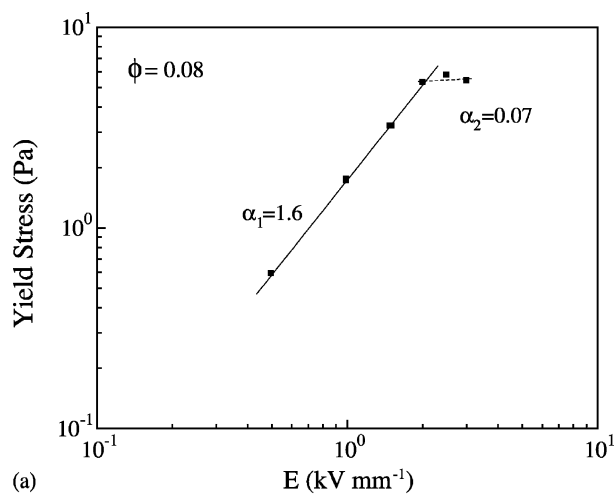


Fig. 5. (a) Yield stress (found by extrapolation) as a function of the dc electric field (E) for the asphaltene suspension ($\phi = 0.08$). (b) Yield stress (obtained from the maximum of the viscosity) as a function of E , for the system shown in (a).

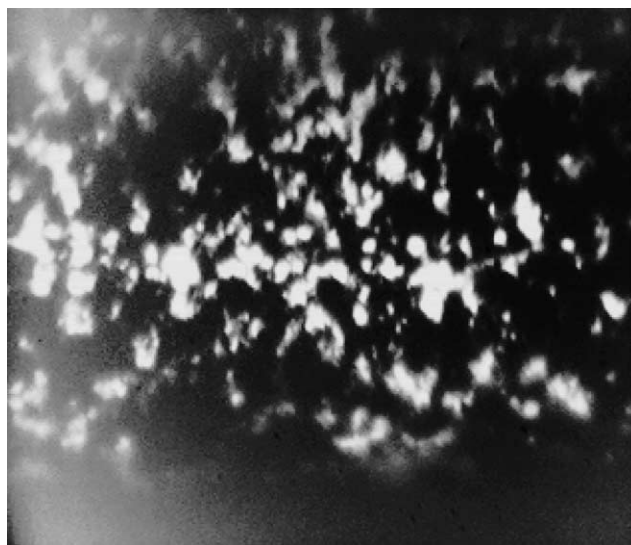


Fig. 6. Structural arrangements observed in the asphaltene suspension ($\phi = 0.08$) at 0 kV mm^{-1} .

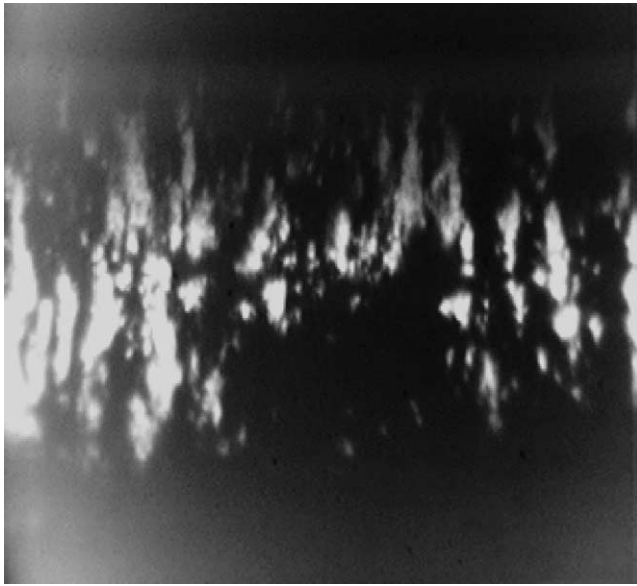


Fig. 7. Structural arrangements in the asphaltene suspension ($\phi = 0.08$) at 1 kV mm^{-1} .

These aggregates are broken when the electric field is applied and consequently this leads to the formation of fibrous structures. The structure of the fibers that present different arrangements depends on the electric field strength and is responsible for the increase in the suspension viscosity ($0.5\text{--}2 \text{ kV mm}^{-1}$). When the electric field reaches values (3 kV mm^{-1}) higher than the critical value (2 kV mm^{-1}), the suspension becomes less structured, as shown in Fig. 9. In this case, motion of the particles (electrophoretic-like effect) occurred in the suspensions, and this motion is directed toward the electrode of the opposite charge. Consequently, the structures are weakened and the viscosity growth ceases, as shown in the results presented in Fig. 3. These observations clearly demonstrate

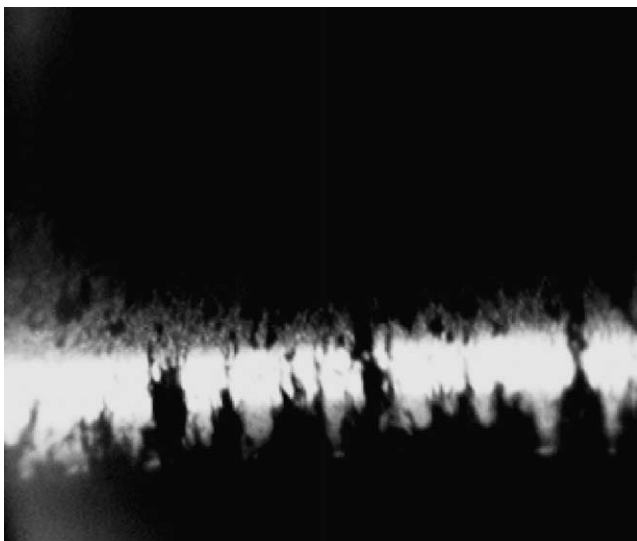


Fig. 8. Structural arrangements in the asphaltene suspension ($\phi = 0.08$) at 2 kV mm^{-1} .

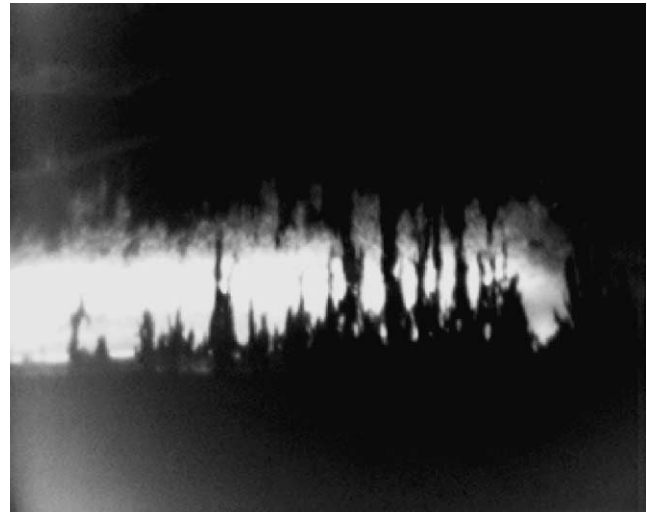


Fig. 9. Structural arrangements in the asphaltene suspension ($\phi = 0.08$) at 3 kV mm^{-1} .

the relationship between the structure induced by the electric field and the behavior of the viscosity and yield stress of the suspensions.

3.3. Dielectric properties

Generally, the dielectric spectrum gives information on the collective response of the microscopic polarization process under external electric fields. The presence of any dielectric relaxation corresponds to the manifestation of polarization mechanisms that occur in a microscopic scale. The polarization mechanisms commonly observed in suspensions at relatively low frequency are the interfacial polarization and Debye polarization. The interfacial polarization is the dominant mechanism arising from differences in conductivity between silicon oil and asphaltene particles (see Table 1). In Fig. 10, the dielectric loss tangent ($\tan \delta$) is shown as a function of frequency for the asphaltene

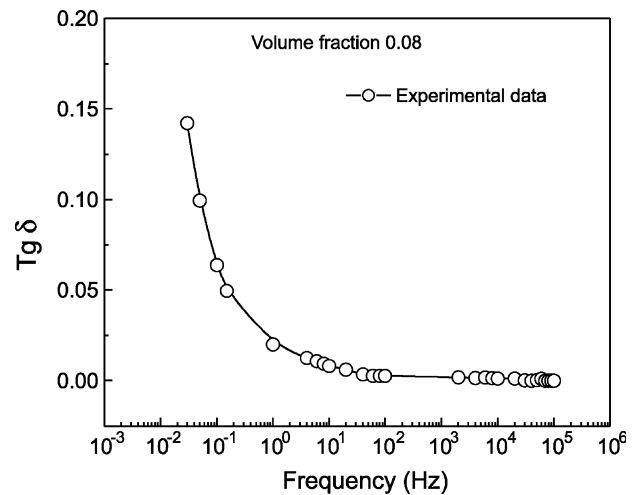


Fig. 10. Frequency variation of the loss tangent ($\tan \delta$) in asphaltene suspensions.

suspension. Hao and coworkers [15] found that in ER fluids, a value of $\tan \delta$ under 0.1 at 1 kHz is representative of a weak ER response. In our case, $\tan \delta$ is equal to 0.002 at this frequency. The formation of the fibrous structure caused by polarization forces in the asphaltene suspensions may then be ascribed in part to the ionic species present in the asphaltene, since $\tan \delta$ decreases inversely with the frequency. This dielectric behavior has been observed in systems having migrations of free-ionic species [16].

4. Conclusions

Rheological and structural arrangement studies on asphaltene suspensions were presented. The asphaltene suspensions show a weak electrorheological (ER) response, which depends on the electric field intensity and concentration. This response is not substantial for concentrations lower than 0.08 volume fraction.

The suspensions show a Bingham plastic behavior and the yield stress varies as a power of the electric field, which indicates that the ER behavior can be explained on the basis of the formation of weak aggregated structures. An asymptotic behavior of the viscosity and yield stress with the electric field is found at a critical electric field. This is due to the disruption of the aggregated structures caused by particle motions at high electric fields. Thus, the structural arrangements are strongly dependent on the magnitude of the applied electric field.

Although the formation of fibrous structures under electric fields in petroleum-based dispersed systems has been observed before 1940 [17], the present results have highlighted the effect of polarization forces of the asphaltene aggregate under electric fields in a flowing

system, adding more evidences of electrokinetic effects observed in asphaltene dispersions.

Acknowledgements

The authors are thankful to CONACYT (Project No. 31123-U), IIE (Project No. 11794) and IMP (Project No. D00337) for the financial support.

References

- [1] Mansoori GA. Arab J Sci Engng 1996;21:707–23.
- [2] Katz DL, Beu KE. Ind Engng Chem 1945;37:195.
- [3] Dykstra H, Beu KE, Katz DL. Oil Gas J 1944;43:79.
- [4] Evdokimov IN, Eliseev N Yu. Nauka I Tehnologiya Uglevodorodov 2000;2:54–8.
- [5] Sams GW, Zaouk M. Energy Fuels 2000;14:31–7.
- [6] Teixeira PIC, Tavares JM. Telo da Gama M.M. J Phys: Condens Matter 2000;12:R411–34.
- [7] Telo de Gama MM, Tavares JM. J Phys: Condens Matter 2000;12: A471–6.
- [8] Marshall L, Zukoski F, Goodwin JW. J Chem Soc Faraday Trans 1989;85:2785–95.
- [9] Rejon L, Ponce MA, De La Luz C, Nava R, Castaño VM. J. of Mat. Sci: Mat Electron 1996;7:433–6.
- [10] Deinega YF, Vinogradov GV. Rheol. Acta 1984;23:63619.
- [11] Gast AP, Zukoski CF. Adv Colloid Interface Sci 1989;30:153.
- [12] Boissy C, Atten P, Foulc JN. J Int Mat Syst Struct 1996;7:599–603.
- [13] Otsubo Y, Sakine M, Katayama S. J Rheol 1992;36:479–96.
- [14] Rejon L, Castañeda-Aranda I, Manero O. Colloids Surfaces A: Physicochem Eng Aspects 2001;182:93–107.
- [15] Hao T, Akiko K, Fumikazu I. Langmuir 1998;14:1256–62.
- [16] Barnikas R, Eichhorn RM. Engineering dielectric volume IIA, ASTM. 1983. p. 61–5.
- [17] Clayton W. The theory of emulsions and their technical treatment, 4th ed. ; 1943.