

Effect of the Addition of Water-Soluble Polymers on the Structure of Aerosol OT Water-in-Oil Microemulsions: A Fourier Transform Infrared Spectroscopy Study

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Using Fourier transform infrared (FT-IR) spectroscopy and electrical conductivity measurements, the study of water-in-oil (w/o) microemulsions of Aerosol OT dissolved in toluene with different water contents, in the absence and in the presence of poly(vinylpyrrolidone) (MW 10 000), PVP K15, and poly(sodium 4-styrenesulfonate) (MW 75 000), PSS, has been carried out. Conductivity measurements show attractive interactions between droplets of w/o microemulsions without polymers containing high water contents, $w_0 \geq 25$. The addition of polymers prevents these interactions even at the lowest polymer concentration used in this work, 2%. From FT-IR spectra different micellar structures were detected in the absence of polymers, and vibrational modes of the surfactant molecule allow structural information to be obtained of each kind of aggregate. The structure of each kind of aggregate has a great dependence on the water content. Infrared spectra of the surfactant molecule of microemulsions containing different concentrations of PVP K15 and PSS were also recorded. The comparative analysis of these spectra with those in the absence of polymers permits, in a first place, localization of the polymer in the aqueous core and, later, study of the structural changes induced by the addition of these polymers.

Introduction

The reverse micelles and the w/o (water-in-oil) microemulsions modified by addition of water-soluble polymers are routinely used in synthesis of microparticules,¹ polymerization and separation processes,² and oil recovery.³ However, there is not enough information about the polymer–surfactant interaction or about the effects of the polymer on the droplet structure, size, and shape. Most of the works have studied these microemulsions in the domain of the gel formation using the gelatin agents,^{4–6} but a better understanding of such systems requires modified conditions of formation for these microemulsions, i.e., varying the kind of polymer, the polymer content, or the water composition.

Therefore, the aim of this work is to obtain structural information of the w/o microemulsion perturbed by the addition of two different water-soluble polymers, poly(vinylpyrrolidone), PVP K15 (MW 10 000), and poly(sodium 4-styrenesulfonate), PSS (MW 75 000). The water-in-oil microemulsion was made using bis(2-ethylhexyl) sodium sulfosuccinate, Aerosol OT, AOT, as surfactant and toluene as solvent. The water content, given as water–surfactant ratio, $w_0 = [\text{H}_2\text{O}]/[\text{S}]$, was modified between $w_0 = 0.34$ and $w_0 = 35$. The polymer content, expressed as polymer–water fraction in weight, $R = w_p/w_{\text{water}}$, was also modified in the range 2–20% (w:w). Particularly, the specific objectives of the investigation are to study the effect of the addition of these polymers on the structure of the water pool, on the rotational isomerism, and on the chain packing of the Aerosol OT molecule into aggregates.

To obtain this information, FT-IR spectroscopy has been used. This technique is noninvasive, functional group selective, and particularly suitable to detect the changes of the microenvironmental properties, and it has been used by others authors to study the structure of some nonperturbed w/o microemulsions.^{7–10} In particular, we discuss the spectrum of the water of the micellar core, *water pool*, the skeletal hydrocarbon bands of the surfactant molecule, and the carbonyl and sulfonate vibrational modes of the surfactant head group. The comparative analysis of spectra corresponding to microemulsions with and without polymers, allows structural information to be obtained of these new microemulsions and of the effects of changes on the water and polymer contents.

On the other hand, in nonperturbed w/o microemulsions attractive interactions between droplets have been detected at high values of w_0 .¹¹ In general the addition of water-soluble polymers decreases these interactions,^{12,13} whereas oil-soluble polymers increase them.¹² It is known that electrical conductivity measurements can be used to predict qualitatively the interaction between droplets. w/o microemulsions exhibit a small conductivity as water droplets are separated by the surfactant layers; however, when the water content increases beyond a certain critical value, the conductivity increases sharply. These conductivity values have been related with an increase of attractive interactions, because these interactions produce an increase of the lifetime of two or more associated droplets which facilitate the migration of the surfactant counterions along connected paths through the microemulsions, leading finally to the electrical percolation phenomenon.^{11–13} Therefore, in order to know the effect of the addition of PVP K15 and PSS on the interactions

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(1) Arriagada, F. J.; Osseo-Asare, K. *J. Colloid Interface Sci.* **1995**, 178, 8.

(2) Sheu, E.; Goklen, K. E.; Hatton, T. A.; Chem, S. H. *Biotechnol. Prog.* **1987**, 4, 175.

(3) Caponetti, E.; Lizzio, A.; Triolo, R.; Compere, A. L.; Griffith, W. L.; Johnson, J. S. *Langmuir* **1989**, 5, 357.

(4) Rees, G. D.; Robinson, B. H. *Adv. Mater.* **1993**, 5, 608.

(5) Quellat, Ch.; Eicke H. F.; Gehrke, R.; Sager, W. *Europhys. Lett.* **1989**, 9, 293.

(6) Petit, G.; Zemb, Th.; Pilani, M. P. *Langmuir* **1991**, 7, 223.

(7) Mac Donall, H.; Bedwell, B.; Gulari, E. *Langmuir* **1986**, 2, 704.
(8) Jain, T. K.; Varshney, V.; Maitra, A. *J. Phys. Chem.* **1989**, 93, 7409.

(9) Onori, G.; Santucci, A. *J. Phys. Chem.* **1993**, 97, 5430.

(10) Morán, P. D.; Bowmaker, G. A.; Coeney, R. P. *Langmuir* **1995**, 11, 738.

(11) Van Dijk, M. A.; Castelein, G.; Joosten, J. G. H.; Levine, Y. K. *J. Chem. Phys.* **1986**, 85, 626.

(12) Suárez, M. J.; Levy, H.; Lang, J. *J. Phys. Chem.* **1993**, 97, 9808.

(13) Suárez, M. J.; Lang, J. *J. Phys. Chem.* **1995**, 99, 4626.

between droplets, electrical conductivities of all w/o microemulsions were determined.

Experimental Section

Materials. Bis(2-ethylhexyl) sodium sulfosuccinate, Aerosol OT, AOT, was purchased from Fluka. It was purified according to the published method.¹⁴ After the sample was dried, some water molecules remain bound to the surfactant. The analysis of the water concentration of the stock solution of AOT in toluene with a Karl-Fisher titrator revealed the presence of 0.34 mol of residual water/mol of surfactant. This water content was taken into account for the calculation of the w_0 ratio. Toluene, spectroscopic grade from Fluka, was stored in sodium.

The samples of PVP K15 (Fluka) and PSS (Aldrich) had molecular weight of 10 000 and 75 000 g/mol, respectively, provided by the manufacturers.

Methods. Reverse micelles and w/o microemulsions were prepared by adding the appropriate amount of water to a stock solution of 0.08 mol dm⁻³ of AOT in toluene and stirring until the solution became transparent. In the presence of polymers, aggregates were prepared by adding the appropriate volume of a concentrated aqueous polymer solution to a steady w/o microemulsion and stirring until all the polymer was incorporated to the micellar core, and the solution became transparent. All microemulsions were stable at least for several months.

To study the effect of the composition on the structure of the microemulsion, the water and the polymer contents have been systematically modified. All the spectra were recorded at 25.0 °C.

Spectroscopy. Infrared absorption spectra were recorded with a Perkin-Elmer 1730 FT-IR spectrophotometer. A spectral range of 4000–1000 cm⁻¹ and an effective resolution of 2 cm⁻¹ was used. In order to obtain a good quality of the spectra, a minimum of 20 scans were accumulated. Due to the high quality of the spectra, no smoothing has been necessary. A cell of CaF₂ windows of variable path length has been used. The path length was around 0.0675 mm and was determined with the interference fringes method.¹⁵ In all cases the bands of toluene have been subtracted.

In order to quantify the components of the hydroxyl and carbonyl stretching bands and their changes with water and polymer contents, spectra have been subjected to a deconvolution process in Gaussian bands. The deconvolution procedure used considers the spectral contour as composed of a number N of Gaussian bands, allowing an expression of the absorbance $A(\nu)$ as a function of the frequency, ν , in the following way:

$$A(\nu) = \sum A_i(\nu) \exp\{-\ln 2[(\nu - \nu_i)/\delta_i]^2\}$$

where A_i is the maximum absorbance at each band central frequency, ν_i , and δ_i is the half-width. The fit process has been carried out with a computer program developed in this laboratory.¹⁶

Conductivity Measurements. The electrical conductivity was measured using a CDM 83 (Radiometer, Copenhagen) conductometer and a low-conductivity cell. The cell constant was calibrated with solutions of KCl of a known concentration.¹⁷

Results and Discussion

Electrical Conductivity Measurements. Figure 1 shows the variation of the specific electrical conductivity, κ , as a function of the water concentration, for nonperturbed w/o microemulsions and for microemulsions composed of AOT in toluene containing two different polymer contents, given as polymer–water fraction in weight: 3% of PVP K15 and 2% of PSS.

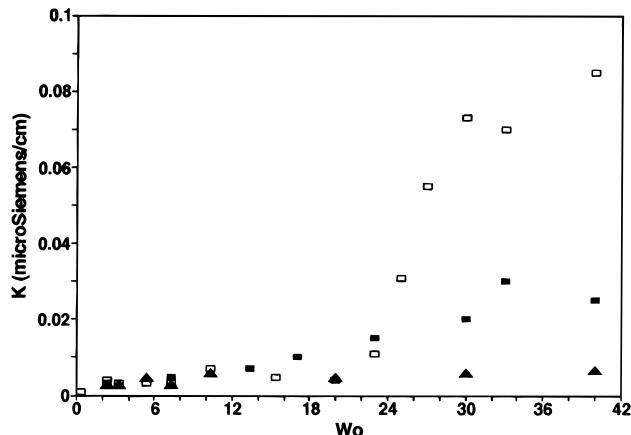


Figure 1. Variation of the electrical conductivity with the water content of the following w/o microemulsions: □, AOT/toluene 0.08 M; ▲, AOT/toluene 0.08 M 2% PSS; ■, AOT/toluene 0.08 M 3% PVP K15.

In the absence of polymers, the specific conductivity increases until a w_0 value of 25. At a greater water content a sharp increase of the conductivity is observed. These results may show the presence of attractive interactions between droplets of w/o microemulsions with water content higher than 25.

In the presence of PVP K15 and PSS the specific conductivity also increases as w_0 ; however, it does not increase sharply in the whole range of w_0 studied. This behavior is observed at all polymer contents used in this work. The results may indicate that the presence of polymers prevents attractive interactions between droplets and are consistent with data in literature.^{12,13} The origin of this behavior was explained in other microemulsions assuming that the addition of water-soluble polymers decreases the droplet size, decreasing the interpenetration of the interfacial layer of two colliding droplets and, as consequence, the attractive interactions.¹²

Infrared Spectroscopic Study of the Structure of w/o Microemulsions in the Absence of Polymers. The following section deals with the infrared spectra of Aerosol OT aggregates containing different polymer compositions in comparison with those of nonperturbed aggregates. Therefore, in first place it is necessary to discuss the spectra of microemulsions without polymer. These spectra are discussed in this section.

The following regions of infrared spectra of AOT aggregates in toluene with different water contents have been examined: (a) the OH stretch band, 3100–3700 cm⁻¹; (b) the carbonyl stretching region, 1700–1750 cm⁻¹; (c) the sulfonate stretching region, 1210–1245 cm⁻¹; (d) the CH wagging and scissoring bands, 1100–1500 cm⁻¹.

The Water Bands. The OH stretching band is an asymmetrical band that can be fitted to a minimum of four Gaussian functions centered around 3321, 3450, 3550, and 3635 cm⁻¹, with half-widths of 65, 80, 60, and 45 cm⁻¹ respectively. Results for the resolved spectra are shown along with the experimental data in Figure 2. The low-frequency peak is due to the OH stretch in a hydrogen-bonded polymeric chain.¹⁸ The 3450 cm⁻¹ peak is assigned to the hydrogen-bonded dimers bound at the interface.¹⁸ The 3550 cm⁻¹ band has been assigned to the stretch of non-hydrogen-bonded water molecules which have penetrated into the surfactant layer,⁷ and the high-frequency

(14) Menger, F. M.; Yamada, K. *J. Am. Chem. Soc.* **1979**, *101*, 6731.
(15) See for example: Skoog, D. A.; Leary J. J. In *Principles of Instrumental Analysis*, 4th ed.; Saundier Coll. Pub.: New York, 1992; p 274.

(16) González-Hierro, P.; Velázquez, M. M.; Cachaza, J. M.; Rodríguez, L. J. *J. Pharm. Biomed. Anal.* **1987**, *5*, 395.

(17) Lind, J. E.; Zwolenik, J. J.; Fuoss, R. M. *J. Am. Chem. Soc.* **1959**, *81*, 1557.

(18) D'Aprano, A.; Lizzio, A.; Turco Livery, V.; Aliotta, F.; Vasi, C.; Migliardo, P. *J. Phys. Chem.* **1988**, *92*, 4436.

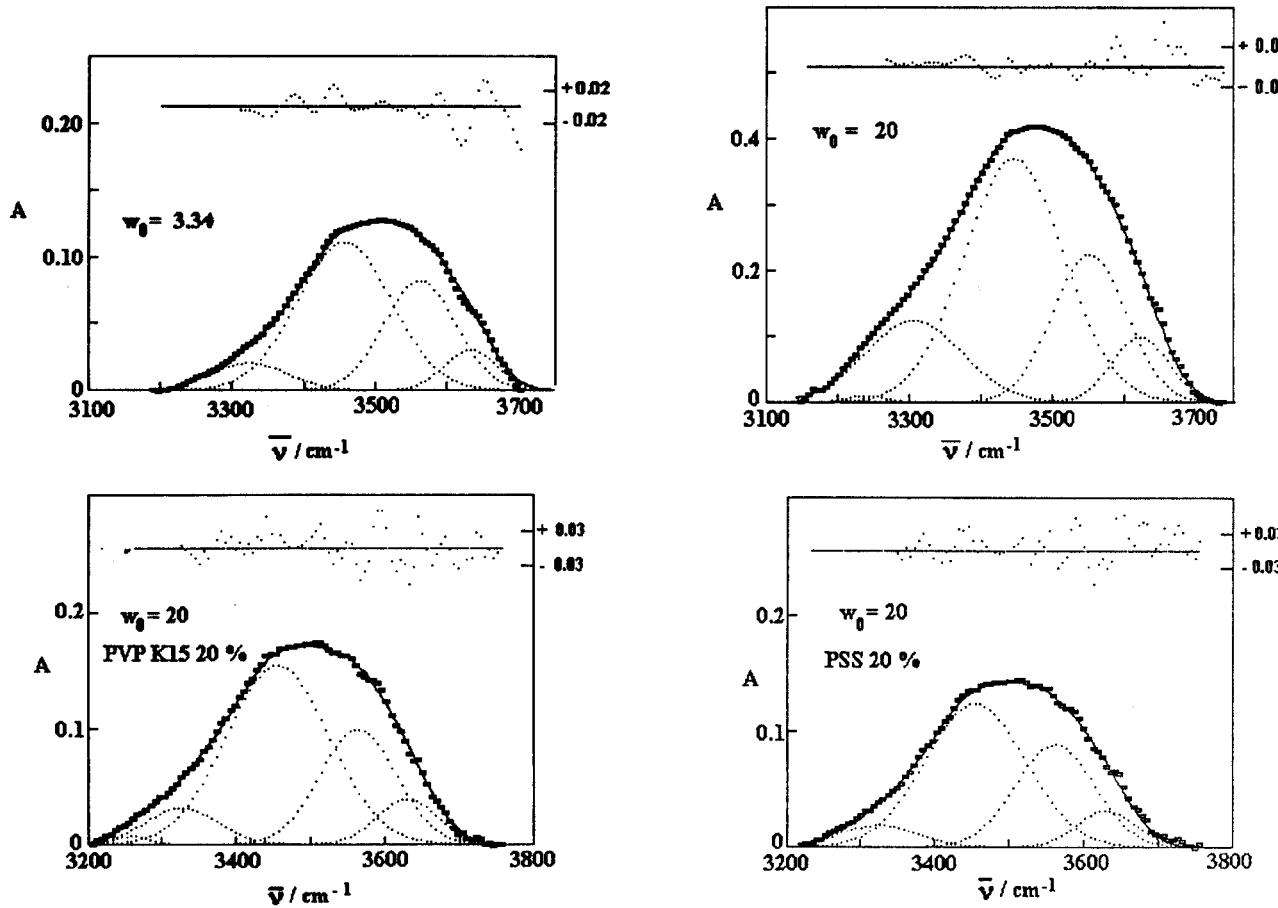


Figure 2. Deconvolution of OH stretching vibration band of water contained in w/o microemulsions at selected water and polymer contents. Dotted lines are Gaussian component bands and the full line is the calculated spectrum contour. Upper line is the absolute deviation from experimental line.

peak at 3635 cm^{-1} is ascribed to monomeric water observed in pure water.¹⁹

These results differ from those obtained for AOT microemulsions dissolved in heptane, carbon tetrachloride, and isoctane by other authors,⁷⁻⁹ in that four Gaussian peaks are obtained in the deconvolution process of the OH stretching band, whereas only three Gaussian bands have been detected in other w/o microemulsions. The presence of four kinds of water molecules has not been detected by infrared spectroscopy by other authors; however, by using a variety of physical techniques, such as NMR, electron spin resonance spin labeling, or differential scanning calorimetry, several types of bound water species have been detected.²⁰ It seems that IR spectroscopy reveals only some of different kinds of the microemulsion water molecules.

In our case, the fourth Gaussian peak is centered around 3550 cm^{-1} . This band was observed in AOT microemulsions⁷ and has been ascribed to the OH stretching of monomer water molecules at the interface. The presence of two types of water molecules at the interface, monomers and dimers, may be attributed to the different hydration shells corresponding to the sulfonate surfactant group and sodium counterion.²⁰

These results are consistent with the three-state model proposed by Tamura²¹ and Goto.²² In this model, water exists in three phases: the phase s_1 , is the water at the

interface; the phase b , is the water existing in the core, and the third phase, existing between the b and the s_1 phases, is called phase s_2 .

The spectroscopic data obtained in this work for AOT in toluene may indicate that in the phase s_1 , interfacial water, two different water molecules, dimers and monomers, are incorporated; the phase b is formed by monomer water molecules inside the aqueous core, and the s_2 phase is formed by a structured hydrogen-bonded polymeric chain water shell between b and s_1 phases. These results are also consistent with theoretical molecular dynamics studies of the stucture and dynamics of water in the vicinity of a charged biomembrane.²³

The total peak area of the OH stretching increases with w_0 , but this increase is different for each water species. To better detect these differences, fractions of each water species, P_i , have been calculated from the area of each Gaussian with respect to the total peak area, assuming that the total area is the sum of the area of the distinct states of water.⁸ Fractions of water species cannot be precisely calculated from the integrated area of the vibrational band, as no coupling effects have been considered.²⁴ However, we use these values for comparative purposes as a measure of the relative abundance of the different species.

Plots of P_i vs w_0 in Figure 3 show that polymeric chain bonded water molecules increase with the increase of the

(19) Tso, T. L.; Lee, E. K. C. *J. Phys. Chem.* **1985**, *89*, 1612.
(20) Hauser, H.; Haering, G.; Pande, A.; Luisi, P. L. *J. Phys. Chem.* **1989**, *93*, 7869.

(21) Tamura, T.; Schelly, Z. *J. Am. Chem. Soc.* **1981**, *103*, 1018.
(22) Goto, A.; Yoshiota, H.; Kishimoto, H.; Fujita, T. *Langmuir* **1992**, *8*, 441.

(23) Bopp, P. In *Intermolecular Forces: An Introduction to Modern Methods and Results*; Huyskens, P. L., Luck, W. A. P., Zeegers, T., Eds.; Springer-Verlag: Berlin, 1991; Chapter 14.

(24) Zeegers-Huyskens, T. In *Intermolecular Forces: An Introduction to Modern Methods and Results*; Huyskens, P. L., Luck, W. A. P., Zeegers, T., Eds.; Springer-Verlag: Berlin, 1991; Chapter 6.

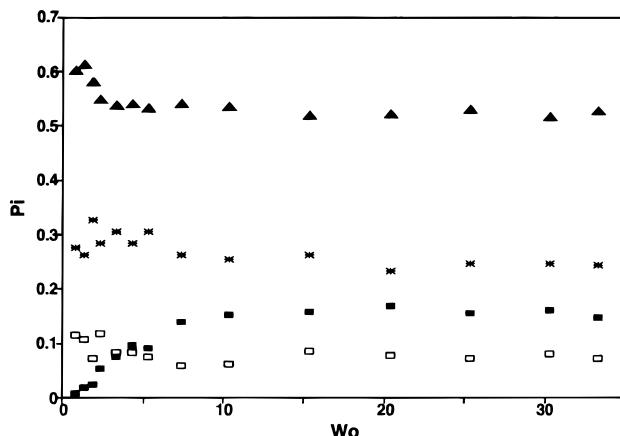


Figure 3. Variation of fractions of the different kinds of water molecules with the water–surfactant ratio, w_0 : ■, polymeric chain bonded; ▲, dimers at the interface; *, monomers at the interface; □, free monomers.

water content until $w_0 = 7$. At higher w_0 values this fraction reaches a constant value. For dimer and monomer molecules at the interface and for the monomer molecules inside the water pool, the behavior is reversed. At a water content lower than 7, the fraction of these kinds of water molecules decreases with the water content, but for values higher than 7, the fraction remains constant.

This is consistent with microstructural changes in micellar aggregates. At the lowest water contents, $w_0 \leq 3$, aggregates have a low aggregation number,²⁵ and water molecules are highly immobilized due to a strong electrostatic interaction between the counterion and the surfactant head group,²⁰ so the fraction of water dimers at the interface is higher, ≈ 0.6 . At $w_0 \geq 3$, fractions of dimers and monomers at the interface decrease. This fact is associated to the growth of micellar aggregates, probably due to the decrease of the electrostatic interaction between the ions at the interface. Simultaneously, the size of the structured shell increases with the total water content until reaching a w_0 value of 7, where swollen reverse aggregates are predominant, and the fraction of all kinds of water molecules remains constant.

It must be noted that when attractive interactions between droplets are predominant ($w_0 > 25$), no significant changes are detected on water molecule bands as compared to the corresponding ones observed in swollen reverse micelles. This fact may indicate that interactions between droplets do not modify the structure of the water pool of these microemulsions.

The Carbonyl Bands. The carbonyl group of the Aerosol OT molecule gives rise to a strong asymmetric infrared band. This band was fitted to a sum of two Gaussian functions centered around 1737 and 1720 cm^{-1} , with half-widths of 8.2 and 9.3 cm^{-1} , respectively. Figure 4 shows some of these resolved spectra. These bands correspond to different conformations about the acyl bond of the succinate backbone. The band centered around 1737 cm^{-1} has been assigned to the *gauche* conformation and the band centered around 1720 cm^{-1} to the *trans* conformation.^{8,10,26} The *trans* conformation is related with a weak interaction between the sodium cation and the carbonyl group.¹⁰ Fractions of each conformer, corresponding to microemulsions with different water contents, have been calculated from the area of each Gaussian with respect to the total area. Results show that both fractions of *gauche* and *trans* conformers remain constant in the

whole range of w_0 studied. This fact may indicate that the addition of water does not modify the interaction between the sodium cation and the carbonyl group, even when the interaction between droplets takes place. The fraction of the *gauche* conformer (63%) is always greater than the fraction of the *trans* conformer (27%).

The Sulfonate Bands. The infrared spectrum of the surfactant sulfonate group is composed of a band centered around 1050 cm^{-1} attributed to a symmetric stretching mode and of a doublet centered around 1212 and 1242 cm^{-1} , ascribed to the antisymmetric stretching mode. The position of the band corresponding to the symmetric stretching mode and the splitting of bands corresponding to the doublet have been related to the separation between the sodium ion and the sulfonate group and between the adjacent sulfonate groups.¹⁰ The increase in the separation between these ions is accompanied by a shift lowering the wavenumber of the symmetric stretching mode band and simultaneously by the decrease of the splitting of bands ascribed to the antisymmetric mode.¹⁰

The variation of the maximum of the symmetric sulfonate stretching band of AOT in toluene with respect to w_0 is plotted in Figure 5. Results presented in this figure show that this band is shifted from 1051 to 1047 cm^{-1} as the water content increases until reaching a w_0 value around 3–4. At higher w_0 values the band position remains constant. A similar trend is observed with respect to the antisymmetric mode bands. The splitting of these bands is around 40 cm^{-1} at low water content, $w_0 = 0.34$, and decreases until a value of 20 cm^{-1} , when the water content increases and swollen reverse micelles are predominant.

All results may indicate that the separation between ions increases when swollen reverse micelles are formed. This behavior was observed in other w/o microemulsions of AOT dissolved in cyclohexane or in isoctane¹⁰ and was associated to the hydration of micelles, which results in the removal of sodium counterion from the sulfonate group of the surfactant.

Attractive interactions between droplets do not affect the separation of the sulfonate and sodium ions.

The CH_2 Wagging Bands Progression and the CH_2 Scissoring Vibrations. The methylene wagging band progression is a series of weak and regularly spaced bands in the region of 1180–1370 cm^{-1} which results from the wagging vibration of the hydrocarbon chain.²⁷ Results obtained in this work show that the surfactant spectrum of microemulsions with low water content, $w_0 = 0.34$, does not contain the wagging band progression. This fact is characteristic of the fully extended hydrocarbon chains of liquid *n*-paraffins. At w_0 values between 1 and 15, a broad band centered around 1360 cm^{-1} and two new bands centered at 1338 and 1100 cm^{-1} appear. These bands are due to the presence of some *trans* conformation in the hydrocarbon chain.²⁷ At $w_0 > 20$ the band centered around 1360 cm^{-1} is shifted to 1356 cm^{-1} . This band has been assigned to *gauche* (GG) conformations.²⁷ The presence of some GG configurations is always related to an increase of the degree of disorder on the hydrocarbon chain. Taking into account that attractive interactions between droplets were observed in these microemulsions, the increase of the conformational disorder could be due to the interpenetration of interfacial layers of two colliding droplets.

All spectra present two bands centered at 1313 and 1375 cm^{-1} . These bands are ascribed to a CH_3 rocking vibration and a CH_3 symmetric deformation, respectively.^{27,28}

(25) Ueda, M.; Schelly, Z. A. *Langmuir* **1988**, *4*, 653.

(26) Martin, C. A.; Magid, L. J. *J. Phys. Chem.* **1981**, *85*, 3938.

(27) Snyder, R. G. *J. Chem. Phys.* **1967**, *47*, 1316.

(28) Susi, H.; Pazner, S. *Spectrochim. Acta* **1962**, *18*, 499.

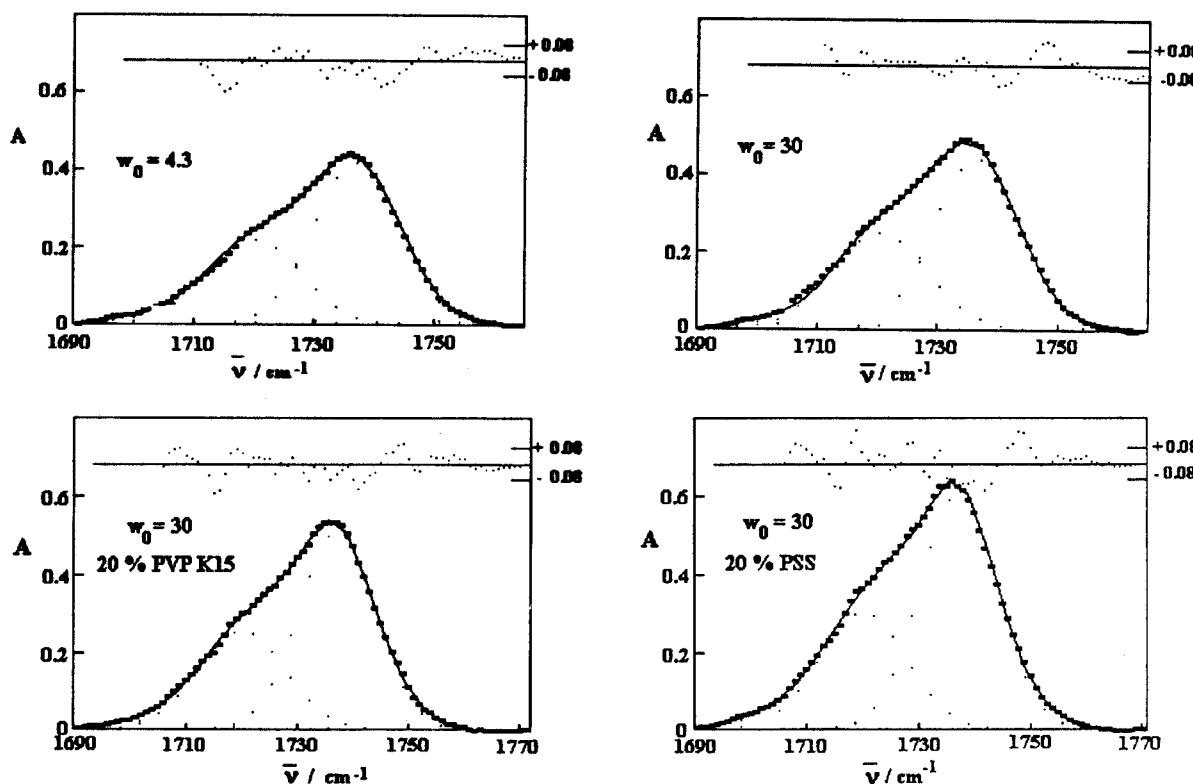


Figure 4. Deconvolution of the carbonyl stretching vibration band of surfactant in water/AOT/toluene microemulsions at selected water and polymer contents. Dotted lines are Gaussian component bands and the full line is the calculated spectrum contour. Upper line is the absolute deviation from experimental line.

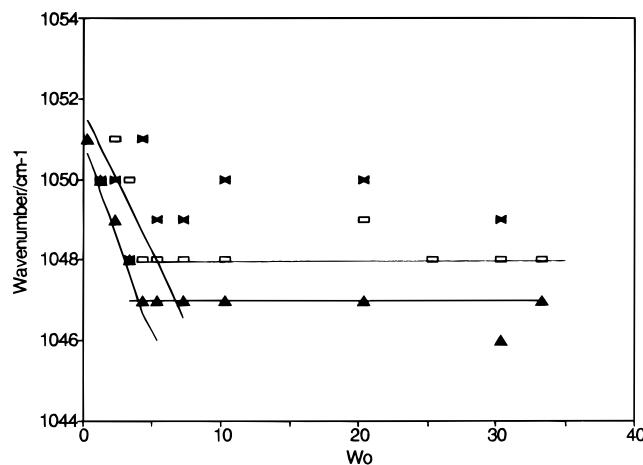


Figure 5. Variation of the band position corresponding to the symmetric sulfonate stretching mode with w_0 : ▲, without polymer; ×, 2% of PVP K15; □, 2% of PSS.

On the other hand, CH_2 scissoring vibrations, located in the region of $1460\text{--}1480\text{ cm}^{-1}$, are characteristic of the nature of the packing of the hydrocarbon chain.²⁹ Infrared spectra of the surfactant molecule present two bands centered at 1462 and 1466 cm^{-1} and a shoulder at 1455 cm^{-1} . These bands were observed on spectra corresponding to systems with a certain degree of packing, i.e., phospholipids in orthorombic or monoclinic crystal lattice.³⁰

The information obtained from IR spectra shows a great dependence of the structure of aggregates with the water content w_0 . At $w_0 \leq 3$ aggregates have low aggregation numbers and results obtained in this work may indicate

that (i) there is a relatively great interaction between Na^+ and $-\text{SO}_3^-$ ions, (ii) that the water contained in the aqueous pool is highly immobilized, and, (iii) that the surfactant chain have a certain degree of conformational order, with some all trans segments in the hydrocarbon chain.

A second type of aggregate is that with w_0 values ranged between 3 and 7. In these aggregates dimer water molecules at the interface decrease with respect to aggregates containing low aggregation number, and the water inside the micelle is reorganized by forming a structured shell of hydrogen-bonded polymeric chain water molecule. The separation between the sodium counterion and the sulfonate surfactant ion increases and the hydrocarbon chain conformation is similar to that corresponding to micelles of low aggregation number.

Finally, at water content greater than 7, reverse micelles or microemulsions are predominant. Results obtained in this investigation indicate that these aggregates have the following properties: a relatively weaker interaction between sodium and sulfonate ions, and a steady water pool organization, where the fraction of each water state that constitutes the aqueous core remains constant. Two different hydrocarbon chain conformations have been observed. At $w_0 < 15$ the hydrocarbon chain conformation has a certain degree of order due to the presence of some all trans bond segments, whereas microemulsions with water contents $w_0 > 20$ present some GG configurations on the surfactant hydrocarbon chain. This indicates an increase of the hydrocarbon chain conformational disorder probably due to the presence of attractive interactions between these microemulsions.

Infrared Spectroscopic Study of the Structure of w/o Microemulsions Perturbed by the Addition of Water-Soluble Polymers. The Water Bands. The addition of water-soluble polymers to w/o microemulsions produces changes on the shape of the OH stretching

(29) Umemura, J.; Cameron, D. G.; Mantsch, H. H. *Biochim. Biophys. Acta* **1980**, *602*, 32.

(30) Snyder, R. G. *J. Mol. Spectrosc.* **1961**, *7*, 116.

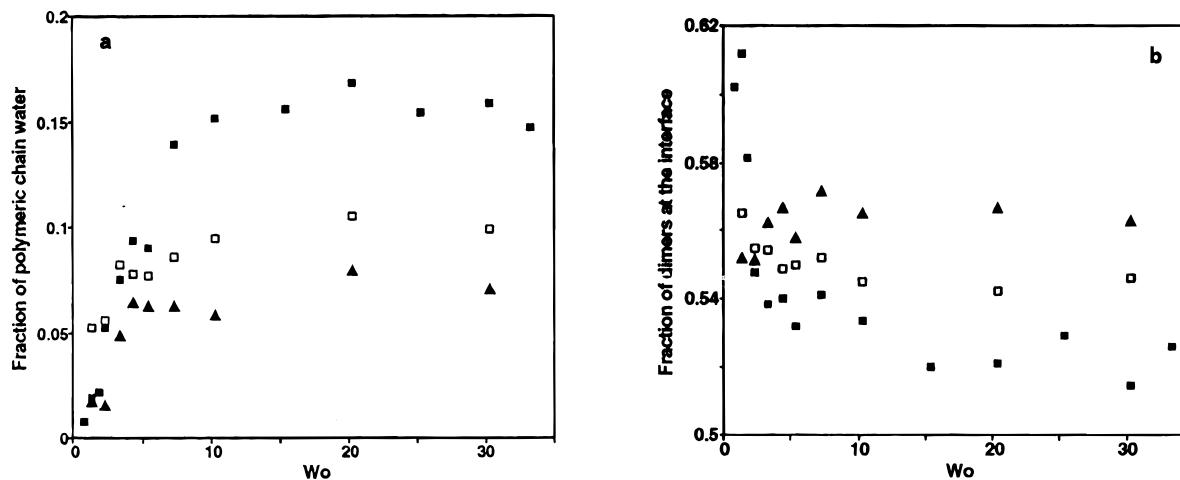


Figure 6. Variation of fractions of some different kinds of water molecules with the water content: (a) hydrogen-bonded polymeric chain water molecules, (b) water dimers at the interface; ■, without polymer; □, 12% PSS, ▲, 2% PVP K15.

band.³¹ The deconvolution process in Gaussian bands applied to the OH band of water molecules of these perturbed aggregates gives results similar to those in the absence of polymer, Figure 2. The aforementioned four Gaussian functions fit the OH spectral contour. The position of these bands is the same as in nonperturbed aggregates and they have also been ascribed to the hydrogen-bonded polymeric chain, the dimer and the monomer water molecules at the interface, and the free water molecules, respectively.

In the first place the effect of the addition of water to microemulsions containing constant polymer content has been analyzed. The fractions of each kind of molecule at different water and polymer contents have also been determined as the quotient between the area of each Gaussian with respect to the total peak area. These values are represented versus w_0 , at each polymer content. Figure 6 shows some of these results.

Some significant differences as regards results obtained in w/o microemulsions without polymers have been detected. The addition of polymers decreases the fraction of hydrogen-bonded polymeric chain water molecules, Figure 6a. This fact can be understood if it considers that polymers are solubilized in the water pool region where these kinds of water molecules are localized, the layer between the interface and the inner core. Thus, the presence of polymers in this region prevents the formation of the water pool structured layer decreasing the number of hydrogen-bonded polymeric chain water molecules. As in w/o microemulsions without polymers, the fraction of this kind of water molecule increases with w_0 and reaches a constant value at high water contents, in the range of $w_0 = 5-10$.

(31) To get a deeper insight of these results it is important to know the ratio of filled micelles to empty micelles at different w_0 values. This ratio can be calculated by using the Poisson distribution, but it is necessary to know the aggregation number of aggregates with different water concentrations. A rough estimation of this ratio could be calculated assuming that, at each w_0 value, the aggregation number of filled micelles is the same to that corresponding to empty reverse micelles. Taking into account this assumption, values calculated show that PVP K15 filled micelles are only predominant at high values of water and polymer contents. However, when PSS is added to reverse micelles, empty micelles are always predominant, i.e., 77% of empty micelles in microemulsions with 20% PSS and $w_0 = 30$. These facts are not consistent with results obtained in this work. Electrical conductivity values and IR spectra of aggregates containing 2% of PSS or 2% of PVP K15 show significant changes as regards to the empty microemulsions. Therefore, filled reverse micelles must be predominant even at the lowest polymer content used in this work. This is only possible if the aggregation number of filled aggregates decreases as compared to that of the empty micelles.

Table 1. Variation of the Fraction of Each Kind of Water Molecule with the Polymer Content at a Fixed w_0 Value of 20

| polymer content | hydrogen-bonded polymeric chain | dimers at the interface | monomers at the interface | free monomers |
|-----------------|---------------------------------|-------------------------|---------------------------|---------------|
| 0.00 | 0.17 | 0.52 | 0.23 | 0.08 |
| 2% PVP K15 | 0.07 | 0.56 | 0.28 | 0.09 |
| 3% PVP K15 | 0.06 | 0.55 | 0.29 | 0.10 |
| 5% PVP K15 | 0.06 | 0.56 | 0.29 | 0.09 |
| 20% PVP K15 | 0.07 | 0.56 | 0.27 | 0.10 |
| 2% PSS | 0.09 | 0.55 | 0.29 | 0.07 |
| 5% PSS | 0.11 | 0.56 | 0.27 | 0.06 |
| 12% PSS | 0.10 | 0.54 | 0.31 | 0.05 |
| 14% PSS | 0.08 | 0.55 | 0.30 | 0.07 |
| 20% PSS | 0.09 | 0.56 | 0.30 | 0.05 |

Fractions of dimer water molecules increase as compared to those corresponding to nonperturbed microemulsions, Figure 6b. A weakly increase of water monomer molecules at the interface was also observed. These results are consistent with aforementioned changes on hydrogen-bonded polymeric chain water molecules. If the addition of polymers gives a significant reduction of these molecules, water molecules must be displaced from the structured water pool layer to other water pool regions, in this case to the micellar interface.

On the other hand, fractions of both dimer and monomer water molecules at the interface remain constant with the water content, whereas in nonperturbed microemulsions these fractions decrease with water concentration until reaching a w_0 value of 7, where they remain constant. At the present time only a speculative explanation of this effect can be given. In order to obtain thermodynamically stable aggregates, polymer molecules might force an organization on the interface which is not altered by the addition of water.

The free monomer molecules fraction is practically unaffected by the addition of polymers, remaining constant to a value around 0.08.

To study the effect of the polymer concentration on reverse micelles, the variation of fractions corresponding to different kinds of water molecules with the polymer concentration at a fixed w_0 value has been analyzed.

Table 1 presents some of these results. In order to compare results corresponding to swollen micelles without attractive interactions, the w_0 value selected was 20, just to avoid effects of very high or very low w_0 values.

Results of Table 1 confirm the behavior discussed above, i.e., the decrease of hydrogen-bonded polymeric

chain water molecules and the simultaneous increase of dimer and monomer water molecules at the interface induced by the addition of polymers. The free monomer water molecules do not show significant variations with respect to the empty micelles.

Finally, it can be noted that values of fractions for each type of water molecule remain constant with the addition of different polymer concentrations. This fact suggests that polymer molecules can be incorporated to aggregates and that the incorporation to micelles gives a water pool structure unaffected by the polymer concentration in the whole range of polymer contents used in this work.

The Carbonyl Bands. The addition of these water-soluble polymers to the AOT/toluene/water microemulsions does not modify the spectral contour of the carbonyl band of the surfactant as regards the corresponding one to nonperturbed microemulsions; i.e., the asymmetrical band is deconvolved in two Gaussian functions centered around 1737 and 1720 cm⁻¹, respectively, Figure 4. These bands were also ascribed to the gauche and trans conformations, respectively. The fraction of each conformer has the same value as in the absence of polymer, 63% of gauche and 27% of trans conformers, respectively. The position and the area of each band are also unaffected by the addition of different polymer and water contents. This shows that polymers are not localized near the carbonyl group, so that no changes on the stereospecific position around the carbonyl group were expected.

The Sulfonate Bands. The antisymmetric doublet and the symmetric stretching sulfonate bands of microemulsions of AOT perturbed by the addition of polymers were investigated. Figure 5 shows the position of the symmetric stretching band at every w_0 and at a R value of 2% for PVP K15 and PSS. Two different behaviors as a function of the kind of polymer were observed. In the case of aggregates containing PSS, the variation of position of this band with w_0 shows a trend similar to that corresponding to aggregates without polymer. The maximum of the band is shifted from 1051 to 1048 cm⁻¹ as w_0 increases until a value of around 4. Up to this value the position of the band remains constant. A small difference in the band position was detected at high w_0 values. The band is centered around 1047 cm⁻¹ in empty microemulsions and around 1048 cm⁻¹ in the filled ones. This indicates that the separation between the surfactant sulfonate and the sodium ions is smaller in perturbed aggregates than in nonperturbed ones. This behavior is observed at all polymer concentrations studied.

When PVP K15 is added the position of the band does not change with the increase of w_0 , remaining constant at a value of 1050 cm⁻¹. This value is intermediate between the corresponding ones to microemulsions and low aggregation number aggregates without polymer. This correlates well with the value of the splitting of the antisymmetric stretching sulfonate bands. In the presence of PSS, the behavior is similar to that corresponding to nonperturbed aggregates. However when PVP K15 is added, the splitting of bands remains constant at a value of 29 cm⁻¹. This value is also intermediate between those corresponding to micelles of low aggregation number and nonperturbed microemulsions. All these results may indicate that, in PVP K15 filled microemulsions, the separation between the Na⁺ counterion and the sulfonate surfactant ion is intermediate between the corresponding one to low size micelles and swollen reverse aggregates without polymers and is unaffected by changes in the water composition.

The CH₂ Wagging Bands Progression and the CH₂ Scissoring Vibrations. The addition of PVP K15 and PSS to microemulsions made with AOT dissolved in toluene

and with different water contents does not change the CH₂ scissoring vibrations as compared to corresponding ones to nonperturbed micelles. This behavior may indicate no changes on the packing of the hydrocarbon chain when polymers are added.

On the other hand, significant changes on the CH₂ wagging bands were observed. Results can be summarized as follows: (a) At low PVP K15 concentration, $R < 5\%$, the wagging spectrum is composed of three bands centered around 1100, 1338, and 1361 cm⁻¹. This spectrum is characteristic of a hydrocarbon conformation with some all-trans segments. The conformation is the same to that of aggregates without polymers and with water content, w_0 , in the range of 1–15. The addition of water does not affect the conformation. (b) At high concentrations of PVP K15, $R \geq 5\%$, two kinds of conformations appear as a function of the water content. At w_0 values between 1 and 3, a new band centered at 1082 cm⁻¹ appears and a significant increase on CH₃ symmetric deformation band, 1380 cm⁻¹, is observed. The band at 1082 cm⁻¹ has been observed in some phospholipid hydrocarbon chains and is assigned to short all-trans segments connected by a single gauche bond.³² Some of these groups of bonds have a GTT conformation, responsible for the increase of the intensity of the band centered around 1380 cm⁻¹. At $w_0 > 3$, the band centered around 1361 cm⁻¹ is shifted to 1355 cm⁻¹, and simultaneously the intensity of bands centered at 1338 and 1380 cm⁻¹ decreases. This behavior is characteristic of the presence of some GG conformations and shows an increase of the conformational disorder at these w_0 values. (c) The position and the intensity of wagging bands of the surfactant corresponding to microemulsions with low PSS contents, $R \leq 12\%$, suggest that the hydrocarbon conformation is similar to that corresponding to aggregates with high PVP K15 content and low w_0 values. The characteristic of this hydrocarbon chain conformation has been discussed in section b. (d) Infrared spectra of aggregates containing PSS concentrations greater than 12% and $w_0 > 2$ have the following group of bands: 1100, 1338, and 1361 cm⁻¹. These bands indicate the presence of all-trans segments in the surfactant hydrocarbon chain, in a similar configuration to that corresponding to nonperturbed aggregates with water content in the w_0 range of 1–15 or to filled micelles with low PVP K15 content. Finally at $w_0 < 2$, bands centered at 1082 and 1368 cm⁻¹ appear and simultaneously the intensity of the band at 1380 cm⁻¹ increases. Bands centered at 1082 and 1380 cm⁻¹ correspond to GTT configurations and were discussed in previous sections, and the third band, centered around 1368 cm⁻¹, corresponds to the wagging vibration of a GTG conformation.²⁷ The presence of these bands on the spectrum might indicate the existence of both GTG and GTT conformations in these microemulsions.

Conclusions

Attractive interactions between reverse aggregates of Aerosol OT dissolved in toluene at high water contents, $w_0 \geq 25$, have been detected. FT-IR spectra detected different structures in nonperturbed aggregates. These structures have a strong dependence of the water content.

No attractive interactions between droplets were detected in polymer-filled aggregates at all the water and polymer contents studied in this work. This behavior shows that the addition of PVP K15 and PSS in reverse aggregates prevents the interaction between these reverse micelles.

From FT-IR spectra the location of polymers in the aqueous core can be made. Polymers are solubilized in a region localized between the interface and the most internal layer of the water pool. The sulfonate stretching band corresponding to the surfactant molecule shows that PVP K15 and PSS molecules force the sodium and sulfonate ions to a greater closeness than in empty aggregates. However, this effect is more accused in PVP K15 filled microemulsions. Finally, the addition of these polymers to aggregates increases the degree of disorder

in the conformation of hydrocarbon chains of the surfactant. The kind of conformation has a great dependence of the structure of the polymer and of the water and polymer contents.

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