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STUDY OF ASPHALTENE SOLUTIONS BY ELECTRICAL CONDUCTIVITY MEASUREMENTS

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CONDUCTIVITÉ ÉLECTRIQUE DES SOLUTIONS
D'ASPHALTÈNES

Les interactions des asphaltènes avec leur environnement moléculaire dans des solutions modèles ont été étudiées par la mesure de la conductivité électrique de ces solutions. Les interactions avec le n-heptane, des résines, des tensioactifs, l'eau, le phénol et le chlorure de sodium ont été explorées. Les conclusions tirées de cette étude ont confirmé certaines hypothèses faites sur les mécanismes d'agrégation des asphaltènes en solution, en particulier dans le cadre de la théorie des solutions colloïdales.

STUDY OF ASPHALTENE SOLUTIONS BY ELECTRICAL
CONDUCTIVITY MEASUREMENTS

The asphaltene interactions in model solutions were studied using a technique based on the electrical conductivity measurement. Interactions with n-heptane, resins, surfactants, water, phenol and NaCl were investigated. The conclusions drawn from this study confirmed previous opinions on aggregation mechanism of asphaltenes in solutions. They confirmed also the interpretation of asphaltene behaviour in terms of colloidal solution theories.

CONDUCTIBILIDAD ELÉCTRICA DE LAS SOLUCIONES
DE ASFALTENOS

Se ha procedido al estudio de las interacciones de los asfaltenos con su entorno molecular en soluciones modelo, por la medición de la conductibilidad eléctrica de éstas. También se han explorado las interacciones con el n-heptano, las resinas, los tensioactivos, el agua, el fenol y el cloruro de sodio. Las conclusiones que se derivan de este estudio han venido a confirmar ciertas hipótesis establecidas acerca de los mecanismos de agregación de los asfaltenos en solución, y básicamente, situándose en el marco de la teoría de las soluciones coloidales.

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INTRODUCTION

The asphaltenes are one of the most polar parts of the crude oil. The polyaromatic core of asphaltenes containing nitrogen, sulfur, oxygen, vanadium and nickel strongly interacts with the external electrical field. The resulting migration of asphaltenes leads to the electrical conductivity as was first reported by Lichaa and Herrera (1975).

The mechanism of this migration is not completely explained up to this day. Recently Fotland *et al.* (1993) proposed to determine asphaltene precipitation with a technique based on measurement of electrical conductivity of the crude oil. It was demonstrated that the abrupt change of the electrical conductivity occurring during precipitation phenomena made it possible to determine not only the precipitation point but also the relative amounts precipitated.

In this study we used electrical conductivity of asphaltenes to characterise their molecular interactions in model solutions. Asphaltenes were obtained from asphalts derived from various crude oils and furnished by the *Institut français du pétrole*. Solutions were prepared by dissolving the asphaltenes in polar solvents. The high solvent polarity increases the electrical conductivity of asphaltenes and facilitates measurements.

Measurements were carried on with tetrahydrofuran and nitrobenzene. Both compounds are excellent solvent for asphaltenes.

1 EXPERIMENTAL SECTION

1.1 Experimental set-up

The apparatus is shown on Figure 1. Measurements were performed in a glass sample cell (a) of the volume $V = 250 \text{ cm}^3$ equipped with a magnetic stirrer (b). The temperature was maintained constant to within $\pm 0.1 \text{ }^\circ\text{C}$ by a double jacket surrounding the cell and connected to the Lauda RM6 thermostat (c). A platinum resistance probe (PT 100) with a Hewlett-Packard digital multimeter (34401 A) was used to measure the cell temperature (d). The conductivity measurements were carried out using an electrode immersed in the solution and connected to a Tacussel CDM 92 conductimeter (e). The working frequency of this apparatus ranged from 94 Hz to 50 kHz (conductivity from $10 \text{ nS} \cdot \text{cm}^{-1}$ to

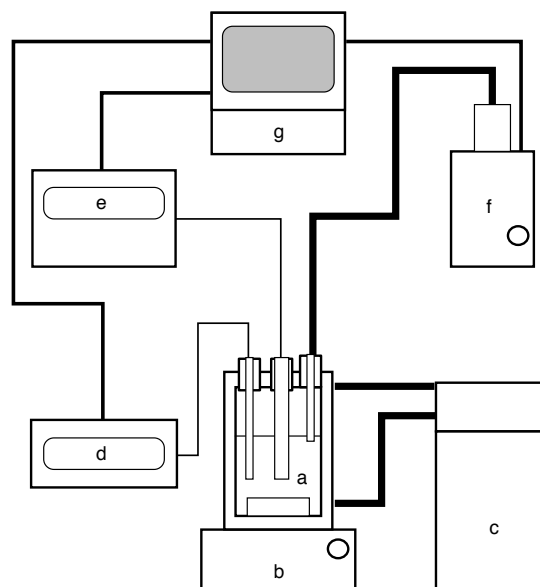


Figure 1

Experimental setup (a: sample cell; b: magnetic stirrer; c: thermostat; d: multimeter; e: conductimeter; f: piston buret; g: PC computer).

$6 \text{ S} \cdot \text{cm}^{-1}$ when using a cell constant of 1 cm^{-1}) and enabled the conductivity studies of both low and high conductivity solutions. An automatic piston burette (Schott T90/20) was used to modify the initial quantity of the solvent (f). The piston burette, the multimeter, the conductimeter and the magnetic stirrer were connected with the four serial ports of a PC computer via the standard RS-232 interface (g). Measurement control and data acquisition was automated via the computer.

1.2 Experimental procedure

A known mass of asphaltenes was dissolved in 50 ml of solvent. The solution was stirred during approximately 3 hours up to the stability of the measured conductivity was obtained. The measurement was performed every 2 seconds during 1 minute after the stirring was stopped. The mean value was retained and compared with the new conductivity measurement obtained after the next stirring-measuring cycle. Next, the solvent was introduced into the cell (0.1-2.5 ml) by an automatic piston buret and the measurement was performed as described above. Usually the experiment was stopped when 50 ml of solvent was added. All experiment was controlled by PC computer.

2 RESULTS

2.1 Conductivity of asphaltenes in nitrotoluene and in tetrahydrofuran

Measurements were performed with solution of asphaltenes in nitrotoluene (initial concentration was $C_{asph} = 11.3 \text{ g/l}$) and in tetrahydrofuran ($C_{asph} = 7.27 \text{ g/l}$). Results obtained are presented in Figure 2. The specific conductivity presented in this figure is defined as the ratio of the conductivity to the concentration of asphaltenes in the solution. The specific conductivity in nitrotoluene is less important than in THF in spite of the higher polarity of the former. This can be attributed to the higher viscosity of nitrotoluene. In both cases the specific conductivity is sharply increasing in diluted solutions. This phenomenon corresponds probably to the dissociation of asphaltene aggregates. It can be supposed that the limiting conductivity value corresponds to monomeric species. Active sites of asphaltenes are the most accessible in the monomeric form and become shielded when the aggregation rate

increases. They are supposed to be responsible for the electrical conductivity. Therefore in more concentrated solutions where asphaltenes are more aggregated a smaller specific conductivity is observed. Consequently, analysing the conductivity curve during dilution can afford arguments to modelling the aggregation mechanism of asphaltenes.

2.2 Conductivity of asphaltenes + resins in nitrotoluene

The initial solution was prepared with 0.5654 g of asphaltenes and 0.1547 g of resins in 50 ml of nitrotoluene. Therefore, the concentration in asphaltenes and resins were respectively 10.13 g/l and 3.24 g/l. Results obtained are given in Figure 3 together with results obtained previously without resins. The pattern of both curves is very similar but the conductivity in presence of resins is significantly lowered. Probably resins are bound to certain active sites. It can be observed that the limiting conductivity remains unchanged. Therefore asphaltene-resin complex

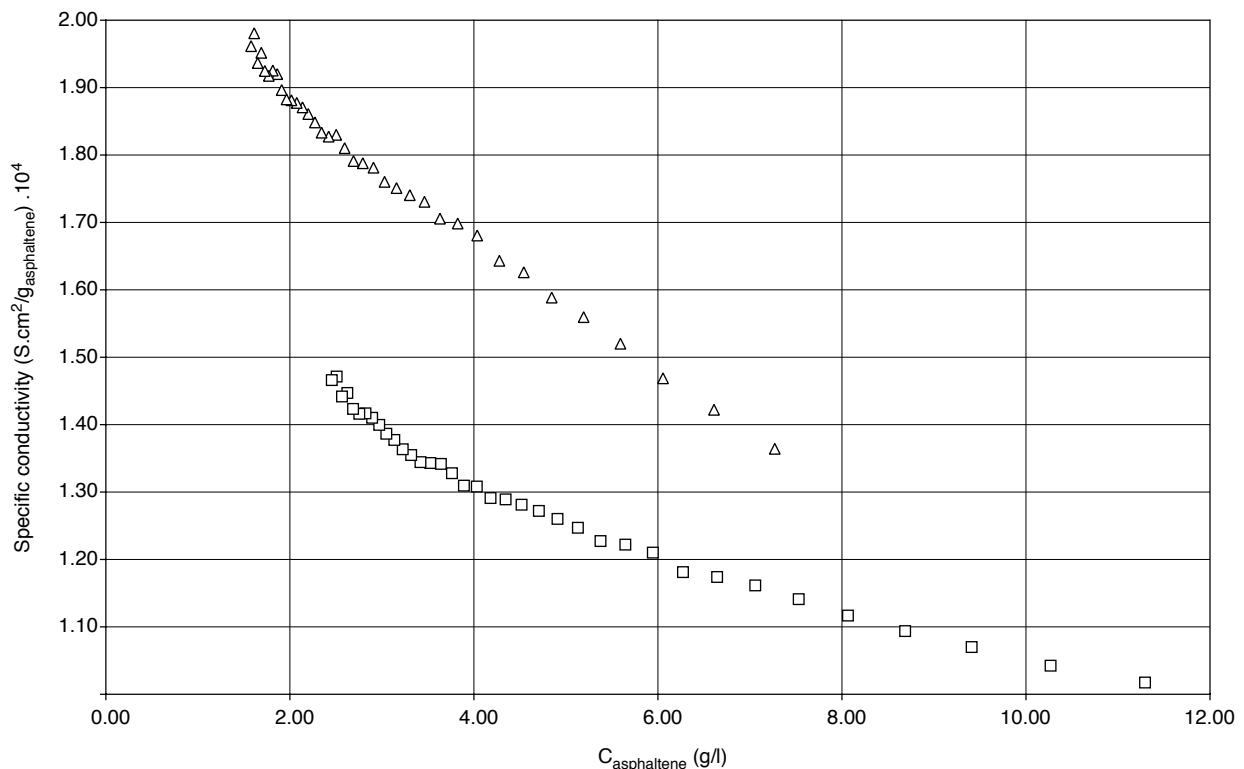


Figure 2

Specific conductivity of asphaltenes versus asphaltene concentration in: (Δ) THF solution, (\square) nitrotoluene solution.

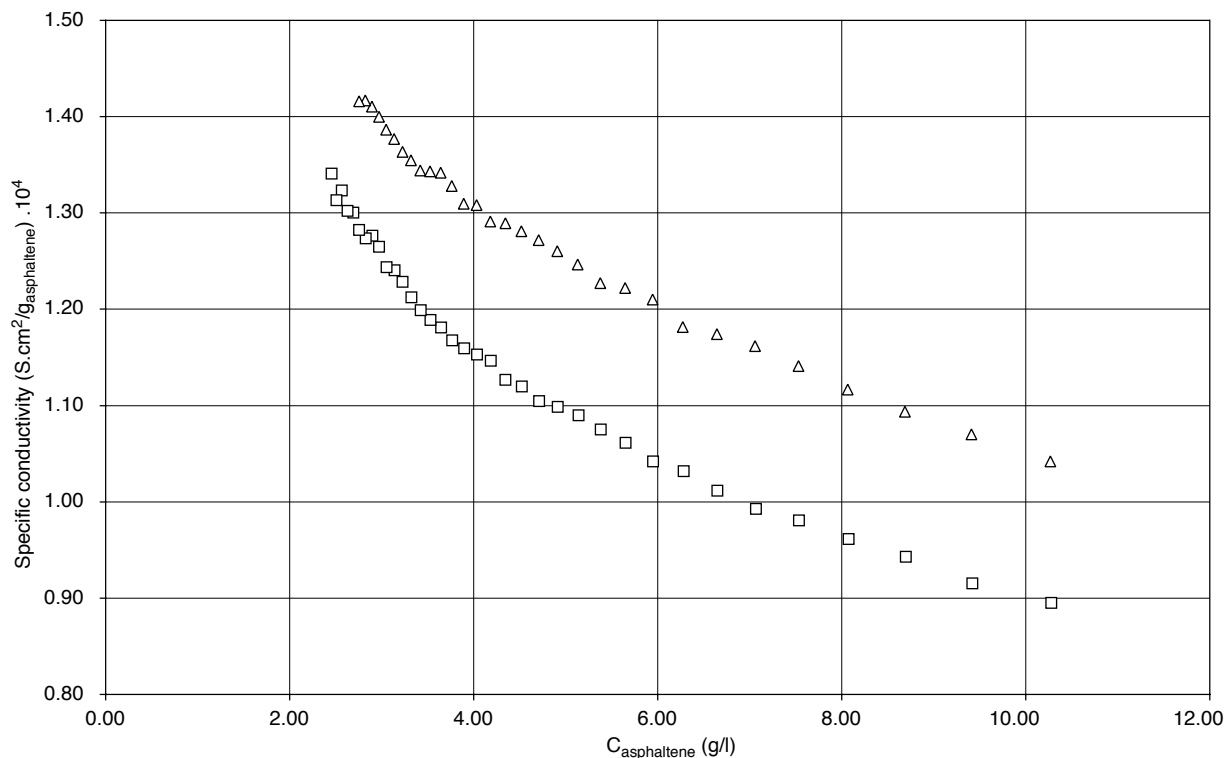


Figure 3

Specific conductivity of asphaltenes versus asphaltene concentration in (Δ) nitrotoluene, (◻) nitrotoluene + resins.

dissociates at high dilution. The influence of resins on the conductivity confirms the previous conclusions concerning the relationship conductivity/aggregation. The comparison of both curves lead to the quantitative interpretation to these results. In fact, supposing that the loss of the conductivity can be attributed to the asphaltene-resin binding the following relationships can be written:

$$m_{ads} = C_{asp} - C_{(asp+res)} \quad (1)$$

The mass of asphaltenes bound with resins m_{ads} is calculated as a difference of asphaltenes concentrations $C_{asp} - C_{(asp+res)}$ (in g per liter of solvent) determined at the same solution conductivity.

$$X_{ads} = m_{ads}/C_{res} \quad (2)$$

X_{ads} is a mass ratio of bound asphaltenes and of the total quantity of resins present in the solution. The plot of X_{ads} versus asphaltene concentration is given in Figure 4. After an initial abrupt rise in the range of

diluted solutions X_{ads} remains almost constant for asphaltene concentrations higher than 4 g/l. This value is close to the CMC of asphaltene in toluene (3.24 g/l at 298.2 K) as reported by Andersen and Speight (1993). It is clear from Figure 4 that approximately 1.9 g of asphaltenes is bound with 1 g of resins at concentration higher than 4 g/l.

2.3 Flocculation of asphaltenes from tetrahydrofuran solutions with n-heptane.

Initial solutions of asphaltenes in tetrahydrofuran containing respectively 2.58, 5.19 and 13.6 g/l of asphaltenes were diluted with n-heptane. The corresponding curves are presented in Figure 5. Their shape is very similar to this obtained by Fotland *et al.* (1993) with crude oil conductivity. The characteristic slope changes of the conductivity curve which was attributed by Fotland *et al.* to the beginning of the flocculation process occurs at the volumetric ratio of n-heptane/THF being 0.30, 0.29 and 0.27 respectively for three solutions studied. Therefore, the beginning of

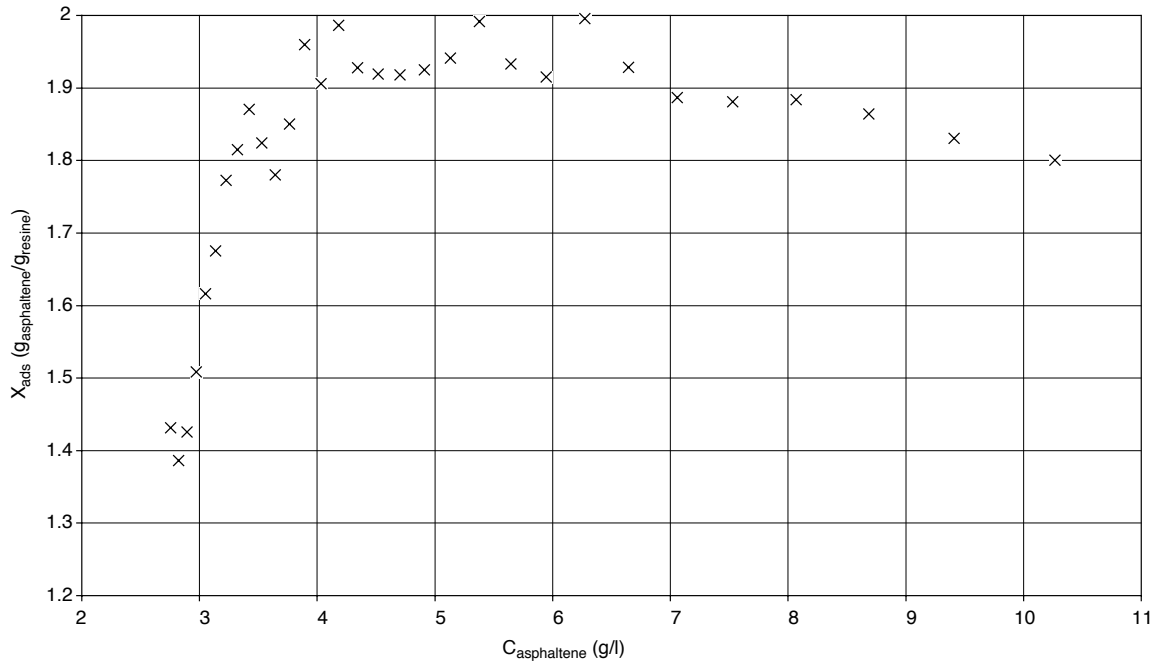


Figure 4
Asphaltene-resin binding in function of asphaltene in THF concentration.

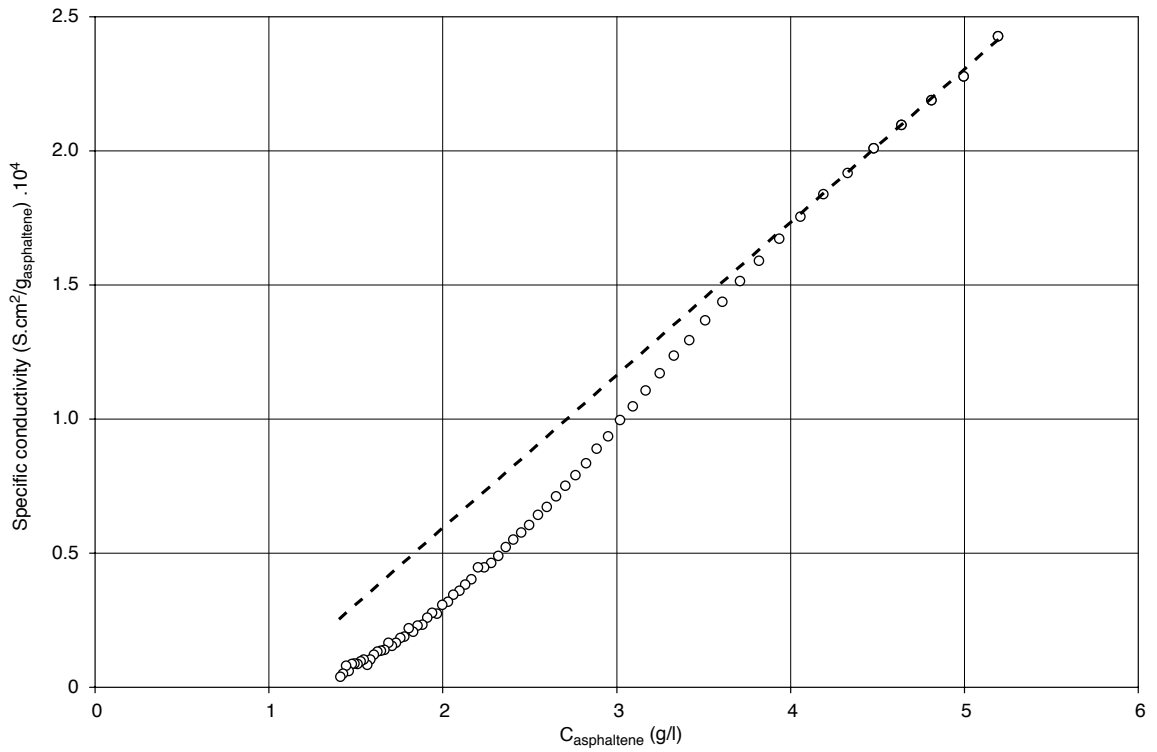


Figure 5
Flocculation of asphaltenes from THF solution with *n*-heptane.

flocculation is nearly insensitive on the initial asphaltene concentration and occurs at almost the same *n*-heptane/solvent ratio. This observation is important for the comprehension of the flocculation mechanism.

2.4 Flocculation of asphaltenes from tetrahydrofuran/water solutions with *n*-heptane

The knowledge of interactions of water with asphaltenes is an important topic. In fact, the important polarity and the hydrophobicity of asphaltenes let expect the existence of complex entropy driven structures. THF is an ideal solvent for this study dissolving both water and asphaltenes.

The mass of 0.260 g of asphaltenes was dissolved in 60 ml of solvent containing 50 ml of THF and 10 ml of water ($C_{asph} = 4.33$ g/l). This solution was diluted with *n*-heptane. Results are presented on Figure. 6. The presence of water increases the dielectric constant of the solutions and makes rise its conductivity. The curve break corresponding to the beginning of flocculation occurs at the *n*-heptane/solvent ratio of 0.32. Surprisingly the presence of water in the solvent makes

the solution more stable in regards of flocculation (previously for the same amount of asphaltenes the ratio 0.29 was obtained). Moreover, the comparison of the shape of both curves indicates that the amount of asphaltenes flocculated is less important in this case (for details of argumentation see Fotland *et al.*, 1993). Consequently, it can be thought that water-asphaltenes interactions lead to structures involving both components and increasing their stability in the solution. However, the solution seems to be metastable and flocculates with time.

2.5 Flocculation of asphaltenes from tetrahydrofuran/water/surfactant solutions with *n*-heptane

This experiment was carried out in the same way as the former one. A small quantity of an anionic surfactant (SDS, $2.8 \cdot 10^{-5}$ mole/l) was added to the mixed solvent (50 volume parts of THF and 10 volume parts of water). Resulting conductivity curve is given in Figure 6. In this case the conductivity changes with concentration nearly linearly. The small curve break is observed at concentration corresponding to *n*-heptane/

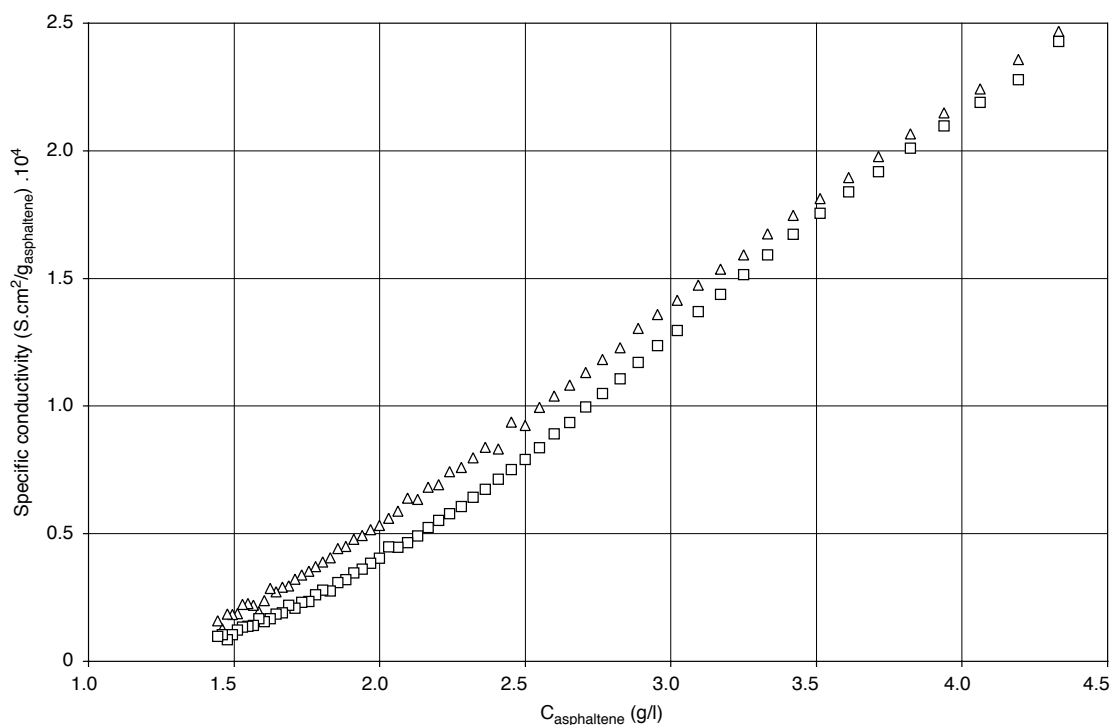


Figure 6

Flocculation of asphaltenes with *n*-heptane from: (Δ) THF-water solution, (◻) THF-water-SDS solution.

solvent ratio of 0.52. Therefore, about 40% more of *n*-heptane is needed to initiate the asphaltene precipitation. Moreover, the analysis of this curve shape indicates that the quantity of asphaltenes deposited is significantly smaller than in the former case.

2.6 Conductivity of the system (asphaltenes + THF) + (H₂O + Phenol)

The influence of water on the asphaltene stability in solution encouraged us to continue studies on this problem. In the present experiment a solution of asphaltenes dissolved in THF was diluted either with water either with the solution of phenol in water (9.66 g of phenol per liter of water).

In the later case phenol was used to follow the availability of binding sites of asphaltenes. This method was proposed by Barbour and Petersen (1974) to characterise the basicity of asphalt and can be applied

to asphaltenes also. It can be considered that the amount of bound phenol expresses the basicity of asphaltenes and the number of available binding sites.

Following systems were studied:

A: asphaltenes + THF + water + phenol

B: asphaltenes + THF + water

C: THF + water + phenol

D: THF + water

Conductivity of systems C and D were determined as reference for A and B.

In the case of systems A and B measurements were performed for three initial concentrations of asphaltenes being respectively 3.23, 4.50 and 8.76 g/l. In Figure 7 conductivity curves obtained in function of water or water/phenol solution added are presented. The contribution of phenol and THF to the total conductivity is small as is evident from C and D curves behaviour. The main contribution to the conductivity is due to the presence of asphaltenes. The increase of the

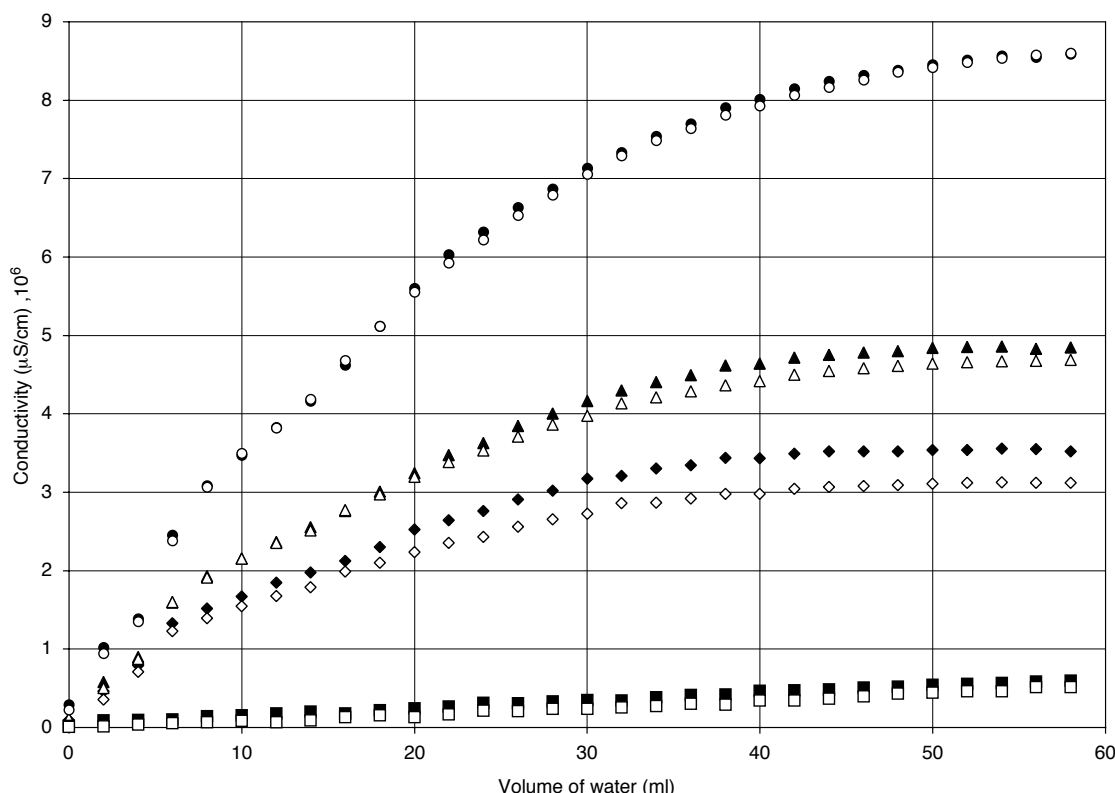


Figure 7

Conductivity of the system (asphaltene + THF) + (water + phenol)

- ◆ THF + water + phenol + asphaltenes (3.23 g/l)
- ◇ THF + water + asphaltenes (3.23 g/l)
- ▲ THF + water + phenol + asphaltenes (4.50 g/l)
- △ THF + water + asphaltenes (4.50 g/l)

- THF + water + phenol + asphaltenes (8.76 g/l)
- THF + water + asphaltenes (8.76 g/l)
- THF + water + phenol
- THF + water

dielectric constant of the solvent gives rise to the abrupt increase of the conductivity. When the initial volume of solvent is doubled the conductivity becomes nearly constant. In spite of the important water content no asphaltene deposition was observed during experiments. The phenol presence diminishes, as expected, asphaltene conductivity in the case of lower concentration of asphaltenes (3.23 g/l). This is probably due to the asphaltene-phenol binding. At higher concentration this phenomenon is no more observed. It can be explained by increasing auto-aggregation of asphaltenes but also by a probable formation of asphaltenes/water/THF structures involving active sites of asphaltenes.

2.7 Conductivity of the system asphaltenes + H₂O + NaCl

The strong interactions of ions with colloidal species and their influence on aggregation and flocculation processes justify a study of asphaltene-ion system conductivity.

In the present experiment two asphaltene solutions in THF with concentration 3.8 g/l and 9.4 g/l respectively were diluted by the water or aqueous solution of NaCl (3.44 g/l). For each asphaltene concentration two series of measurements were performed:

A: asphaltenes + THF + NaCl/H₂O

B: asphaltenes + THF + H₂O

The total conductivity of A is composed of the contributions of NaCl and of asphaltenes. We define the difference:

$$\chi_{(\text{NaCl}/\text{Asph})} = \chi_A - \chi_B \quad (3)$$

as the conductivity due essentially to the salt. The corresponding specific conductivity is given by:

$$\Lambda(\text{NaCl}/\text{Asph}) = \chi_{(\text{NaCl}/\text{Asph})} / \chi_{(\text{NaCl}/\text{Asph})} \quad (4)$$

with $\chi_{(\text{NaCl}/\text{Asph})}$ being the concentration of the salt in the solution.

The third series of measurements

C: THF + NaCl/H₂O

was performed to determine $\Lambda_{(\text{NaCl})}$, the conductivity pattern of NaCl without asphaltenes. The corresponding specific conductivity was defined as in Equation 4. In Figure 8 $\Lambda_{(\text{NaCl}/\text{Asph})}$ and $\Lambda_{(\text{NaCl})}$ are plotted in function of salt concentration. The observed decrease of the

NaCl conductivity can be attributed to the NaCl-asphaltene binding. Therefore, it can be assumed that the mass of the bound salt is given by expression defined at the constant specific conductivity:

$$m_{\text{ads}}(\text{NaCl}) = c_{(\text{NaCl})} - c_{(\text{NaCl}/\text{Asph})} \quad (5)$$

Amount of bound salt in function of salt concentration is reported in Figure 9. In the range of diluted salt solutions this amount is small and nearly constant when salt composition increases. Moreover nearly the same value is observed with both asphaltene concentrations. This behaviour changes for salt concentrations higher than 0.8 g/l. The amount of the salt retained increases exponentially with the salt concentration. This rise is smaller in the case of more concentrated asphaltene solution. This is probably due to a higher auto-aggregation.

CONCLUSION

Measurements of the electrical conductivity were used to study molecular interactions of asphaltenes in solutions. This technique can be applied to quantitative characterising of binding phenomena also.

The most important conclusions concerning asphaltenes behaviour can be summarised as follows:

- asphaltenes aggregate in diluted solutions and this tendency is only slightly dependant on their environment;
- at low concentration (below 3-4 g/l) behaviour of asphaltenes is significantly different than at higher concentration; the limit between the two domains corresponds probably to the CMC;
- at higher concentrations asphaltenes seem to be more sensible to their chemical environment and they are able to form organised structures including polar molecules;
- water can be involved in the structures stabilising asphaltenes in solution.

All above formulated opinions should be confirmed by further investigations.

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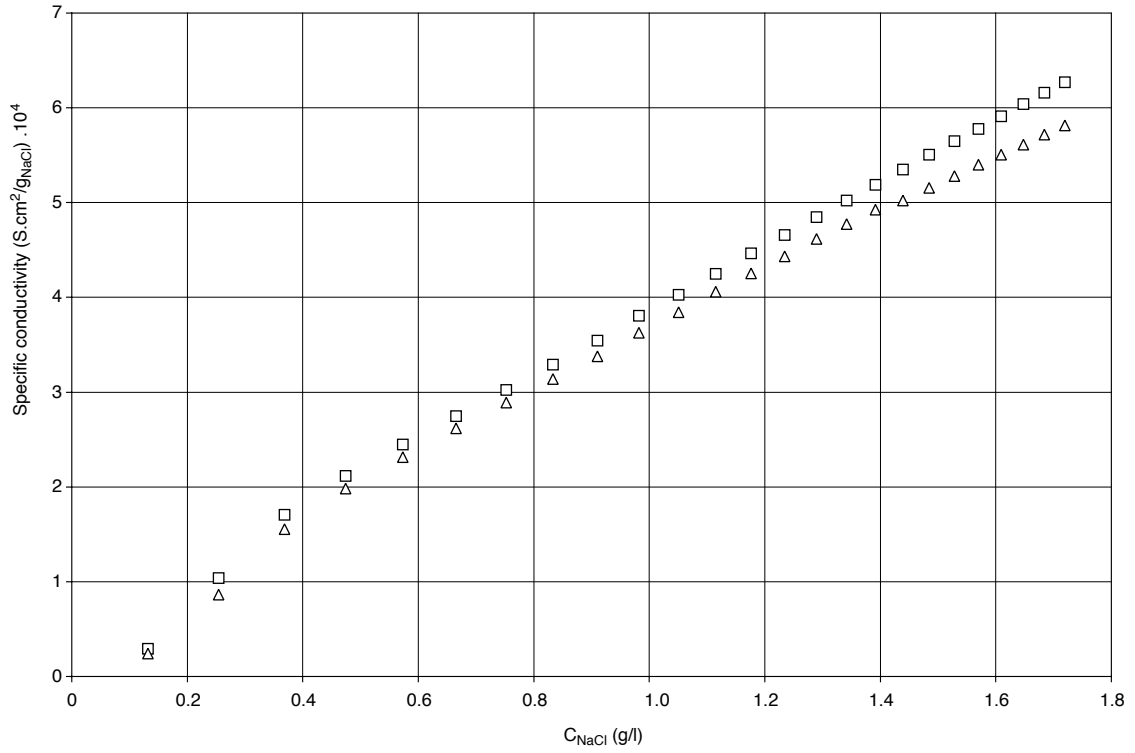


Figure 8
Specific conductivity of: (□)THF + NaCl/H₂O solution and (Δ)THF + NaCl/H₂O + asphaltene.

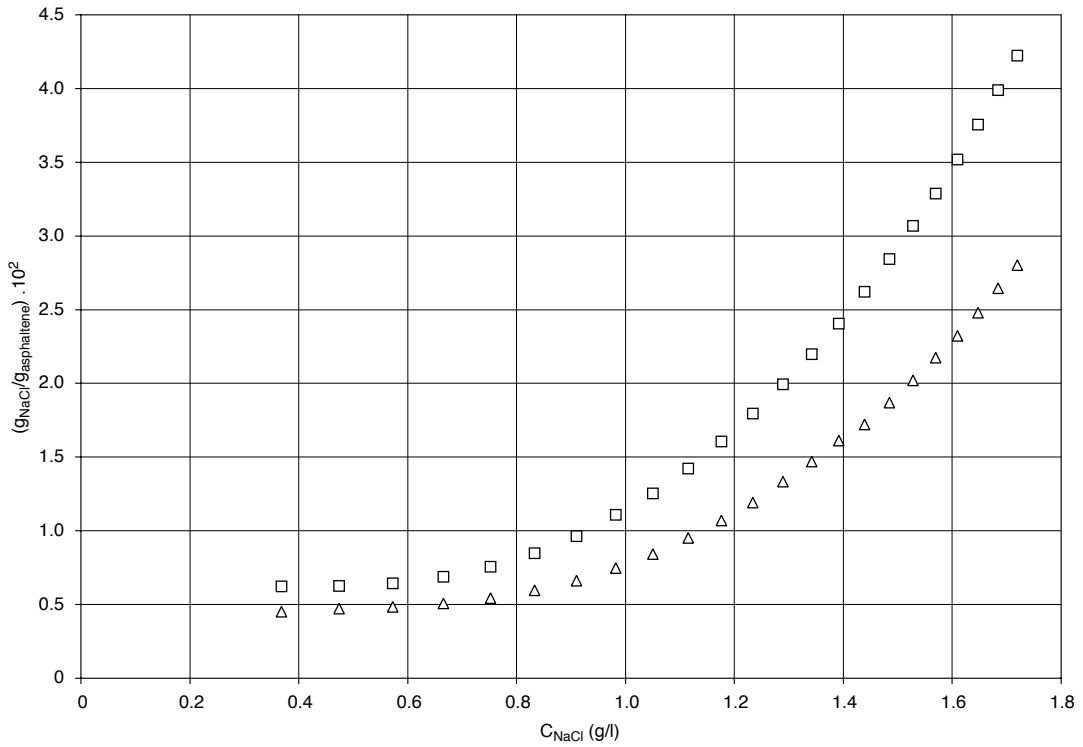


Figure 9
Asphaltene-NaCl binding in function of the salt concentration. The initial concentration of asphaltenes in THF (Δ) 3.8 g/l, (□) 9.4 g/l.

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