Investigation on the conformations of AOT in water-in-oil microemulsions using 2D-ATR-FTIR correlation spectroscopy

Zuliang Lai, Peiyi Wu *

The Key Laboratory of Molecular Engineering of Polymers (Ministry of Education), Department of Macromolecular Science, Fudan University, Handan Road 220, Shanghai 200433, People's Republic of China

Abstract

The carbonyl groups of sodium bis(2-ethylhexyl) sulfosuccinate (AOT) in the water-in-oil (W/O) microemulsions of AOT/tetrachloromethane/water were investigated by using two-dimensional attenuated total reflection Fourier transform infrared (2D-ATR-FTIR) correlation spectroscopy under a perturbation of temperature. The results of a traditional curve fitting method were compared with the 2D correlation spectra results. The peaks at 1718 and 1736 cm^{-1} were assigned to different carbonyl groups in *trans* conformation and *gauche* conformation of AOT molecules, respectively. With the increase of temperature, the *trans* conformation increased quickly at the lower temperature below 35 °C and decreased slowly at the higher temperature. The special phenomenon owed to the composition and decomposition of the hydrogen bonding between water of the inner polar core and carbonyl groups of AOT molecules. Two new peaks at 1707 and 1747 cm^{-1} in the 2D correlation spectra implied the process of the transition of AOT molecule conformation and the deviation of correlation coefficients of curve fitting method. 2D-ATR-FTIR correlation spectroscopy exhibited the superiority over the traditional curve fitting method.
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1. Introduction

Aerosol-OT (AOT, sodium bis(2-ethylhexyl) sulfosuccinate) forms inverted micelles when dissolved in nonpolar solvents such as isooctane and tetrachloromethane [1–4]. With a special molecular structure of polar head and nonpolar hydrocarbon chains tail, AOT exhibits a remarkable ability to solubilize large quantities of water-in-oil without help of cosurfactant [5]. It is of interest to study the microstructure of AOT microemulsions because the structure of AOT molecule is similar to the phospholipid and is able to form bimolecular film in particular environment [6–8]. Recently, the nanoparticle synthesis in the AOT microemulsion becomes another hot issue [9–11]. Many theoretical and experimental viewpoints were proposed to delineate the structures of AOT microemulsions [12–15]. Generally speaking, in AOT water-in-oil (W/O) microemulsions, the sulfonate and ester head groups are pointed toward the polar side of aqueous core and the hydrocarbon chains are extended outside toward the oil phase [16]. Water is solubilized in the polar core, forming a so-called "tank", which is usually used as a microreactor of polymerization [17,18]. The key factor to characterize the microemulsion is W (H$_2$O:AOT, molar ratio). These systems are often referred to as reversed micelles if the W is smaller than 12 and as water-in-oil microemulsion if W is larger than 12 [19]. Zhou et al. reported that at $W < 20$, the effective head-group area increases with W increasing; when $W > 20$, it slightly decreases [2]. Other researches also pointed out that $W = 20$ is an important dividing point of AOT microemulsions [16,20].

Many theoretical models have been proposed to describe the microstructures of AOT microemulsions for

* Corresponding author. Tel.: +86 21 65643255; fax: +86 2165640293.
   E-mail address: peiyiwu@fudan.edu.cn (P. Wu).

decades. A hot-spot topic of AOT microemulsion is the assignment to the carbonyl groups in various conformations of the AOT molecule [2,8,16,21,22]. One viewpoint concluded by Jain et al. [16] and Ikushima et al. [8] was that there were two kinds of carbonyls, which corresponded to *trans* conformation and *gauche* conformation, and the peak positions of them were at 1736 ± 5 and $1719 \pm 5 \, cm^{-1}$, respectively. Another viewpoint was proposed by Moran et al., considered that $1735 \, cm^{-1}$ was assigned to the *gauche* conformation and $1723 \, cm^{-1}$ to *trans* one [21]. The contradiction should be clarified by further research with more reliable method.

Fourier transform infrared spectroscopy (FTIR) is proved to be a suitable method to characterize microstructures in the AOT microemulsions [2,8,14,16,23–26], but the key problem of FTIR is the separation of overlapped peaks. Zhou et al. obtained the same conclusion as C. González-Blanco by using the least-squares curve fitting to resolve the broad peaks for hydroxyl of water, and proposed another model of conformations of carbonyl group in the AOT W/O system [2]. Although the curve fitting is a powerful method to separate overlapped peaks in vibrational spectroscopy, it is hard to avoid errors for artificialness, such as the quantity and positions of fitted peaks [27]. To avoid the artificial factors of curve fitting, a mathematical method called two-dimensional correlation spectroscopy, which proposed by Noda in 1989, was applied to study the complicated systems such as aqueous solutions and polymers [28]. The construction of 2D correlation IR spectra is based on the detection of dynamic changes of a system under an external perturbation such as temperature, concentration, pressure and so on [29,30]. The main advantages of 2D correlation analysis are: simplification of complex spectra consisting of overlapped peaks; enhancement of spectral resolution by spreading peaks over the second dimension; and providing interaction and dynamic information of functional groups in the system [31]. By using this powerful method, the carbonyl groups of AOT molecules in W/O microemulsions ($W = 20$) were investigated by 2D-ATR-FTIR correlation spectroscopy with perturbation of temperature. The method was compared with a traditional curve fitting and the results obtained in previous works by other researchers were discussed.

2. Experimental

2.1. Materials

Sodium bis(2-ethylhexyl) sulfosuccinate (AOT, 98%) was obtained from Aldrich and was used without further treatment. CCl_4 was refluxed with addition of $CaCl_2$ for 6 h and then distilled. AOT/CCl_4 solution was prepared at a concentration of 0.1 m, than was stirred for 30 min in the presence of P_2O_5 (99%) purchased from Sigma to ensure the complete removal of residual water. The dehydration procedure was proved not to chemically transform the solution [1,9]. The $H_2O/AOT/CCl_4$ solution at W ($H_2O:AOT$, molar ratio) = 20 was prepared by adding purified water into former AOT/CCl_4 solution. The solution was stable and transparent at room temperature (25 °C) and was kept for more than a week before test.

2.2. ATR-FTIR measurements

A Nicolet Nexus 470 FTIR spectrometer equipped with a DTGS-KBr detector was used in the measurements. An Attenuated total reflection (ATR) cell with a horizontal ZnSe crystal and an angle of incidence of 45° was mounted to obtain the ATR infrared spectra. Each single-beam mid-IR spectrum resulted from a 64 scans average. All the FTIR spectra of different $H_2O:AOT$ molar ratio W were obtained between 4000 and 650 cm^{-1} at a resolution of 4 cm^{-1} at room temperature. The $H_2O/AOT/CCl_4$ solution of $W = 20$ ($H_2O:AOT$) was used to collected the temperature-dependent IR spectra from 27 to 45 °C with a 2 °C increments. The measurement was repeated twice to decrease the error, and one of the data was chosen for detailed study.

2.3. 2D-IR correlation analysis and curve fitting

OMNIC 6.0 (Thermo Nicolet) and Origin 7.5 (Origin-Lab) were used to generate all the spectra. Two-dimensional infrared correlation spectra and contours were calculated by *2Dshige* version 1.3 (programmed by Shigeaki Morita, Yukihiro Ozaki and Isao Noda, Japan), according to theory of I. Noda's 2D correlation method. The reference spectra on the side and top of the 2D contour maps were average spectra calculated over the entire temperature range. The negative cross-peaks in 2D contour maps were shaded using the standard shading convention. Only the top left parts of 2D contours were discussed because of the symmetry of the spectra. The curve fitting was performed by using Origin 7.5. Gauss function was chosen to fit the overlapped peaks.

3. Results and discussion

Fig. 1 shows the staggered conformations of AOT molecule in W/O microemulsions in Newmann projection. Rotamer A is *trans* conformation and rotamer B is the *gauche* one. In *trans* conformation, one ester group and the sulfonic group are directed to the polar side, while in the *gauche* conformation, both of the ester group are in the apolar region of surfactant monolayer. The third rotamer has poor amphiphilicity and scarcely exists in microemulsion [21,22].

FTIR absorbance spectra of AOT W/O microemulsion ($W = 20$) at the temperature from 27 to 45 °C with 2 °C increments are shown in Fig. 2. Table 1 was the general assignment of AOT W/O microemulsion.

It was observed that the intensity of hydroxyl stretching bond decreased with the increase of temperature, while in the spectral region between 900 and 1800 cm^{-1}, most of
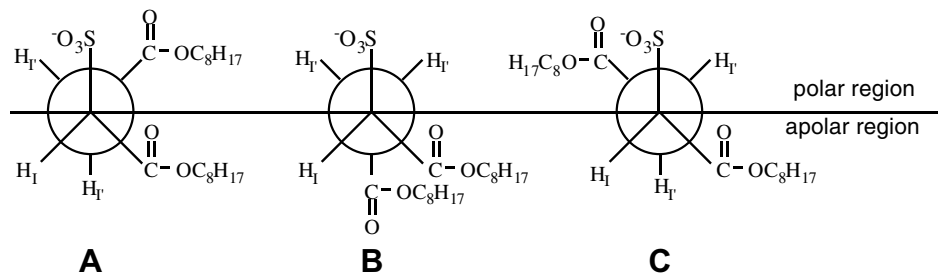
Fig. 1. The staggered conformations AOT molecule in Newmann projection [2].
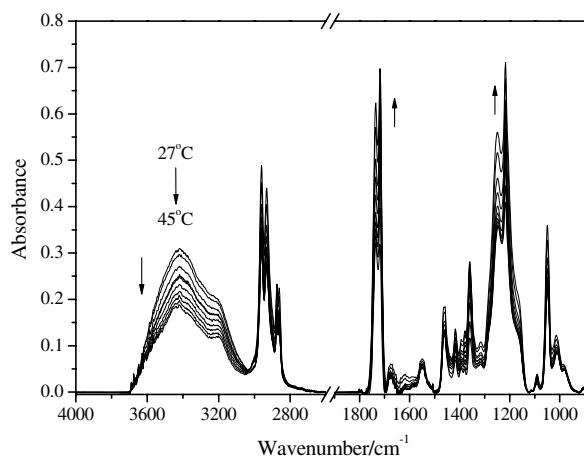

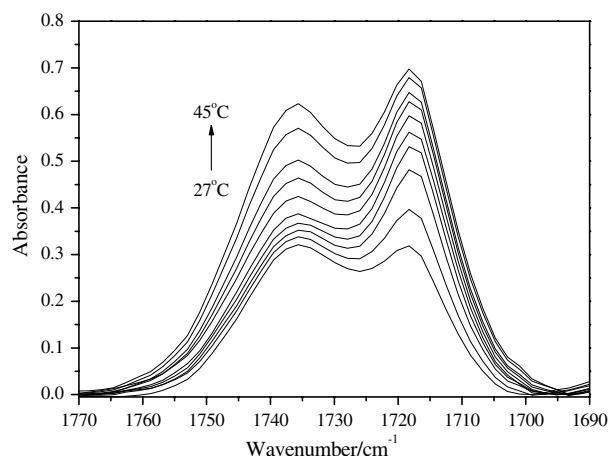Fig. 2. FTIR spectra of AOT W/O microemulsion ($W = 20$) under different temperatures.

Fig. 3. Temperature-dependent FTIR spectra of AOT W/O microemulsion in the range of 1690–1770 cm^{-1}.

Table 1
IR wavenumber and assignment of AOT W/O microemulsion

v (cm^{-1})	Assignment	v (cm^{-1})	Assignment
3200–3600	v(H$_2$O)	1461	δ_{as}(CH$_3$), CH$_2$ sciss
2960	v_{as}(CH$_3$)	1393	δ_s(CH$_3$)
2932	v_{as}(CH$_2$)	1380,1360	CH$_2$ wag
2874	v_s(CH$_3$)	1217, 1245	v_{as}(–SO$_3^-$)
2861	v_s(CH$_2$)	1169	v_s(C–O)
1736, 1718	v_s(C=O)	1094	CH$_2$ twist
1640	δ(H$_2$O)	1050	v_s(S=O)

Note: v, stretching vibration; δ, bending; s, symmetrical; as, asymmetrical
Ref. [25].

Fig. 4. Curve fitting result of the C=O stretching vibration region of AOT W/O microemulsion at 27 °C.

peaks increased. Fig. 3 shows the temperature-dependent FTIR spectra of C=O stretching vibration of AOT in the range of 1690–1770 cm^{-1}. Two overlapped peaks were easy to identify at 1718 and 1736 cm^{-1}. If the number of sub-peaks were set as two, the overlapped peaks could be separated by a traditional curve fitting method, using Gauss function. (Fig. 4 is an example of curve fitting result of the FTIR spectrum at 27 °C.)

The curve fitting results are listed in Table 2. It could be seen that with the increase of temperature, the intensities of peaks at 1718 and 1736 cm^{-1} increase simultaneously. If the peaks at 1718 and 1736 cm^{-1} were assigned to the carbonyl groups in two different kinds of conformations of
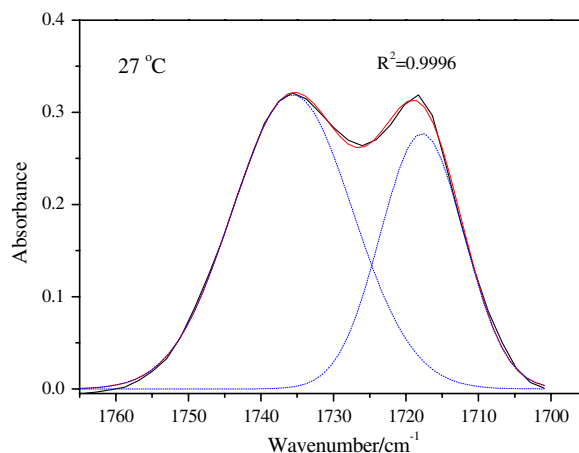
AOT molecule, thus the ratio of two conformations could be described as the ratio of peak height (I1736/I1718) or peak area (A1736/A1718) of the peaks at 1736 and 1718 cm^{-1}. The peak height and area ratio as a function of temperature are plotted in Fig. 5. Interestingly, the ratio of two AOT conformations was strongly related to the temperature when the value of W was 20. When the temperature was below 35 °C, the intensity of the peak at

Table 2
Peak parameters of curve fitting in the range of 1695–1765 cm^{-1}

$T/°C$	1718 cm^{-1}			1736 cm^{-1}			R^{2b}
	Area	Height	FWHM[a]	Area	Height	FWHM	
27	3.9978	0.27738	11.500	6.6375	0.31946	16.578	0.9992
29	4.8059	0.34023	11.270	7.1574	0.33443	17.706	0.9986
31	6.0179	0.42162	11.389	7.6386	0.34849	17.787	0.9978
33	6.7065	0.46575	11.489	8.2478	0.36292	18.133	0.9975
35	7.3005	0.49573	11.750	8.6810	0.38028	18.214	0.9979
37	7.5845	0.51407	11.772	9.9186	0.41431	19.102	0.9972
39	8.2387	0.54544	12.052	10.531	0.45217	18.582	0.9972
41	8.6060	0.55908	12.282	11.349	0.48875	18.527	0.9970
43	9.1789	0.57914	12.646	12.891	0.55228	18.623	0.9964
45	9.4856	0.58808	12.870	14.098	0.60013	18.744	0.9962

[a] FWHM, full-width at half-maximum.
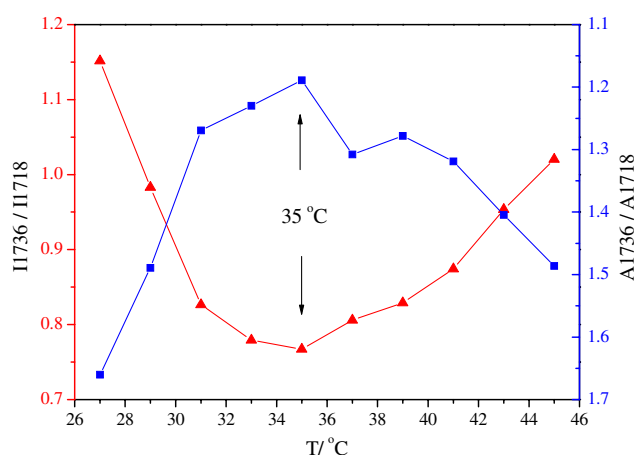[b] R^2, correlation coefficient of curve fitting.

Fig. 5. I1736/I1718 peak height ratio as a function of temperature (red line, trigonal points, left axis) and A1736/A1718 peak area ratio as a function of temperature (blue line, foursquare points, right axis). (For interpretation of the references in colour in this figure legend, the reader is referred to the web version of this article.)

1736 cm^{-1} increased rapidly with the increase of temperature, while temperature was beyond 35 °C, the intensity of the peak at 1718 cm^{-1} increased slowly. It was clear that 35 °C was a dividing point of the transition of two AOT conformations.

Although the correlation coefficients R^2 of curve fitting were close to 1 at low temperature, they became poor at higher temperature. Besides the error of baseline shift, were there any inner factors of the deviation of curve fitting? 2D-IR correlation spectra provided another reason of the deviation of R^2.

In the 2D synchronous spectrum (Fig. 6A), two auto-peaks could be seen at 1718 and 1736 cm^{-1}, identical with the results of curve fitting. Only a positive cross-peak at 1736/1718 cm^{-1} was found in the synchronous spectrum. Because the peaks in the synchronous spectrum were also overlapped, the peaks in the asynchronous spectrum became important to distinguish the overlapping peaks in the original spectra. The 2D asynchronous spectrum (Fig. 6B) was more complicated than the synchronous one. There were two positive cross-peaks at 1747/1736 cm^{-1} and 1716/1707 cm^{-1} and a large negative cross-peak at 1736/1716 cm^{-1}. With the IR resolution of 4 cm^{-1}, the peak at 1716 cm^{-1} was considered to be the
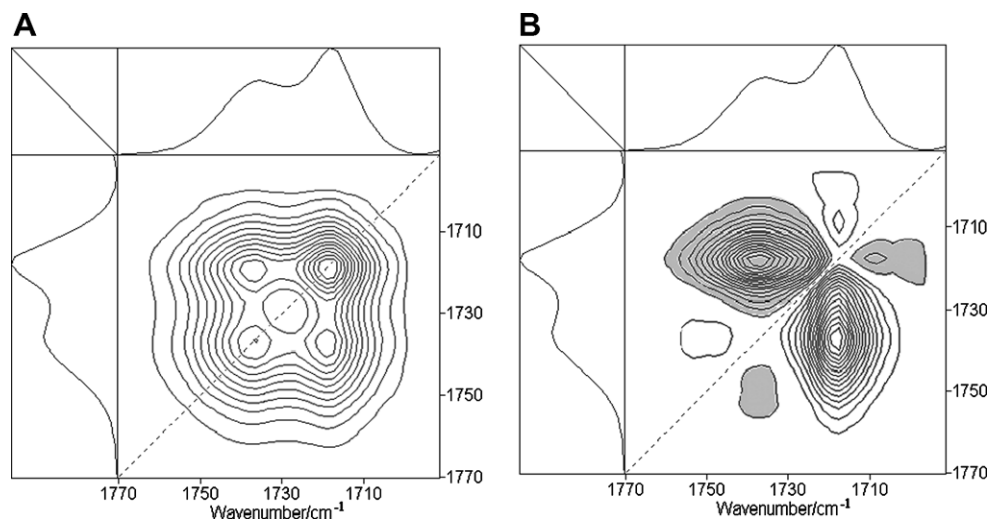

Fig. 6. 2D correlation IR spectra of AOT W/O microemulsion in the range of 1690–1770 cm^{-1}. (A) Synchronous spectrum; (B) asynchronous spectrum.

same as the one at 1718 cm^{-1} in the synchronous spectrum. Surprisingly, the peaks at 1707 and 1747 cm^{-1} distinguished by 2D-IR correlation spectra were not observed before. The presence of the new peaks implied two new kinds of C=O in the system. As we all known, if the functional group of C=O has interaction with other kind of functional group, the wavenumber of C=O stretching vibration may shift to a lower frequency. In this case, the peak at 1736 cm^{-1} was probably assigned to *gauche* conformation, because both of the C=O group were in the apolar region and have rare interaction of each other. The peak at a lower frequency of 1718 cm^{-1} should be assigned to *trans* conformation because one C=O group transferred to apolar region of the microemulsion and might have some weak interaction with hydroxyl group of H$_2$O. According to this idea, the peak at 1747 cm^{-1} was possible to a free C=O stretching vibration mode and the peak at 1707 cm^{-1} was probably assigned to the C=O group which had strong interaction with H$_2$O.

Why can we find these four kinds of C=O in the system? One reason was that the value of W was 20, which was generally believed to be a dividing point of AOT conformation transformation in many previous researches [14,16,20]. When $W = 20$, the system was seen to be a microemulsion, so the polar region constructed by water and polar heads of AOT molecules was large enough and H$_2$O molecules were excessive. Another important reason was the thermal perturbation of the system. In Fig. 5, it was clear that 35 °C was a dividing point of the transition of two AOT conformations. At low temperature, I1736/I1718 is larger than 1, suggested the *gauche* conformation took the advantage. With the increase of temperature, the *trans* conformation increased quickly. It could be explained that the interaction of apolar solvent of ester was broken and the hydrogen bonds between C=O and OH were formed with the increase of temperature. While beyond 35 °C, the unsteady hydrogen bond was broken for the high temperature, and the free C=O stretching vibration mode in the apolar region and a strong hydrogen bond with OH in the polar region were formed. The existence of the dividing point at 35 °C was mainly for the reason that when the value of W was fixed, the number of H$_2$O molecules in the surface area of polar core was stationary, so the number of hydrogen bonds between C=O and OH were limited. While at higher temperature, the hydrogen bonds were decomposed and the number of *trans* conformation C=O decreased. The speed of the transition of different AOT conformations at high temperature was slower than that at low temperature because the process at high temperature was the composition and decomposition of the hydrogen bonds between water of the inner polar core and carbonyl groups of AOT molecules, not a rotation of AOT molecules at lower temperature. The two new bonds formed at the high temperature caused the R^2 of curve fitting results deviating. If the sub-peaks were set as four, much better results of curve fitting would be obtained. (The results were not showed in this paper.) While former researches were based on the low temperature and concentration perturbation, only two main kinds of C=O could be found in the system [2,16,21].

4. Conclusion

Four peaks, which assigned to four different kinds of C=O stretching vibration modes, were found in the range of 1690–1770 cm^{-1} with the increase of temperature in AOT W/O microemulsions ($W = 20$) by 2D-ATR-FTIR correlation spectroscopy. The transition of *trans* and *gauche* conformations seemed to be sensitive to the temperature when the value of W was 20. At $T < 35$ °C, the *trans* conformation increased rapidly with the increase of temperature; while $T > 35$ °C, it reduced slowly. Two new peaks at 1707 and 1747 cm^{-1} appeared at the high temperature, came from two new kinds of C=O, which were probably assigned to strong hydrogen bonding C=O and free C=O stretching vibration mode, respectively. The presence of the new modes of C=O was strongly related to the temperature perturbation and the value of W. The 2D correlation spectroscopy was more advantageous compared with the traditional method of curve fitting because of the elimination of artificial errors.

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