



EFFECT OF THE CONCENTRATION OF IONIC SURFACTANTS ON THE ELECTROKINETIC BEHAVIOR OF ASPHALTENE PRECIPITATED FROM A MAYA MEXICAN CRUDE OIL

EFFECTO DE LA CONCENTRACIÓN DE SURFACTANTES IÓNICOS EN EL COMPORTAMIENTO ELECTROKINÉTICO DE ASFALTENO EXTRAÍDO DE UN CRUDO MAYA MEXICANO

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Abstract

In this work we show the behaviour of the zeta potential of asphaltene when different concentrations of two cationic surfactants (cetylpyridinium chloride and dodecylamine hydrochloride) and one anionic surfactant (sodium dodecyl sulphate) interact with asphaltene particles at different pH in the aqueous phase. Asphaltene, precipitated from a Maya Mexican crude oil, was observed by Transmission electron micrographs showing that asphaltene is constituted of nanometric particles smaller than 50 nm in diameter. By changing the concentration of cetylpyridinium chloride, dodecylamine hydrochloride and sodium dodecyl sulphate from 0.01 mM to 1 mM, we were able to reverse and control the sign of the zeta potential of asphaltene, demonstrating the presence of both electrostatic and hydrophobic interactions at the asphaltene surface. These interactions were also observed by interfacial tension measurements at the toluene - water interface. It has been noticed that for low and high pH in the aqueous phase, the presence of dodecylamine hydrochloride and sodium dodecyl sulphate were not determinant on the asphaltene interfacial tension. On the contrary for pH near the IEP and pH neutral, these surfactants were more effective. The presence of cetylpyridinium hydrochloride in the aqueous phase changed the asphaltene interfacial tension to very low values independent of the pH.

Keywords: asphaltene, zeta potential, ionic surfactants, interfacial tension, pH.

Resumen

En este trabajo se muestra el efecto de la interacción de dos surfactantes catiónicos (cloruro de cetilpiridinio e hidrocloreto de dodecilamina) y un surfactante aniónico (dodecilsulfato de sodio) en el potencial zeta de asfalto en diferentes pH. El asfalto fue extraído de un crudo Maya y fue observado en Microscopía de transmisión, observándose partículas de tamaño promedio de 50 nm. Variando las concentraciones de los surfactantes de 0.01 a 1 mM, pudimos controlar la carga de las partículas de asfalto y se pudo demostrar la existencia de interacciones electrostáticas e hidrofóbicas al variar el pH en la solución acuosa. El efecto de los surfactantes en la interfase asfalto agua fue más significativo alrededor del punto isoeléctrico del asfalto lo cual fue determinado por tensiometría interfacial. Por el contrario, a pH bajo y alto se observó una disminución del efecto de los surfactantes en la tensión interfacial, predominando las moléculas de asfalto en la interfase.

Palabras clave: asfalto, potencial zeta, surfactantes ionicos, tension interfacial, pH.

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1 Introduction

The crude oil may be considered as a colloidal system, composed of four major fractions: saturated hydrocarbons, aromatic hydrocarbons, resins, and asphaltene (Guiliano *et al.*, 2000; Baginska and Gawel, 2004). Many of the problems associated with processing of heavy crude oils come from asphaltene. Conventionally asphaltene is defined as the fraction of crude oil insoluble in n-alkanes such as n-heptane or n-pentane but soluble in aromatic solvents such as toluene or benzene (Pietrau and Cramb, 2003). This component is the heaviest and polar fraction of crude oils and formed by condensed polyaromatic structures containing small aliphatic side chains, polar heteroatoms such as oxygen, sulfur, and nitrogen, and some metals such as iron, vanadium, and nickel (Marczewski and Szymula, 2002; Grijalva-Monteverde *et al.*, 2005). Many studies have indicated the presence of carboxylic acid, carbonyl, phenol, pyrrole, and pyridine functional groups in asphaltene (Östlund *et al.*, 2004). These characteristics provide the character hydrophilic and hydrophobic of asphaltene to confer an important surface activity.

It has long been suggested that in the crude oil system, the asphaltene is associated into large structures or aggregates which are stabilized by resins, which are polar species soluble in n-alkanes; therefore, keeping asphaltene in suspension and maintaining the colloidal stability of crude oil (Sheu and Storm, 1995). If the resin separates from the asphaltene, it is possible that self-association of asphaltene molecules occurs, leading to aggregation and even precipitation causing colloidal destabilization. Asphaltene deposition and precipitation have undesirable consequences during production, transport and refining of petroleum. Aggregation and precipitation of asphaltene molecules also occurs during the processing, transportation and application of aqueous asphalt emulsions, which are widely used in the field of road construction and maintenance, thus causing problems to the optimum performance of these products (Jada and Salou, 2002). One of the most common problems related to crude oil production is the formation of stable water-in-oil emulsions (Sjöblom *et al.*, 1990; Yarranton *et al.*, 2000; Havre and Sjöblom, 2003; Sztukowski *et al.*, 2003; Zhang *et al.*, 2003; Acevedo *et al.*, 2005; Poteau and Argillier, 2005).

Water is normally present in crude oil reservoirs or is injected as steam to stimulate oil production (Peña *et al.*, 2005). Surface active materials of crude oils such as asphaltene and resin are known to adsorb at water-oil interfaces building a rigid and protective interfacial film around the water droplets (Zhang *et al.*, 2003; Poteau and Argillier, 2005; Peña *et al.*, 2005; Spiecker *et al.*, 2003; Zhang *et al.*, 2005). This interfacial film acts as a barrier that prevents droplets from coalescing and confers stability against phase separation. Aggregation and film formation are likely driven by polar heteroatom interactions, such as hydrogen bonding, which allow asphaltene to adsorb, consolidate, and form cohesive films at the oil-water interface (Spiecker *et al.*, 2003).

The study of the interfacial properties of asphaltene has been extensively studied (Rodríguez-Abreu *et al.*, 2000; Chaverot, *et al.*, 2008) because asphaltene is responsible for physical and chemical properties of crude oils and lead to major problems encountered during production, transportation, refining, and utilization of crude oils. There is a strong interest in furthering the understanding of the aggregation/dispersion characteristics of asphaltene for better control of crude oil stabilization and demulsification of water-in-oil emulsions (Sztukowski and Yarranton, 2005; Sheu *et al.*, 1992). During the last years, researchers have considered that many of the important colloidal properties of crude oils are determined directly or indirectly by the electrical charge and potential on asphaltene particles; however, the mechanisms of surface charge development on asphaltene are not fully understood (Abraham *et al.*, 2002; González *et al.*, 2003; Jada and Chaou, 2003). One of the most important tools used to gain information about the electrical characteristics (charge and potential) of colloidal particles has been the measurement of their electrophoretic mobility (Hunter, 1981). These measurements allow an indirect determination of the electrical charge at the surface, and delineation of the effect of simple ions, multivalent ions, surfactants, polymers and even proteins on both the surface charge and potential. Electrokinetic data are valuable for predicting conditions to maximize or minimize the repulsive forces between colloidal particles, thus inducing their dispersion or aggregation, respectively (Sztukowski and Yarranton, 2005).

The electrokinetic behavior of asphaltene dispersed in aqueous and non aqueous solvents has been investigated by several researchers. In aqueous solutions, the electrophoretic mobility (or zeta potential) of asphaltene is negative above about pH 4 (Abraham *et al.*, 2002; González *et al.*, 2003; Kokal *et al.*, 1995; Parra-Barraza *et al.*, 2003), whereas it is positive in toluene (González *et al.*, 2003) and in nitromethane (Kokal *et al.*, 1995). The magnitude and the sign of the zeta potential of asphaltene dispersed in aqueous solutions can be modified upon the addition of anionic and cationic surfactants (Parra-Barraza *et al.*, 2003). In spite of the reported electrokinetic results, the effect of chemical additives on the zeta potential of asphaltene in aqueous and non aqueous solvents as well as phenomena responsible for the self-aggregation of asphaltene lack of complete understanding.

Other important characteristics as the size and shape of asphaltene have received considerable attention. Size and shape properties of asphaltenes have been reported using several techniques. Transmission electronic microscopy (TEM) provides this information and images of the ordering of asphaltene molecules, resulting in a precise test for establishing the importance the stacking in precipitated asphaltenes. With this method, it has been reported that the asphaltene aggregates are formed by nanometric particles having an average diameter of 50 nm. Agglomeration of these particles can reach diameters from 200 to 550 nm approximately, and in some cases asphaltene particles show a graphitizing tendency; in addition, graphene-like layers having a morphology similar to a cauliflower with an average separation between layers of 39 nm are also found (Perez-Hernandez *et al.*, 2003;

Acevedo, *et al.*, 2008; Trejo *et al.*, 2009; Camacho-Bragado *et al.*, 2002). Also some authors have reported the existence of fullerenes of around 1.4 nm (Mordkovich *et al.*, 2000).

In a recent paper (Salmón-Vega *et al.*, 2009) we have investigated the effect of the addition of ethylene glycol on the electrokinetic behavior of solid asphaltene particles dispersed in aqueous 1.0 mM NaNO₃. We demonstrated that ethylene glycol can affect the charge of asphaltene particles and can help to control the undesired phenomena of asphaltene aggregation and precipitation and contribute to the stabilization of oil-in-water emulsions. In this work we are interested to investigate the effect of the concentration of cationic (cetylpyridinium chloride and dodecylamine) and anionic (sodium dodecyl sulfate) on the electrokinetic behavior of asphaltenes for different pH. Interfacial tension measurements between asphaltene in toluene and ionic surfactants in water were also performed by axisymmetric tensiometry. Asphaltene particles were observed by transmission electron microscopy.

2 Experimental

2.1 Materials

Asphaltene samples were precipitated from a Maya Mexican crude oil (KU-42) provided by the Instituto Mexicano del Petróleo (Mexico City). All chemicals used were reagent grade (Sigma Aldrich, Mexico). Cetylpyridinium chloride, dodecylamine, and sodium dodecyl sulfate were used without any further treatment. The characteristics of the surfactants used are given in Table 1.

Table 1. Description of surfactants used in the present work

Surfactant	Chemical formula	pK_a	Ion	Critical micelle concentration, mM (25 °C)
Cetylpyridinium chloride	C ₂₁ H ₃₈ ClNH ₂ O	—A	RNH ₂ ⁺	0.96 B ^a , 1.03 B ^b
Dodecylamine hydrochloride	C ₁₂ H ₂₅ NH ₃ Cl	≈10.6 C	RNH ₃ ⁺	12.0 C
Sodium dodecyl sulfate	C ₁₂ H ₂₅ O ₄ SNa	< 3 A,D	RSO ₄ ⁻	7.75 A ^a , 7.70 A ^b 8.2 E, 8.D, F ^a

R represents a hydrocarbon chain. ^{a,b} The critical micelle concentration, values obtained by the methods of conductance and microcalorimetry, respectively.

A: Yoon and Jordan (1986); B: Chatterjee *et al.* (2001); C: Laskowski (1999); D: Leja (1982); E: Fuerstenau and Palmer (1976); F: Goddard and Benson (1957)

Sodium nitrate was selected as electrolyte to maintain the initial ionic strength of the dispersion constant because it acts as indifferent electrolyte. Sodium hydroxide or nitric acid solutions were added to adjust the pH. Water used was triply distilled (conductivity around 3 $\mu\text{mhos/cm}$). The pH of the asphaltene dispersions were measured with a Corning pH/ion meter 450 using a Corning high performance combination electrode. All experiments were performed open to the atmosphere at 25 ± 1 °C.

2.2 Extraction of asphaltene from crude oil

Asphaltene was precipitated from crude oil following the ASTM D2007-80 standard method (ASTM, 1983) with some modifications. A mixture of crude oil and n-heptane, 1:40 volume ratio, was hand shaken for 10 min and left during two days at ambient conditions to ensure precipitation of the insoluble asphaltene fraction. After this period, the mixture was centrifuged at 2400 rpm during 10 min. The precipitate was removed from the centrifuge tube with a small amount of n-heptane and subsequently separated from this liquid by vacuum filtration using a membrane filter of 0.45 μm . Asphaltene samples were dried in air, then grounded to fine particles in an agate mortar and stored in air.

2.3 Electrophoretic measurements of asphaltene

The electrophoretic mobility (U , $\text{m}\cdot\text{s}^{-1}/\text{V}\cdot\text{cm}^{-1}$) of asphaltene particles was measured with a Zeta-Meter 3.0+ unit (Zeta-Meter, Inc., New York). Electrophoretic mobility of asphaltene was converted into zeta potential (ζ , mV) automatically by the microprocessor of the Zeta-Meter System using the Smoluchowski equation $\zeta = \frac{4\pi\eta U}{D}$, where η and D are the viscosity and the dielectric constant of the aqueous medium, respectively (Hunter, 1981).

Aqueous dispersions of asphaltene were prepared as follows: First, 5 mg of asphaltene powder was suspended in 100 ml aqueous 1.0 mM NaNO_3 solution. This suspension was sonicated for 1 min in an ultrasonic bath. Then, the dispersion was agitated with a magnetic stirrer and the pH was adjusted to the desired value, the agitation continued during 20 min. For

experiments with ionic surfactants, the required volume of aqueous cetylpyridinium chloride or sodium dodecyl sulfate solution was added after adjusting the pH of the asphaltene dispersion. For the case of dodecylamine hydrochloride solutions, the required volume was added before adjusting the pH of the asphaltene dispersion. After a 20 min conditioning period, the pH of the dispersion was measured and the asphaltene dispersion was transferred to the Zeta-Meter cell. The electrophoretic mobility was averaged with at least 20 different measurements.

2.4 Interfacial tension of asphaltene

Axisymmetric drop tensiometry was used to determine the dynamic interfacial tension measurements at the toluene - water interface with the drops of asphaltene in toluene solutions in the upward direction. The drop was formed at the tip of a stainless steel needle (0.5 mm i.d.) immersed in water at different pH, 1.0 mM NaNO_3 and 0.1 mM concentration of the same surfactants used for electrophoretic measurements. The equipment used was a Tracker tensiometer (I.T. Concept, France) capable of real time surface tension measurements with an accuracy of 0.01 mN/m. The needle is immersed into a quartz cuvette (103.051F-Og, 20-10, Hellma, Germany). The measurement of the interfacial tension is based on the digital profile of the drop image and the solution of the Gauss-Laplace equation. The software used for the axisymmetric drop shape image analysis was the Win Drop software (I.T. Concept, France). Temperature was kept constant at 25 ± 0.1 °C. Asphaltene concentrations used were 0.04 and 0.1 w/w % and was kept constant in all experiments. All measurements were repeated at least three times with an average error of 3 %.

2.5 Transmission electron microscopy (TEM)

Microstructure and morphology of the asphaltene was examined by transmission electron microscopy (TEM) using a JEOL JEM-2010F electron microscope. Asphaltene suspension samples were prepared adding the appropriated amount of wet asphaltene (wet in ethanol), immediately obtained after the mentioned vacuum filtration process. The suspension was sonicated for 5 min in an ultrasonic bath (Branson 2510)

and after this, two drops were sprayed over a copper microgrid for TEM observation, which was put under a high vacuum chamber to eliminate humidity.

3 Results and discussion

3.1 Microstructure and composition

Fig. 1 shows a typical transmission electron microscopy (TEM) image of asphaltene. We observe that asphaltene aggregates are constituted by irregular nanometric particles smaller than 50 nm and these particles build discontinuous aggregates reaching sizes from 200 to 500 nm approximately. The difference in contrast in this image is probably due to superposition of the material, in such a way that in some regions it is observed partial overlapping or piling up of the asphaltenic material. These results are in agreement with the results of Pérez-Hernández *et al.* (2009), who investigated the microstructure and elemental composition of asphaltene, precipitated from Maya crude oil. Dwiggin (1965), Ho and Briggs (1982) and Xu *et al.* (1994) using small-angle X-ray scattering (SAXS), demonstrated the existence of particles with sizes ranging from 3 to 15 nm. Small-angle neutron scattering (SANS) was used by Ravey *et al.* (1988) revealing particle sizes in this same size range. Pederson and Andersen (2000) studied asphaltene from various crudes and found by gel permeation chromatography (GPC) that it is constituted by particles in the size from 5 to 22 nm. In addition, this particles form aggregates of 25 nm approximately, depending on the source of the asphaltene and solvent (Mousavi-Dehghani *et al.*, 2004). The difference in size reported by SAXS, SANS and GPC in contrast with TEM, is probably due to the fact that the former allows particle detection in a wide range of sizes.

The analysis of the chemical spectrum of asphaltene obtained by energy dispersive detector (EDS) is shown in Fig.1a. The asphaltene mass is dominated by carbon, whereas sulphur and oxygen are contained in smaller amounts. These findings are similar to those reported by others investigators (Grijalva-Monteverde *et al.*, 2005). In other works it has been observed that in some cases asphaltene particles show a graphitizing tendency, constituted by carbon atoms arranged in polynuclear aromatic

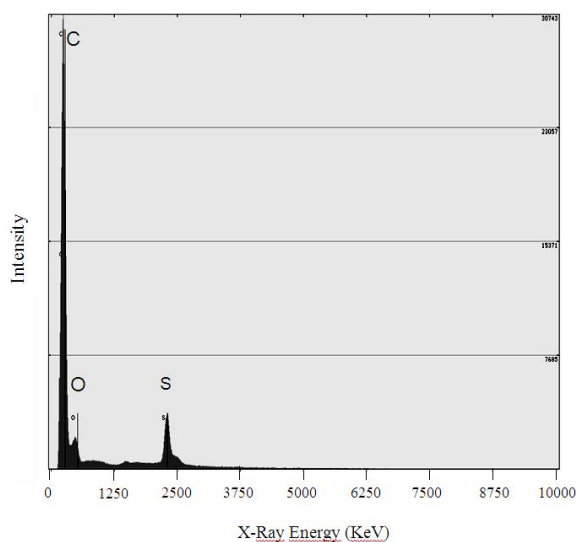
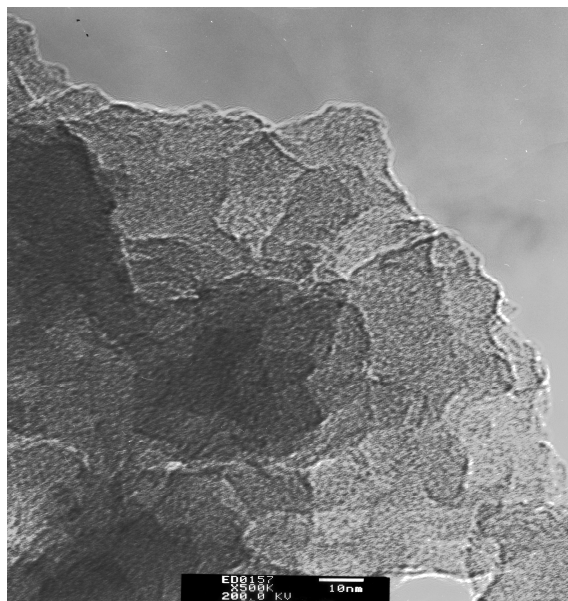


Fig. 1: a) TEM image of asphaltene showing different nanometric aggregates. b) EDS spectrum of asphaltene shows that the mass of asphaltene is mainly constituted by carbon and small quantities of oxygen and sulphur.

hexagonal ring arrays oriented parallel to a crystallographic axis. These arrays form sheets called graphene layers. These arrays, observed by other authors (Perez-Hernandez *et al.*, 2003), could explain the presence of asphaltene layers as can be observed in Fig. 1b.

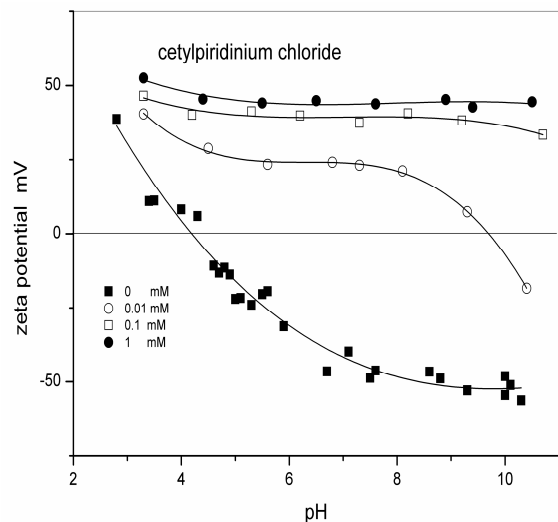


Fig. 2. Zeta potential of asphaltene as a function of pH in 1 mM aqueous NaNO_3 solution, in the absence and presence of cetylpyridinium chloride.

3.2 Effect of pH on the zeta potential of asphaltene

Fig. 2 shows the zeta potential of asphaltene in aqueous solution 1.0 mM NaNO_3 for different pH (dark squares). Sodium nitrate acts as indifferent electrolyte; that is, neither sodium nor nitrate specifically adsorb at the solid asphaltene-aqueous interface (Hunter, 1981; Adamson, 1997). Asphaltene shows an isoelectric point (IEP) at pH 4.5. Below this pH the zeta potential is positive and above this pH the zeta potential is negative up to pH 10.3. The magnitude of zeta potential grows for higher pH values. These results suggest that the surface of asphaltene is positively charged for lower pH values and negatively charged for higher values. The effect of pH on the zeta potential of asphaltene under these conditions can be explained if one considers that the surfaces of this material contain pH-dependent ionizable functional groups (acidic and basic) that can undergo dissociation and protonation (Abraham *et al.*, 2002; Parra-Barraza *et al.*, 2003; Salmón-Vega *et al.*, 2009; Acevedo *et al.*, 1995). Thus, the positive zeta potential of asphaltene might be due to the ionization of basic groups such as amine, amide, pyridine, which have pK_a values > 2 ; whereas the negative zeta potential of asphaltene can be related with the dissociation of acidic functional groups such as carboxylic,

which have pK_a values ≤ 4 (Marczewski and Szymula, 2002; Jada and Salou, 2002). In addition, the protonation of these acid groups may lead to a positive zeta potential in highly acidic solutions. Also, it has been proposed that the structure of asphaltene micelles in solution contains amphiphilic compounds, mainly carboxylic acids (Acevedo *et al.*, 1995). It is speculated that at low pH the asphaltene particles, which are negatively charged, adsorb protons to become neutral or carry a charge close to zero (Kokal *et al.*, 1995). Also it has been suggested that the presence of the IEP at acidic pH indicates a surface exhibiting a high acid character (Chang-Whan and Bernard, 1998). The pH of the IEP of asphaltene in aqueous solutions has been reported to occur at about pH 4.0 in 1.0 mM KCl (Abraham *et al.*, 2002) and in 1.0 mM NaCl (Kokal *et al.*, 1995). In aqueous solutions 1.0 mM NaNO_3 , the IEP of asphaltene has been found to be at about 3.0 (Parra-Barraza *et al.*, 2003).

3.3 Effect of cetylpyridinium chloride (CPCl)

The zeta potential of asphaltene in 1.0 mM NaNO_3 in presence of CPCl is shown also in Fig. 2 as a function of pH. Notice that with a 0.01 mM CPCl concentration, the IEP of asphaltene is shifted from pH 4.5 to 9.7. Below pH 9.7 the zeta potential remains positive and decreases for higher pH values. Above this IEP the zeta potential of asphaltene is negative, but its magnitude is smaller than that without CPCl. When the added CPCl is increased to 0.1 mM the zeta potential of asphaltene is positive in the whole pH range from 3.3 to 10.7, and its magnitude remains practically constant throughout the pH range investigated. In the presence of 1.0 mM CPCl the zeta potential becomes slightly more positive in the pH range from 3.3 to 10.5, but as in the case with 0.1 mM of CPCl, the zeta potential does not change significantly in magnitude. These results indicate both physical and specific adsorption of CPCl in the surface of the asphaltene (Adamson, 1997). Cetylpyridinium cations adsorb on positively charged and uncharged charged asphaltene surfaces by a process that may involve mainly hydrophobic interactions between nonpolar surface sites and the hydrophobic chain of the surfactant cation (Barry *et al.*, 1991). In addition to the hydrophobic interaction,

cetylpyridinium cations seem to adsorb on negatively charged asphaltene by electrostatic attraction. The critical micelle concentration (CMC) of a surfactant in water is determined by the appearance of a break in the variation of some solution property as a function of surfactant concentration; above this threshold, micelles may form (Treiner and Abdelatif, 1992). It is interesting to mention that the CMC obtained for CPCl in aqueous solution at 25 °C was 0.96 mM and 1.03 mM obtained by the methods of microcalorimetry and conductance, respectively (Chatterjee *et al.*, 2001). Therefore, when in our experiments the concentration of CPCl used was 1.0 mM, the micellization process was present. The adsorption via association of nonpolar components between micelles of surfactant and the asphaltene surface probably takes place. These results also indicate that the magnitude of the zeta potentials increases by increasing the surfactant concentration due to increased adsorption of the surfactant at the asphaltene surface, but tend to remain constant near to the CMC. According to the Gibbs equation (Yoon and Yordan, 1986), the surface excess should not increase above a CMC and hence, there should be no further increase in asphaltene the zeta potential.

The electrokinetic behaviour of asphaltene in 1.0 mM NaNO₃, has also been reported by other authors in absence and presence of 0.1 mM CPCl (Parra-Barraza *et al.*, 2003). They found that in the absence of surfactant the asphaltene showed a negative zeta potential in the pH interval from 3 to 10, whereas that in presence of CPCl the asphaltene exhibited positive zeta potential in all the pH interval investigated (Parra-Barraza *et al.*, 2003).

3.4 Dodecylamine hydrochloride (DAH)

The behaviour of the zeta potential of asphaltene dispersed in 1.0 mM NaNO₃ aqueous solution, in the absence and presence of DAH, is shown in Fig. 3 for different pH values. In the presence of 0.01 mM DAH, the IEP of asphaltene shifts from pH 4.5 to 4.8. Below pH 4.8 the zeta potential is positive, above this IEP the zeta potential is negative and its magnitude slightly increases as the pH increases. When the concentration of DAH is increased to 0.1 mM the zeta potential is positive in the pH range from 3.5 to 10, and its

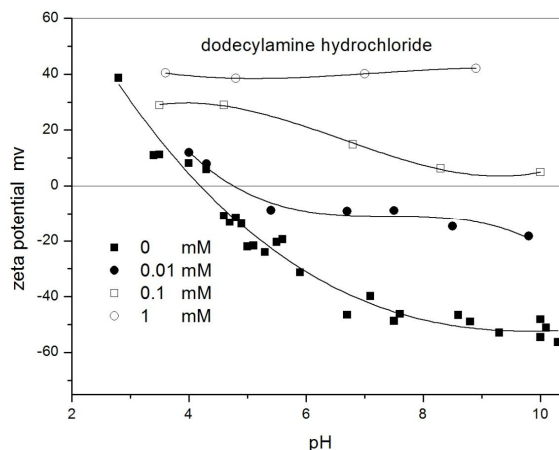


Fig. 3. Zeta potential of asphaltene as a function of pH in 1 mM aqueous NaNO₃ solution in presence of dodecylamine hydrochloride.

magnitude decreases as the pH increases. Finally, with 1.0 mM of DAH the positive zeta potential of asphaltene increases significantly throughout the pH range investigated, but its magnitude tends to remain constant. As in the case of CPCl, the adsorption of DAH cations on asphaltene particles may involve electrostatic as well as hydrophobic interactions depending on the pH.

The hydrolysis plays a more important role when DAH is used in these electrokinetic experiments. In a recent paper (Salmón Vega *et al.*, 2009) we showed the species distribution diagram of the hydrolysis products as a function of pH using different concentrations of DAH; these results are also shown by Yoon and Yordan (1986). There can be observed that for 0.1 mM concentration of surfactant, the concentrations of charged species such as RNH₃⁺, (RNH₃⁺)₂²⁺, and RNH₂–RNH₃⁺ decrease above pH 10.2, while the neutral species, i. e., RNH₂, becomes predominant above this pH. The decrease in the zeta potential as the pH increases may be attributed to the adsorption of neutral hydrolysis products on the asphaltene surface, affecting the zeta potential. However, other mechanisms also may be present.

Some researchers have found that the primary alkylamines are hydrolyzing surfactants with pKa values in the range 10-11 (Barry *et al.*, 1991). They behave as normal cationic surfactants at pH below about but in the range 9-10, while the surface tension of their aqueous solutions passes through a minimum (Castro *et al.*, 1986).

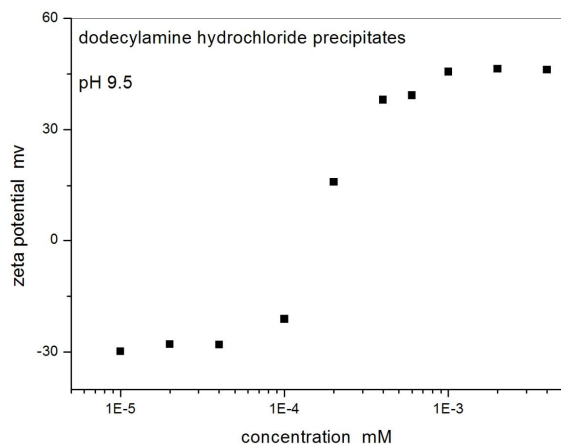


Fig. 4. Zeta potential of dodecylamine hydrochloride colloidal precipitates in aqueous solutions and 1.0 mM NaNO_3 .

This is probably due to a synergism between the cationic aminium ion and the neutral amine similar to the behaviour of the other cationic-nonionic surfactant mixture.

The effect of the pH on the CMC of DAH was investigated by Castro *et al.* (1986). Since the CMC for DAH is 12.0 mM, the concentration used in this work is far below the critical micelle concentration. Therefore in the acidic pH range, the used solutions contain only dodecylamine ions. Free dodecylamine molecules appear in the solution when the pH is increased and solubilization of such molecules into mixed micelles reduces the value of the CMC. Around pH 8, mixed micelles containing both dodecylamine ions and dodecylamine molecules are formed, and around pH 9 phase separation is observed and precipitate appears.

In previous investigations (Dai and Laskowski, 1991), it has been reported that the CMC for solutions of these surfactants decreases from 12.0 mM at pH 5 to 0.3 mM to pH 9. In addition, in the alkaline pH range a colloidal precipitate appears whenever the solubility limit is exceeded. We measured zeta potential of such a precipitate and determined its electrokinetic behaviour. The zeta potential for DAH at different concentrations is shown in Fig. 4. The results are similar to those reported by others researchers (Laskowski *et al.*, 1988). In agreement with the obtained results of zeta potential for dodecylamine precipitates in the range from pH 8 to 10 and especially at higher concentrations (1.0 mM), dodecylamine particles

appear in the solution and precipitate onto the asphaltene surface.

Although the solubility limit for dodecylamine is the 0.02 mM (Janusz and Laskowski, 1999) it has been reported that the precipitation of amine at gas/liquid or solid/liquid interface takes place at much lower concentrations (Laskowski *et al.*, 1989). Ravishankar and Yoon (1995) detected precipitation of dodecylamine at a mica/water interface at 0.005 mM. Electrophoretic studies indicate that the mechanism of interaction between DAH and asphaltene depends strongly of pH and the surfactant concentration.

It has been reported that the zeta potential of bubbles, obtained by using different concentrations of CPCl solutions, is independent of pH, while the zeta potential of bubbles obtained by using DAH is not (Yoon and Yordan, 1986). The reason for this is that, unlike CPCl, DAH is hydrolyzable at alkaline pH values.

Joy and Watson (1964) combined adsorption measurements of DAH on hematite. By using vacuum flotation data and a titration technique, they designed experiments to determine the number of positive and negative sites on hematite in order to study the mechanism of the cationic flotation of this mineral. An important finding was that at pH values below the IEP and at concentrations of DAH greater than 0.01 mM, the quantity of amine adsorbed was much greater than could be accounted for by attachment of amine ions at negatively charged sites. One explanation given was the possibility of an exchange of amine ions for H^+ at these acidic pH values and overall positive mineral charge.

According to the results of zeta potential of asphaltene in presence of the cationic surfactants investigated we can conclude that DAH is less effective than CPCl for reversing the sign of the zeta potential of asphaltene. The longer alkyl chain length of CPCl (16 carbon atoms) may contribute to a more favorable adsorption. The fact that the adsorption of these cationic surfactants to asphaltene particles successively increases with increasing the tail length from C12 to C16, can be explained by an increment of the hydrophobic interaction between the nonpolar surface sites of asphaltene and the hydrophobic tail of CPCl molecules.

Although the higher hydrophobic interaction can be related with the electrokinetic behavior of asphaltene in presence of CPCl, a "hemimicelle"

like process can occur. According with this process, as long as the adsorption density increases, the adsorbed surfactant cations begin to associate through lateral interaction of their hydrocarbon chain (Fuerstenau and Herrera-Urbina, 1991) and under this conditions the zeta potential can become positive because there are more cations in the Slater layer than negative charges at the asphaltene surface. Then, the counterions adsorbed in the Slater layer would consist mainly of ions constituting the hemimicelle and the counterions in the diffuse layer would be chloride ions.

3.5 Effect of sodium dodecyl sulphate (SDS)

SDS belongs to the family of anionic surfactants and it dissociates (ionizes) completely in aqueous solutions above $\text{pH} \sim 3$ (Yoon and Jordan, 1986; Leja, 1982), which means that under the conditions used in this research work, the SDS anion predominates in solution. The zeta potential of asphaltene in 1.0 mM NaNO_3 solution, with and without SDS, is shown in Fig. 5 for different pH values. In the presence of 0.1 mM of SDS no IEP is found since all the zeta potential values of asphaltene are negative in the pH range from 3.1 to 9.7, although small changes were found at pH values higher than 7.5. When the concentration of SDS is increased from 0.1 mM to 1.0 mM, the negative zeta potential is slightly more negative in the pH range between 3.1 and 7.5. Above this pH, the negative zeta potential remains virtually unchanged. This electrokinetic behaviour indicates specific and physical adsorption of SDS onto the asphaltene surface aggregates. Below pH 4.5, which is the IEP of asphaltene in the absence of surfactant, SDS molecules are first attracted to the positively charged sites of asphaltene surface by electrostatic interaction. The larger adsorption around the IEP is probably due to suppressed electrostatic repulsion between the asphaltene molecules; therefore the adsorption of SDS is favored by other interactions. Adsorption of a surfactant ion on a similarly charged surface, which will repel the ion, can be explained considering the interaction of the hydrocarbon chain of the surfactant with a hydrophobic surface site. SDS adsorption on asphaltenes, whose surfaces contain polar and non polar sites, may therefore involve mainly a

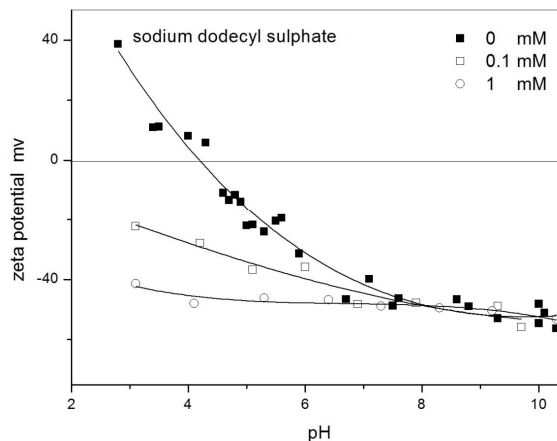


Fig. 5. Zeta potential of asphaltene as a function of pH in 1 mM aqueous NaNO_3 solution, in presence of sodium dodecyl sulfate.

hydrophobic mechanism. Above pH 7.5 changes in the zeta potential of the asphaltene are not observed in presence of SDS, probably due to the electrostatic repulsion between the negative charged SDS head and the negative asphaltene surface, which could be large enough to prevent them from associating in this region.

According to Chatterjee *et al.* (2001), the CMC concentration for SDS is 7.75 mM; therefore with the surfactant concentrations used here, micelles of SDS are not formed and the surfactant molecules exist in solution as monomers and dimers. Studies of the adsorption of SDS onto a hydrophobic C_{18} monolayer revealed that more SDS molecules are adsorbed below the CMC than above the CMC. The reason why this unusual behavior occurs is not understood. The structural arrangement of the adsorbed SDS might provide some insight into the nature of the anomalous adsorption below the CMC (Piasecki, 1994). This explanation can be related with the adsorption of SDS onto the asphaltene surface.

Previous electrokinetic investigations with asphaltenes coming from Mexican Petroleum reported similar results with the dispersed asphaltene in aqueous solution 1.0 mM sodium nitrate in absence and in presence of 1.0 mM SDS in the interval of pH from 3 to 10, approximately (Parra-Barraza *et al.*, 2003). Also electrokinetic characterizations of emulsions have been performed with oil in water emulsions in 10.0 mM NaCl in absence and presence of 0.001 mM to 0.1 mM of SDS. In the absence of surfactant the

oil drops present negative zeta potential. With the addition of SDS, the oil drops exhibit a more negative zeta potential than in absence of this surfactant, which increases the stability of the emulsion with stronger electrostatic repulsion between drops (Stalidis, 1990).

3.6 Interfacial tension of asphaltene at the toluene - water interface

Complementary interfacial tension experiments were performed at the interface between asphaltene in toluene and water at different pH and 0.1 mM surfactant concentration. We used the same surfactants used for the zeta potential measurements. In Fig. 6 we show the behaviour of the interfacial tension of two different asphaltene concentrations at the toluene - water interface at different pH. The asphaltene concentration of 0.04 wt % was chosen far from the asphaltene CMC and the 0.1 wt % was chosen near the CMC (around 0.2 wt %). The behaviour of the surface tension for the 0.1 % asphaltene concentration is very similar to the results found by Rodríguez-Abreu *et al.* (2006) and other researchers (Sheu *et al.*, 1992; Poteau *et al.*, 2005) using a 0.5 wt % solution of asphaltene in toluene. They obtained even a larger reduction of the interfacial tension for pH 12 and 13 produced probably due to the dissociation of the carboxylic groups of asphaltenes at higher pH, which is known to increase the asphaltene surface activity (Gundersen *et al.*, 2001; Xia *et al.*, 2004).

On the other hand the behaviour of the 0.04 wt % asphaltene concentration is interesting. This concentration is away of the CMC of our asphaltene. We observe that for low and high pH solutions, the interfacial tension values are higher than the ones for the 0.1 wt % concentration. This could be a predicted behaviour as also was demonstrated by Rodríguez-Abreu *et al.* (2006) at pH 11. This simply means that a higher asphaltene concentration favours the hydrophobicity at the toluene - water interface and also higher OH⁻ and H⁺ ion concentrations contribute to the asphaltene surface activity. However, the interfacial tension of 0.04 wt % asphaltene in the range of pH between 5 and 7 is lower than the one for asphaltene near the CMC concentration. This is probably due to the relative small concentration of ions at the interface, allowing the neutral and more

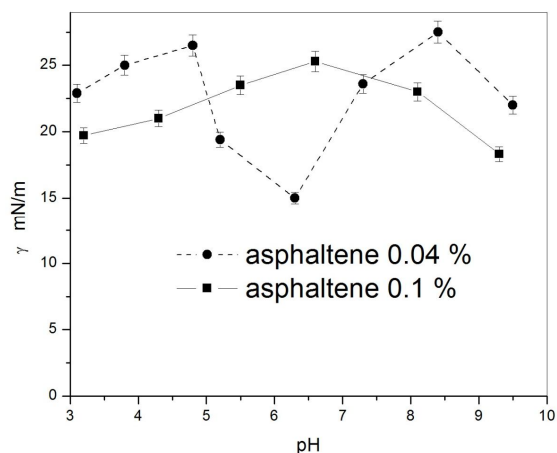


Fig.6 Interfacial tension of asphaltene 0.04 and 0.1 wt % at the toluene-water interface for different pH. Temperature was kept at $25 \pm 0.1^\circ\text{C}$.

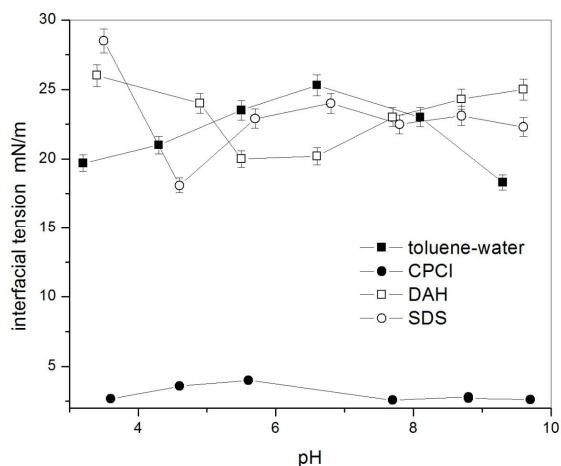


Fig. 7 Interfacial tension of asphaltene 0.1 wt. % in toluene and different surfactants (0.1 mM) in the aqueous phase for different pH. Temperature was kept at $25 \pm 0.1^\circ\text{C}$.

hydrophobic asphaltene groups to remain at the toluene - water interface and decreasing the interfacial tension.

In Fig. 7 we observe the interfacial tension behaviour of asphaltene in toluene and water at different pH and in presence of 0.1 mM concentration of the ionic surfactants used for the zeta potential measurements. A very strong asphaltene - CPCI interaction on the interface is observed by lowering the interfacial tension to around 2-3 mN/m, almost independent of pH. As mentioned before, this surfactant interacts at the asphaltene-water interface in both acidic

and alkaline environments, producing an almost constant and positive zeta potential. On the other hand, the interfacial tension when SDS and DAH are added to the aqueous phase is more sensible to the pH of the solutions. Notice that for pH in the ranges 3-5 and 8-9.6, both surfactants increase the interfacial tension in comparison with the surface tension of asphaltene without surfactants in the aqueous phase. This would corroborate again the observations of Rodríguez-Abreu *et al.* (2006) and others (Sheu *et al.*, 1992; Poteau *et al.*, 2005) in the sense that even when surfactants are present at the interface and modify the zeta potential of asphaltene, pure asphaltene at the toluene-water interface is more hydrophobic at these pH values. On the contrary in the pH range of 5-8 where the interface is relative less charged, the interfacial tension of asphaltene without SDS or DAH in the aqueous phase is higher than the surface tension with these two surfactants in the aqueous phase. In this case the hydrophobicity of the interface is slightly enhanced by the interaction of the SDS and DAH surfactants, independent of the sign of their charge.

Conclusions

In this work we have demonstrated the effect of concentration of some ionic surfactants on the zeta potential of asphaltene particles for different pH. We observed that for a surfactant concentration around 0.1 mM, the zeta potential of asphaltene remains positive for both cetylpyridinium chloride and dodecylamine hydrochloride. Similar behaviour was obtained for 0.1 mM of sodium dodecyl sulphate, keeping the zeta potential negative in the whole range of pH analyzed. This means that we could control the sign of the electrical charge of asphaltene in the range of pH investigated. For all surfactants used, the concentration of 1 mM seemed to be enough to keep the zeta potential nearly constant. TEM showed that asphaltene is constituted by irregular and discontinuous aggregates between 200 and 500 nm, and each aggregates is constituted by aggregates smaller to 50 nm. The results of the interfacial tension of asphaltene in toluene and the ionic surfactants in the aqueous phase showed that asphaltene alone interacts strongly at the toluene - water interface for low and high pH, and the presence of dodecylamine hydrochloride or sodium

dodecyl sulphate does not provoke the decrement of interfacial tension; on the contrary they increase the surface tension. However, in the relative neutral region of pH 5-8 we found that these surfactants slightly decrease the interfacial tension of asphaltene at the toluene - water interface. A different behaviour was found for the effect of the cationic surfactant cetylpyridinium chloride. In this case the interfacial tension decreased significantly to 2-3 mN/m almost independently of the pH, probably due to both electrostatic and hydrophobic higher interactions with asphaltene in comparison with the effect of dodecylamine hydrochloride and sodium dodecyl sulphate.

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