

# Interfacial rheological studies of extra-heavy crude oils and asphaltenes: role of the dispersion effect of resins in the adsorption of asphaltenes at the interface of water-in-crude oil emulsions<sup>α</sup>

Sócrates Acevedo<sup>a\*</sup>, Gastón Escobar<sup>a</sup>, Luis B. Gutiérrez<sup>a</sup>, Hercilio Rivas<sup>b</sup>  
and Xiomara Gutiérrez<sup>b</sup>

<sup>a</sup>Centro de Química Orgánica, Facultad de Ciencias, Universidad Central de Venezuela, Caracas 47102, Venezuela

<sup>b</sup>INTEVEP, S.A. Apdo. 76343, Caracas 1070A, Venezuela

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## Abstract

The interfacial behaviour of a crude oil and an asphaltene system has been studied by a planar rheological method. System S<sub>1</sub> was a 30% (v/v) xylene dilution of extra-heavy Cerro Negro crude oil; the aqueous phase was tridistilled water or an NaCl solution (2% (w/v)). System S<sub>2</sub> was a 3.21% (w/v) dilution of Cerro Negro asphaltene in xylene; aqueous phase as for system S<sub>1</sub>. These systems were studied under creep in the pH range 1.6–9.5. The elasticity ( $E_0$  and  $E_1$ ) and viscosity ( $\eta_1$  and  $\eta_N$ ) surface moduli were obtained from creep compliance measurements. Viscoelastic as well as elastic behaviour was observed. The interfacial rheological behaviour of asphaltene and crude oil systems was found to be very different in the presence and absence of salt. The high values of the moduli, leading to the high stability of water-in-oil emulsions, was attributed to flocculation of asphaltene–resin micelles at the interface. In the absence of resins, asphaltenes were not dispersed and their adsorption at the interface could lead to precipitation and multilayer formation.

*Keywords:* Adsorption; asphaltenes; crude oil emulsions; dispersion; rheology.

## Introduction

Due to their importance in the formation of water-in-crude oil (W/O) emulsions and to the consequences for the oil industry of the presence of these emulsions, native tensoactive compounds, termed natural surfactants (NS), present in crude oils, have attracted the attention of many workers. Reisber and Doscher [1] were among the first to report the presence of such compounds in crude

oils. Seifert and Howells [2] succeeded in extracting carboxylic acids from a light California crude oil. Acevedo et al. [3] have isolated NS from extra-heavy crude oils and from W/O emulsions. The high stability of the W/O emulsions has been attributed to the formation of mechanically strong films of NS around the water droplets. Strassner [4] has reported that these films are formed by adsorption of resins and asphaltenes and that the adsorption of asphaltenes at acidic pH leads to solid films. Kimbler et al. [5] reported compressibility curves ( $\pi-A$ ) vs pH and found low compressibility values for the films except at pH 12.6, where the film apparently disappears. Jones et al. [6]

\*Corresponding author.

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suggested that the low tendency of W/O emulsions to coalesce is due to the low compressibility of the above-mentioned films. Measurement of viscoelastic properties led Eley et al. [7] to conclude that the very high surface viscosities and elasticities found were due to the adsorption of asphaltenes. Cairns et al. [8] studied the rheological behaviour, interfacial tension (IFT) and electrophoretic mobility of two light oils (Zakum and Murban) and one medium oil (Tia Juana). Cairns et al. reported that the usual bell-shaped curve obtained when the IFT is plotted against pH could be reproduced by a hydrocarbon oil containing abietic acid and diphenyl-4-pyridylmethane. The isoelectric points of these crude oils were also reported for the pH range 2.8–4. The rheological studies showed a marked reduction in the surface viscosity  $\eta$  when the pH was increased. For the Murban oil  $\eta$  dropped from 237 (pH 2) to 0.004 (pH 11) m N s m<sup>-1</sup>.

According to many reports, asphaltenes are dispersed in the oil medium by resins [9,11,14]. Thus the idea that asphaltenes exist in crude oils as “micelles” or colloids dispersed by resins is widely held [9,10]. Models for these micelles, in which the asphaltenes and resins are located at the centre and periphery, respectively, have been proposed [10,14,15]. CMC values of asphaltenes in several solvents have been reported [16]. Previous measurements of the IFT of natural surfactants (in crude oil, resins and asphaltenes) have been made at values higher than the apparent CMC of these compounds [3,17,18]. Since the presence of these micelles and the dispersion effect of resins should play important roles in the adsorption of asphaltenes at the crude oil–water interface, the study of these effects can be important for assisting in the interpretation of interfacial behaviour.

In this paper, a planar surface rheological study of xylene dilutions of a Cerro Negro crude oil and its asphaltenes, under conditions where W/O emulsions will prevail, is presented. For these conditions the interfacial moduli instantaneous ( $E_0$ ) and retarded ( $E_1$ ) elasticities, as well as the associated ( $\eta_1$ ) and Newtonian ( $\eta_N$ ) viscosities have been

determined from creep compliance experiments as a function of the aqueous pH.

## Experimental

### Materials

A dehydrated and desalted extra-heavy Cerro Negro crude oil (8.3 API) was employed. Cerro Negro asphaltenes were precipitated, as reported earlier [19], by the addition of 60 volumes of *n*-hexane to a 1:1 dilution of this crude oil in benzene. The precipitated solid was Soxhlet extracted with *n*-hexane to remove the resins.

### Shear viscoelasticity

The viscoelastic properties of the films were studied by subjecting the oil–water interface to shear deformation using a rheometer, model SR-14, designed and constructed by British Petroleum. This apparatus has been described in detail earlier [8]. The experiment is carried out by placing a bob at the interface and applying a shear stress, by means of a motor, through a torsion wire. The aqueous phase of the system is placed in a circular glass flask in a thermostatically controlled room (20°C). Once settled (bottom layer), the oil layer is carefully pipetted over the aqueous phase and the system is allowed to age for 36 h.

Two systems were examined. System S<sub>1</sub> was Cerro Negro crude oil diluted with xylene (30% (v/v)). The aqueous phase was tridistilled water or a sodium chloride solution (2% (w/v)) adjusted to the required pH. System S<sub>2</sub> was a 3.21% (w/v) solution of asphaltenes in xylene and the same aqueous phase as before. These systems afforded very strong films and were studied under creep conditions.

### Creep experiments

In this experiment, a sudden, constant stress is applied and the displacements of a laser beam over

a scale are recorded against time. Displacements are converted to  $\theta$  with use of the following equation

$$\theta = \arctan(x/d) \quad (1)$$

where  $x$  is the displacement, and  $d$  is the mirror-to-scale distance (66 cm). The shearing stress  $\tau$  applied to the interface is related to the torque by

$$\tau = (T/4\pi)(1/R_1^2 - 1/R_2^2) \quad (2)$$

where  $R_1$  (2.81 cm) and  $R_2$  (7.2 cm) are the bob and flask ratios, respectively, and  $T$  is the torque. Surface creep compliance curves are obtained from

$$J(t) = (4\pi/K)(1/R_1^2 - 1/R_2^2)^{-1} \{ \theta(t) / [\alpha - \theta(t)] \} \quad (3)$$

where  $J(t)$  is the creep compliance,  $\alpha$  is the torque angle,  $K$  is the torsion constant ( $43.08 \cdot 10^{-7}$  N m) and  $\theta(t)$  is the angle sweep in time  $t$ . The instrument is calibrated with use of the system serum albumin–0.01 M KCl–petroleum ether at 20°C according to the method of Biswas and Haydon [20]. Various torque angles were tested and a value of  $10^\circ$  (equivalent to a shearing stress of  $6.4 \cdot 10^{-5}$  N m $^{-1}$ ) was found to be satisfactory at the pH values examined. Since no buffer was employed, pH drifts were detected in the pH range

from 4 to 6 and above 10, so the measurements were undertaken at the values shown in Tables 1 and 2. Errors were estimated at pH 1.9, 2.5 and 6.5 where no pH drifting was detected. The values of  $E_0$  and  $\eta_N$  were reproducible within 30%, whereas an error of 30–50% could be expected for  $E_1$  and  $\eta_1$ .

In the cases where the four-body or the two-body models could be used [21], Eqns (4) and (5) were applied respectively

$$J(t) = E_0^{-1} + E_1^{-1} [1 - \exp(t/t')] + \eta_N^{-1} t \quad (4)$$

$$J(t) = E_0^{-1} + \eta_N^{-1} t \quad (5)$$

where  $t'$  is the retardation time given by Eqn (6).

$$t' = \eta_1/E_1 \quad (6)$$

$E_0$  and  $\eta_N$  were determined from the intercept and slope in Eqn (5) when  $J(t)$  was plotted against time. For the case of Eqn (4),  $E_0$  was obtained from the intercept and  $\eta_N$  from the slope of the linear region of  $J(t)$  (see below). The values of  $E_1$  and  $\eta_1$  were determined by the graphic procedure described by Inokuchi [22]. In this an asymptote  $Q(t)$  was drawn and the differences  $Q(t) - J(t)$  were obtained from the  $J(t)$  plot (see Fig. 1). The natural logarithms of these differences were plotted against time and

TABLE 1

Variation of viscoelastic parameters with pH for system S<sub>1</sub>: Cerro Negro oil–xylene (30% (v/v))–aqueous phase, at 20°C

Aqueous phase	pH	$E_0$ (m N m $^{-1}$ )	$E_1$ (m N m $^{-1}$ )	$\eta_1$ (N s m $^{-1}$ )	$\eta_N$ (N s m $^{-1}$ )
Water	1.8	0.5	0.3	0.035	0.40
	2.8	4.0	2.0	0.380	1.60
	3.2	6.7	11.0	0.870	1.90
	3.9	5.7	7.4	0.450	1.90
	6.0	11.0	–	–	–
	6.6	40.0	–	–	–
	8.6	2.2	2.6	0.170	0.40
	2% Sodium chloride	1.9	13.0	14.0	3.2
2.5		23.0	24.0	2.7	14.0
3.5		43.0	–	–	–
3.9		43.0	–	–	–
6.5		40.0	–	–	–
8.9		10.0	15.0	1.1	4.5

TABLE 2

Variation of viscoelastic parameters with pH for system S<sub>2</sub>: asphaltene (3.21%)–xylene–aqueous phase, at 20°C

Aqueous phase	pH	$E_0$ (m N m <sup>-1</sup> )	$E_1$ (m N m <sup>-1</sup> )	$\eta_1$ (N s m <sup>-1</sup> )	$\eta_N$ (N s m <sup>-1</sup> )
Water	1.6	20.0	–	–	–
	2.3	4.9	13.0	0.3	2.1
	3.3	4.4	–	–	0.5
	6.6	5.8	9.4	2.2	4.5
	8.0	4.0	5.4	0.8	3.2
	9.5	2.0	6.5	1.3	1.4
2% Sodium chloride	1.7	43.0	–	–	–
	2.1	46.0	–	–	–
	3.4	46.0	–	–	–
	6.5	5.8	9.4	2.3	4.5
	8.0	5.4	12.6	1.9	7.7
	9.0	2.5	16.2	0.4	1.7

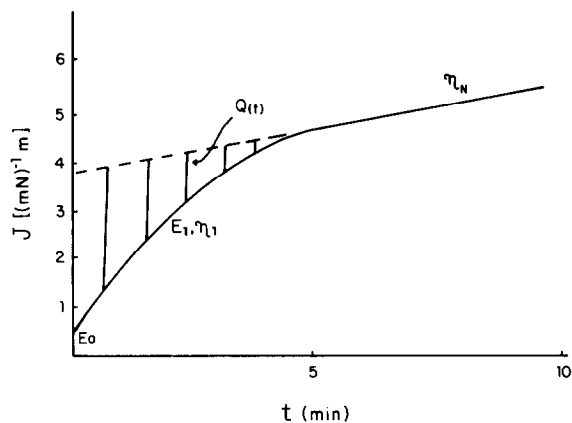


Fig. 1. Creep compliance plot for system S<sub>1</sub>; pH 1.8; aqueous phase, water. The viscoelastic behaviour corresponds to a solid four-body model:  $E_0$ ,  $\eta_N$ ,  $E_1$  and  $\eta_1$ . The values of  $E_1$  and  $\eta_1$  are calculated from those of  $Q(t)$ .

linear plots were obtained in all cases. The variables  $E_1$  and  $t'$  were evaluated from the intercept  $I$  ( $E_1 = e^{-I}$ ) and slope  $s$  ( $t' = s^{-1}$ ) of these linear plots. The associated viscosity  $\eta_1$  was obtained from Eqn (6).

For the viscoelastic films, the shear stress was applied for 40 min or less and  $E_0$  values were estimated from the creep compliance value at 1 min. Those films which gave no significant change in displacement after 1 min were considered elastic under this particular stress. These films recovered

90% or more of the strain when the shear stress was turned off.

#### Preparation of emulsions

Water-in-crude oil emulsions (W/O) were prepared by introducing their components into a Tekman homogenizer, model RW-20, with mixing at about 2000 rev min<sup>-1</sup>.

Routine stability tests for water-in-oil emulsions were performed by placing the fresh emulsion in a graduated test tube in a thermostat (25°C) and measuring the volume of the separated phase after 24 h.

#### Results

The values of the viscoelastic parameters obtained in the present study are shown in Tables 1 and 2. In most cases the rheological behaviour can be represented by a four-body model [21]. An example of this is shown in Fig. 1. A behaviour similar to that of a Maxwell fluid (two-body model) is observed in the case illustrated in Fig. 2. Behaviour resembling that of an elastic or solid film is observed in several cases; here only  $E_0$  can be measured with any certainty (see Tables 1 and

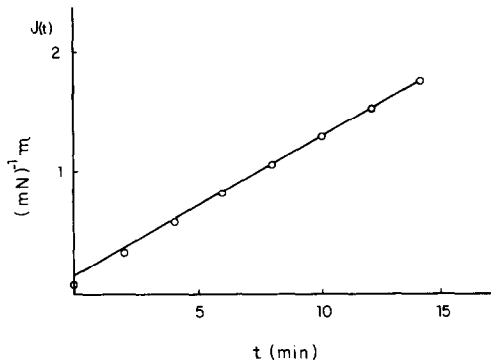


Fig. 2. Creep compliance plot for system  $S_2$ , pH 3.3; aqueous phase, water. The viscoelastic behaviour corresponds to a Maxwell liquid ( $E_0$ ,  $\eta_N$ ).

2). These films present very small displacements ( $d < 0.2$  cm) after 1 min with no significant changes from the initial value after 15 min. It should be mentioned that except for the case illustrated in Fig. 2, the response of the films to shear was always that corresponding to a solid or to a viscoelastic solid (see Tables 1 and 2).

The report of Eley et al. [7] was the only one found with which a comparison can be made. They report the following data for the system asphaltene (Kuwait), 0.014%, in an *n*-heptane–toluene mixture, and aqueous phase:  $E_0 = 14$ ;  $E_1 = 5.0$ ;  $\eta_1 = 2.16$ ;  $\eta_N = 3.2$ . The units are the same as those in Table 2. Comparison with the present results (Table 2; water; pH 6.6) is satisfactory except for values of  $E_0$ . These discrepancies are reasonable in view of the different conditions and sample used, and of the different ways in which  $E_0$  is determined. In Figs 3a and 3b the  $E_0$  values are plotted against pH for the water and salt solutions, respectively. It is important to note that the trends in  $E_0$  as the pH is changed are different for systems  $S_1$  and  $S_2$ , both in the absence and presence of salt. With water as the aqueous phase the  $E_0$  for the crude oil increases sharply in the neighbourhood of neutral pH, leading to solid-like behaviour. For asphaltenes, apart from the  $E_0$  (pH 1.6) value, the other values can be averaged to  $4.2 \pm 1.4 \text{ m N m}^{-1}$ . The addition of salt leads to a substantial increase in  $E_0$  for the  $S_1$  system at all pH values below 8.0.

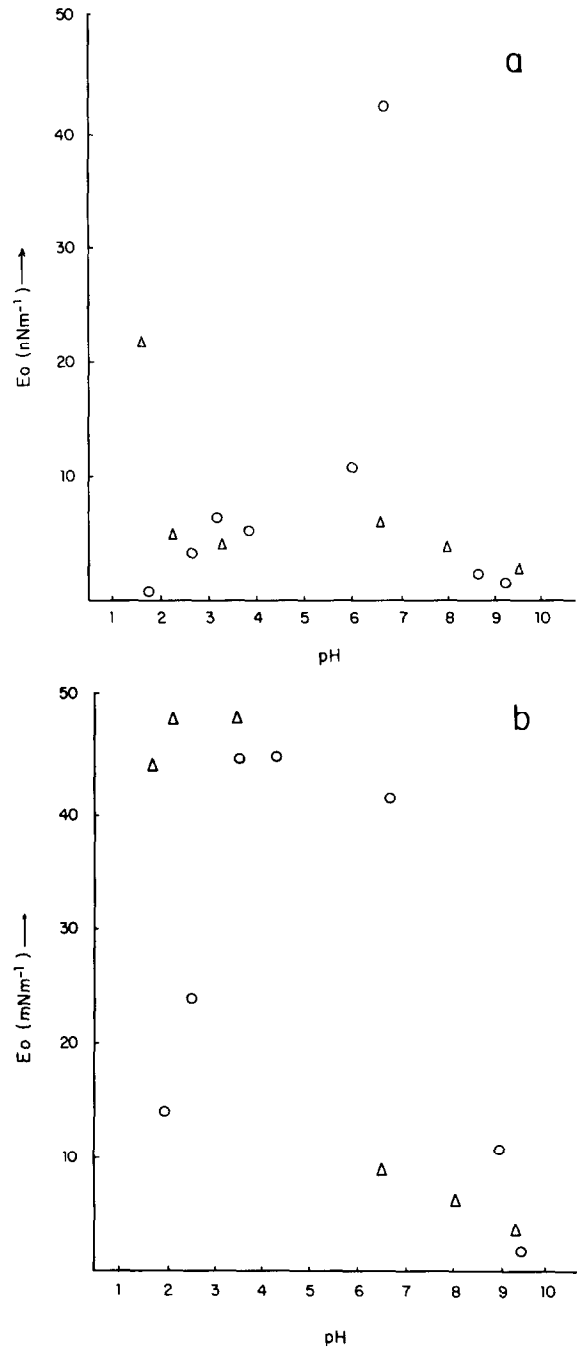


Fig. 3. Comparison of  $E_0$  values for systems  $S_1$  (O) and  $S_2$  ( $\Delta$ ), at various pH values. Aqueous phases: (a) water; (b) 2% NaCl.

Elastic-like films are apparent at pH values of 3.5, 3.9 and 6.5, whereas for asphaltenes, these films are apparent below pH 3.5 (see Table 2 and

Fig. 3b). For the crude system, the viscoelastic parameters increase after the addition of salt. This tendency is opposite to that reported by Cairns et al. [8].

There is some debate regarding the relevance of interfacial viscosities to emulsion stability [23], and evidence has been presented suggesting that only elasticities are important in this respect [24]. As far as the present study is concerned, only  $E_0$  could be measured under all conditions examined and so the discussion below was mainly made in terms of the  $E_0$  values.

## Discussion

The high values obtained for the viscoelastic parameters of both systems are in agreement with the general view that during adsorption at the oil–water interface, the NS form a three-dimensional cross-linked network leading to strong interfacial films, which in turn result in very stable water-in-oil emulsions. As mentioned above, it is believed that the asphaltenes and resins are present in crude oils as micelles in which the former are presumably located at the core, and the latter at the periphery, respectively [10,15]. This micelle formation has been used to justify the greater solubility of asphaltenes in organic solvents in the presence of resins. The above cross-linked network may be the result of flocculation of these micelles at the interface, leading to a better wetting of the interface and to multilayer formation. The interfacial film is thus formed by means of the usual intermolecular interactions common to asphaltenes and resins which, in the present case, are enhanced by hydrophobic effects. In addition, due to the hydrophobic nature of asphaltenes and resins, the above micelles do not enter the aqueous phase.

Due to the absence of resins in system  $S_2$ , it can be expected that the adsorption of NS (asphaltenes in this case) leading to multilayer formation will proceed to a larger extent than in system  $S_1$  since in the former case the asphaltenes will not be dispersed. Therefore the rheological properties of system  $S_2$  will be, in general, less sensitive to

changes in pH (see Fig. 1) than those of system  $S_1$ . The slow changes in the IFT with time reported earlier for crude oil and asphaltenes below pH 10, are consistent with multilayer formation [18]. It has also been found [18] that an asphaltene system similar to  $S_2$  affords very small changes in the IFT with changes in pH below pH 7, whereas the corresponding crude oil systems give the usual bell-shaped IFT–pH curves. This result is consistent with the presence of intermolecular ion pairs at the interface, since such compounds are less sensitive to pH changes than their acid–base components. Presumably, the interfacial concentration of ion pair aggregates in the asphaltene case is higher than in the crude oil. The dispersion effects of resins will keep the aggregation of asphaltenes in the crude oil system relatively low compared with the asphaltene system.

It should be mentioned that the  $E_0$  values may depend strongly on the electrostatic repulsions at the interface and their values should decrease with the imbalance of charges. Apparently this effect is responsible for the lower values of  $E_0$  for system  $S_2$  compared with system  $S_1$ , observed in some cases.

The apparent elastic behaviour found for system  $S_2$  below pH 4 in the presence of salt, as well as the value measured at pH 1.6 in the absence of salt (see Tables 1 and 2), appears to be due to the formation and precipitation of solid chlorhydrates from amines and chloride ions. When the pH is increased, these acids ( $NR_1R_2R_3HCl$ ) are neutralized, the solid disappears and the rheological behaviour changes from elastic to viscoelastic. It can be expected that the resins will hinder such solid formation in system  $S_1$ . In general, the  $E_0$ –pH behaviour for the crude oil system can be accounted for in terms of pH and salt content: at low and high pH values, electrostatic repulsions will be significant and the  $E_0$  values will be low. Addition of salt will lead to double-layer neutralization and higher values of  $E_0$ . At pH values near 7, the positive and negative charges at the interface are almost equal and the NS can approach each

other more closely, affording high  $E_0$  values and elastic films.

Whatever the reasons for the rheological results obtained in this study, there is no doubt that the behaviour of asphaltenes at the oil–water interface will be significantly changed by the presence of resins. Moreover, the properties of water in crude oil emulsions should be a consequence of the adsorption of asphaltenes and resins (probably as micelles) at the interface. If asphaltenes and resins are viewed as a surfactant–cosurfactant pair the above result can be expected. Finally, it should be mentioned that the differences between asphaltenes and resins as compounds capable of playing different roles in crude oil properties have not always been appreciated [25]. According to the present results these differences are enhanced at the water–crude oil interface. It is suggested that the rheological behaviour of the Cerro Negro crude oil systems is due to adsorption at the interface of asphaltenes and resins, probably as micelles. In this case the changes in  $E_0$  with pH and salinity can be accounted for qualitatively in terms of electrostatic and double-layer effects. In the absence of resins the asphaltenes are not adequately dispersed and solid and multilayered films may appear, depending on pH and salt content.

## Conclusions

The high values found for the viscoelastic parameters under conditions where W/O emulsions prevail (pH below 10) are consistent with the high stability of these emulsions and with the solid and solid viscoelastic behaviour of their interfacial films. It is suggested that such strong films are formed as a consequence of flocculation of asphaltene–resin micelles. The different rheological properties of asphaltenes at the oil–water interface in the presence and absence of resins could be due to the dispersion effects of the resins.

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