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Journal of Dispersion Science and Technology

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597266>

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Online Publication Date: 01 May 2005

To cite this Article Luan, Yuxia, Xu, Guiying, Sun, Zhiwei, Dai, Guoliang, Chen, Yijian and Yu, Li(2005)'Comparative Studies of AOT and NaDEHP by Fluorescence Technique and z-Potential () Measurements',*Journal of Dispersion Science and Technology*,26:3,285 — 290

To link to this Article: DOI: 10.1081/DIS-200049572

URL: <http://dx.doi.org/10.1081/DIS-200049572>

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Comparative Studies of AOT and NaDEHP by Fluorescence Technique and z-Potential (ζ) Measurements

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The aggregation behaviors of two surfactants with the same hydrophobic tail, sodium bis(2-ethylhexyl)sulfosuccinate (AOT) and sodium bis(2-ethylhexyl)phosphate (NaDEHP), have been investigated by the fluorescence technique and z-potential (ζ) measurements. Five fine peaks of the pyrene molecule fluorescence spectroscopy appear in the surfactant solution, and the micropolarity at which pyrene locates is monitored from the intensity ratio of the first (I_1) and the third peak (I_3). A wide peak around 475 nm, the emission spectra of the excimer of pyrene molecules, is observed in the NaDEHP solution, while this is not found for the AOT system. The value of I_1/I_3 decreases in a more limited concentration range for the AOT system than for NaDEHP, indicating that small aggregates can be more easily formed by NaDEHP molecules. The z-potential results for the aggregates formed by the two surfactants show that the interaction between AOT and PVP is stronger than that between NaDEHP and PVP.

Keywords AOT, NaDEHP, fluorescence technique, z-potential (ζ)

INTRODUCTION

Sodium bis(2-ethylhexyl)sulfosuccinate (AOT) is a surfactant that is widely used in many fields, such as preparation for nanoparticles, emulsification polymerization, and biological catalysis, due to its special properties of forming the reversed micelle or water-in-oil microemulsion (Casado et al. 1994; Pileni 1993a, 1993b; Cui and Yin 1999). Sodium bis(2-ethylhexyl)phosphate (NaDEHP) is an organic phosphorus extractant widely used in hydrometallurgy and the nuclear industry. Both AOT and NaDEHP contain the same double hydrophobic chains and different polar head groups, but their aggregation behaviors are violently different in oil

(Ruckenstein and Nagarajan 1980; Yu et al. 1992; Yu and Neuman 1994a, 1994b). For example, the reversed micelles formed by AOT are spherical in shape and the size increases with the increase of W_0 (the molar ratio of water to surfactant in the oil) (Ruckenstein and Nagarajan 1980), while NaDEHP in heptane can form giant rodlike reversed micelles and the water acts as both an antimicellization agent and an antimicellar growth agent (Yu et al. 1992; Yu and Neuman 1994a, 1994b). Current studies of AOT and NaDEHP have mainly concerned their behavior in oil phase (Li et al. 1998a, 2000, 2002; Zhou et al. 2001; Kinugasa et al. 2002), but few studies have been carried out on the behavior of the two surfactants in aqueous solution (Luan et al. 2002a, 2002b).

In this work, we investigate the behavior of AOT and NaDEHP in aqueous solution by means of fluorescence probing technique and z-potential measurements. The results may be helpful for exploring the different properties of the two surfactants in the oil phase.

Received 31 August 2004; Accepted 23 October 2004

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EXPERIMENTAL

Materials

AOT and pyrene were bought from Sigma and Fluka, respectively and used as received. Bis(2-ethylhexyl)phosphate (HDEHP, C.R.) and NaCl (A.R.) are products of Shanghai Chemical Co. (China). The preparation of NaDEHP was described elsewhere (Luan et al. 2002a). PVP (polyvinylpyrrolidone, $M_w = 38,000$) and n-pentanol (A.R.) are the products of Beijing Chemical Reagen Co. Water used was triply distilled. The molecular structures of AOT and NaDEHP are shown in Scheme 1.

Methods

Zeta Potential (ζ) Measurements

The z-potential measurements were performed on a ZetaPlus (Brookhaven Instruments Corp.).

Fluorescence Measurements

Fluorescence spectra were recorded on a Perkin Elmer LS-50 spectrophotometer with the excitation wavelength of 335 nm. The hydrophobic index, I_1/I_3 , was defined as the ratio between the intensity at the first ($\lambda = 373$ nm) and at the third ($\lambda = 384$ nm) vibronic peaks in the pyrene (Py) emission spectrum. The surfactant solutions contained a pyrene concentration of 1.0×10^{-6} M.

The solutions were prepared as follows: a known content of methyl alcohol solution of pyrene was put into a test tube and was flushed by N_2 . Then different amounts of the surfactant solutions were added into the test tubes, and the resultant solutions were sonicated for 30 min. Before fluorescence spectrum measurement, the solutions were kept at room temperature for one hour.

RESULTS AND DISCUSSION

Fluorescence Characters of Pyrene in AOT and NaDEHP Solution

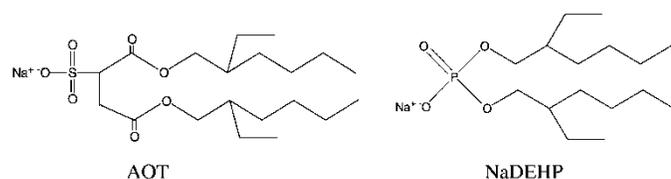
Fluorescence intensities of Pyrene in Different Concentrations of Surfactant Solutions

Fluorescence techniques play an important role in studies of the properties of surfactants. There exist five fine vibronic peaks in the pyrene monomer fluorescence spectrum. The

ratio of the intensities of the first (I_1) to the third vibronic peak (I_3) in the pyrene emission spectrum is known to be a monitor of the pyrene microenvironment polarity (Anghel et al. 2002; Mylonas and Staikos 2001; Christoff et al. 2001; Xu et al. 2000). The value of I_1/I_3 increases with the increase of polarity. For example, the values of I_1/I_3 in hexamethylene, dodecane, isopropyl ether, toluene, pentanol, isopropanol, ethanol, acetic acid, and water are 0.58, 0.62, 0.93, 1.04, 1.05, 1.07, 1.15, 1.39, and 1.87, respectively (Almgren et al. 1980). I_1/I_3 is widely used as a sensitive indicator of the micelle or cluster forming both in the absence and the presence of polymer (Winnik et al. 1991a, 1991b; Löfroth et al. 1991; Turro et al. 1984) and is defined as "hydrophobic index" (Honda et al. 2002; Kalyanasundaram et al. 1974; Kalyanasundaram and Thomas, 1977). The magnitude of I_1/I_3 can clarify the solution structure from the molecular level.

In order to study the difference between AOT and NaDEHP, the fluorescence spectroscopy of the pyrene molecule in different concentrations of AOT and NaDEHP solutions is investigated (shown in Figure 1). It can be seen that there are three obvious peaks in the fluorescence spectra of pyrene molecules. The fluorescence intensity of the probe molecules increases with increasing surfactant concentrations and increases rapidly at the concentrations $C_{AOT} > 3.0 \times 10^{-3}$ M and $C_{NaDEHP} > 1.5 \times 10^{-2}$ M. The critical micelle concentrations (CMC) of AOT and NaDEHP are about 3.0×10^{-3} M and 1.56×10^{-2} M, respectively (Luan et al. 2002a). So this shows that the concentrations at which the fluorescence intensity increases rapidly are approximately equal to their CMC. It is known that pyrene is a hydrophobic probe molecule that can be readily solubilized in the core of the micelles; consequently, most of the probe molecules transfer from the water phase to the micelle phase with the increase of surfactant concentrations. It is interesting to find that a wide peak appears around 475 nm in the NaDEHP solution, suggesting that the excimer of pyrene formed (Honda et al. 2002; Miguel et al. 2001), but this peak is not found in the AOT case. This indicates that the probability of two pyrene molecules in the NaDEHP aggregates is larger than that in the AOT system.

The plots of I_1/I_3 and I_1/I_5 versus concentration of AOT and NaDEHP are shown in Figure 2. The values of I_1/I_3 and I_1/I_5 initially remain constant and then decrease dramatically with the increase of surfactant concentrations. This is attributed to the formation of regular micelles with the rise of surfactant concentrations. The decrease of I_1/I_3 and I_1/I_5 values experiences a narrower concentration range for the AOT system than that for the NaDEHP case. The values of I_1/I_3 and I_1/I_5 decrease with increasing surfactant in the concentration region of about 1.5×10^{-3} – 6×10^{-3} M for the AOT system and 1.0×10^{-3} – 3.0×10^{-2} M for the NaDEHP system. The changes of I_1/I_3 and I_1/I_5 reflect changes of the polarity of the microenvironment experienced by pyrene molecules, i.e., from the bulky aqueous phase to the core of the micelles. It also can be seen that the values of I_1/I_3 and I_1/I_5



SCH. 1. Molecular structures of AOT and NaDEHP.

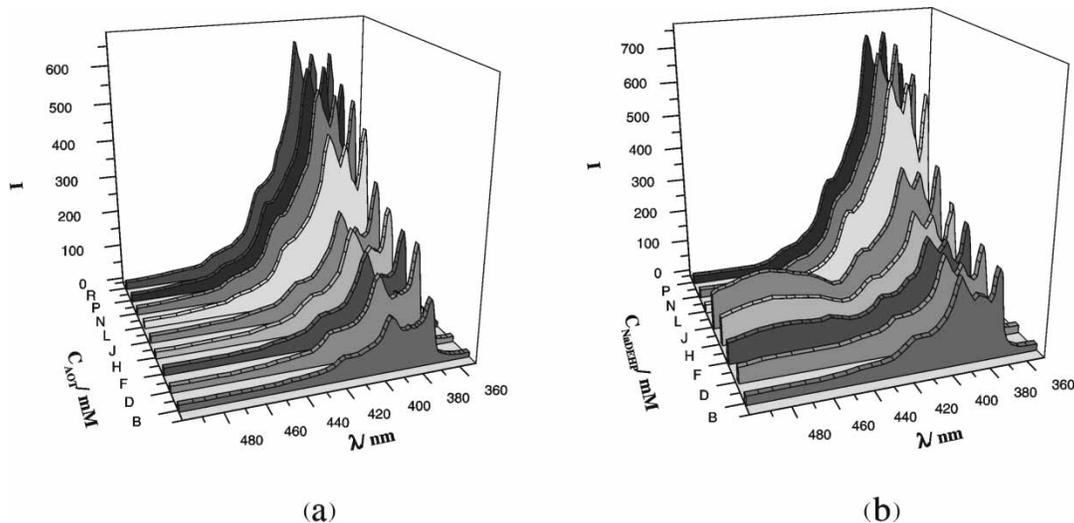


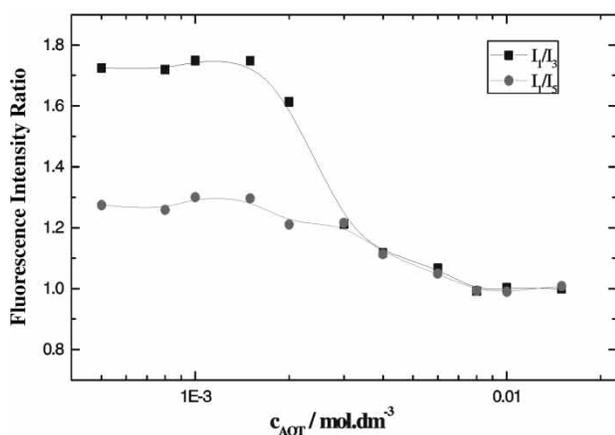
FIG. 1. Fluorescence spectra of pyrene molecule in different concentrations of AOT (a) and NaDEHP (b). AOT concentrations of B, D, . . . , R are 0, 0.5, 0.8, 2.0, 3.0, 4.0, 6.0, 10, 20 mM, respectively. NaDEHP concentrations of B, D, . . . , P are 1, 3, 6, 10, 15, 20, 60, 100 mM, respectively.

for the two surfactants are extremely different at the smaller concentrations, while they intersect at a point with the rise of the concentration. The concentrations corresponding to the points for the AOT and NaDEHP systems are about 3.01×10^{-3} M and 1.53×10^{-2} M, respectively. This result is nearly in agreement with the surface tension measurements (Luan et al. 2002a).

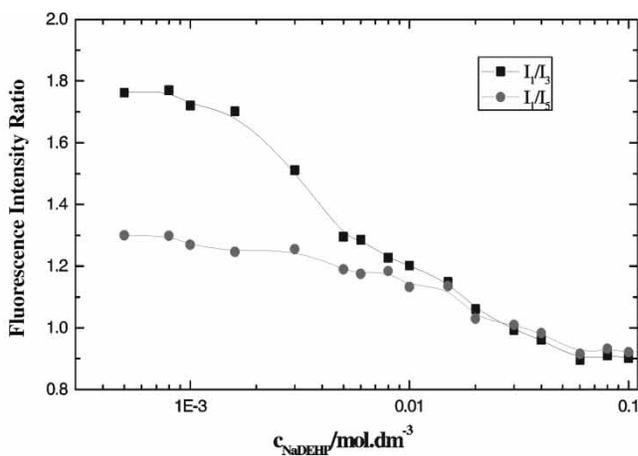
Aggregation Behaviors of AOT and NaDEHP in the Presence of PVP

Here the fluorescence spectrum of pyrene molecules in the PVP solution is first investigated in order to understand

the effect of PVP on AOT and NaDEHP (shown in Figure 3). I_1/I_3 and I_1/I_5 both decrease with the increase of PVP concentration. The value of I_1/I_3 decreases from about 1.55 to about 1.35 when the concentration of PVP increases from 1.0%wt to 5.0%wt. PVP is a good water-soluble macromolecule, which is stretched in water when the concentration of PVP is smaller. PVP molecules can form aggregates due to the hydrophobic interaction of the hydrophobic groups between the inter- and intra-molecules with the increase of concentration. Therefore part of the pyrene molecules can be solubilized in the hydrophobic micro-domain formed by PVP macromolecules, which resulted in the decrease of I_1/I_3 value.



(a) AOT



(b) NaDEHP

FIG. 2. Plots of the I_1/I_3 and I_1/I_5 vs. concentrations of the two surfactants.

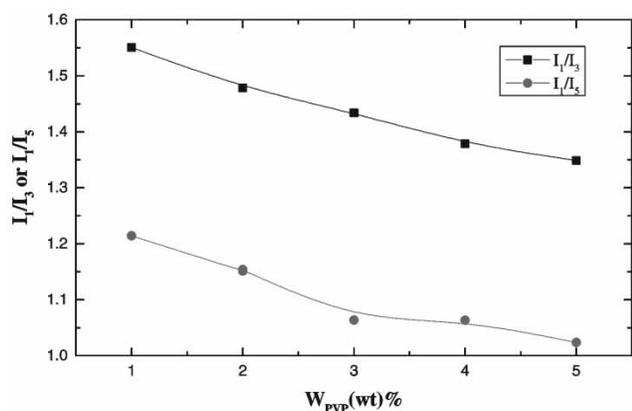
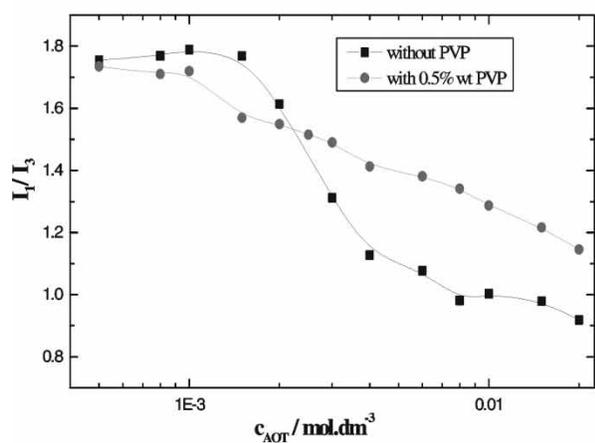
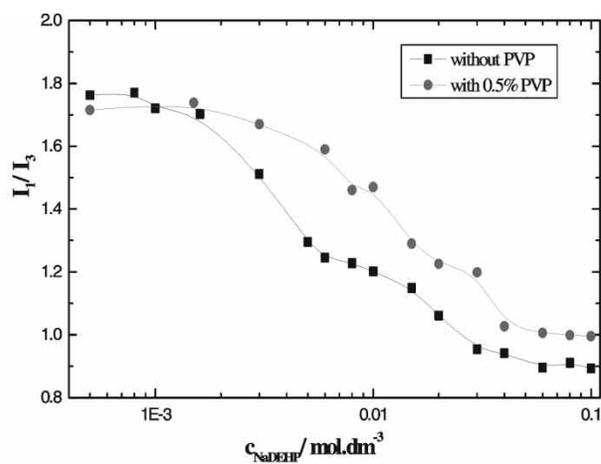


FIG. 3. Dependence of I_1/I_3 and I_1/I_5 on PVP concentration.

The dependence of I_1/I_3 of AOT and NaDEHP solutions in the presence of 0.5%wt PVP on their concentrations is shown in Figure 4. The values of I_1/I_3 in pure surfactant solutions are larger than those in the surfactant-PVP mixed systems at lower surfactant concentrations. This reversed with the increase of surfactant concentrations, that is, the I_1/I_3 values in the presence of PVP are larger than those in pure surfactant systems, indicating that the micelles present a more hydrophobic environment than the PVP-surfactant system. Hence, there are interactions between the surfactants and PVP due to the deviation from the I_1/I_3 of the pure surfactant systems. From the surface tension and electronic spin resonance (ESR) measurements (Luan et al. 2002a; Li et al. 1998b) it is known that the interaction between NaDEHP and PVP is much smaller than that between AOT and PVP. Therefore, the less sharp result for the NaDEHP system might be due to the weak interactions and the formation of premicelles.



(a)



(b)

FIG. 4. Dependence of I_1/I_3 of AOT and NaDEHP solutions on their concentrations.

Apparent z-Potential (ζ) of the Aggregates

Apparent z-Potential of the Two Surfactant Solutions

The dependence of apparent z-potential (ζ) for the aggregates on the surfactant concentration is shown in Figure 5. It is clear that the apparent z-potentials of the aggregates remarkably decrease with increasing surfactant concentrations and the negative z-potential of the AOT system is larger than that of the NaDEHP system. AOT and NaDEHP are both anionic surfactants. The smaller negative z-potential for the NaDEHP system may be caused by two aspects: one hand, the acid that NaDEHP corresponds to is a weak acid and there exists an equilibrium $\text{DEHP}^- + \text{H}^+ = \text{HDEHP}$ in the solution; the HDEHP molecules insert into the micelles and reduce the ζ ; on the other hand, the aggregation number (N) of the aggregates increases with increasing surfactant concentrations. So the surface charges of the aggregates increase with the rise of surfactant concentrations. At the same time, from our fluorescence measurements it is known that the N for the AOT system is much larger than that for the NaDEHP system at the same concentration.

Effect of NaCl on the ζ of the Two Surfactant Solutions

Figure 6 shows the ζ dependence of the aggregates on the NaCl concentration. From Figure 6 that the ζ for both kinds of aggregates increases with the increase of NaCl concentration it is except that the ζ of the AOT system increases more remarkably. The ζ increases from about -100 to -58 mV for the AOT system, while it increases from about -48 to -29 mV for the NaDEHP system when the NaCl concentration increases from 5 to 40 mM. The explanation for this phenomenon is that NaCl is more sensitive to AOT than to NaDEHP molecules. The thickness of the electric double layer of the aggregates is reduced and the surfactant molecules of the

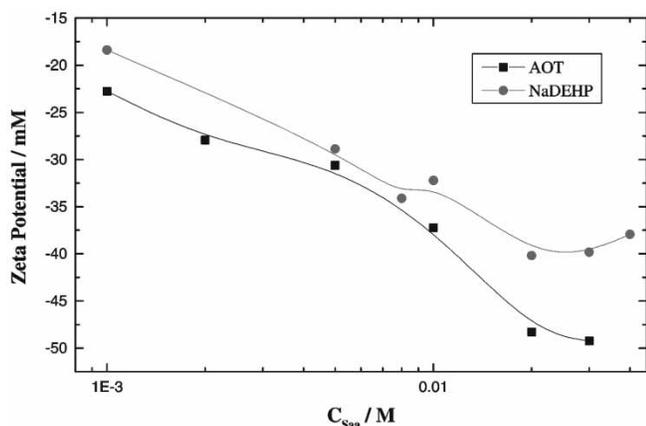


FIG. 5. The z-potential dependence on AOT and NaDEHP concentration.

micelle are packed more tightly with the increase of NaCl concentration.

Effects of PVP on ζ -Potential of the Surfactant Aggregates

The effects of PVP on ζ of the aggregates formed by NaDEHP and AOT are shown in Figure 7. The z-potentials decrease with increasing surfactant concentrations. But the negative z-potential of the AOT-PVP system is smaller than that of the NaDEHP-PVP system, which is more obvious at higher surfactant concentrations. This phenomenon is different from the case of pure surfactants. As is known PVP is a flexible macromolecule and bears weak positive charges. So PVP molecules probably wrap at the interface of the micelles due to the electrostatic interactions between PVP and the head groups of the surfactants. The negative charges are partially neutralized by PVP, and then the ζ value increases. However, the interaction between PVP and NaDEHP is very weak and therefore has little effect on the z-potential of the NaDEHP system.

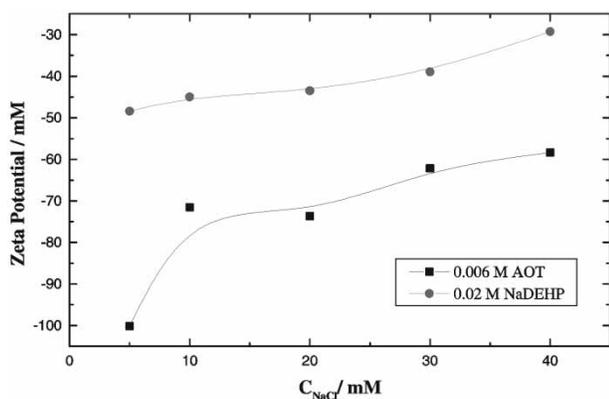


FIG. 6. Effects of NaCl concentration on the ζ of the aggregates.

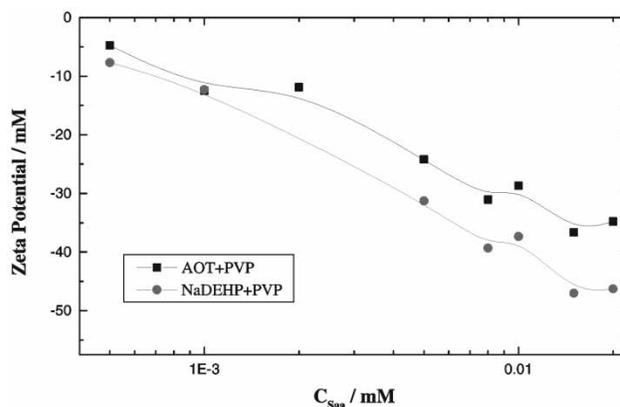


FIG. 7. ζ Dependence of the aggregates on surfactant concentrations in the presence of PVP.

CONCLUSIONS

This article mainly reported the comparative study of the structurally similar surfactants AOT and NaDEHP by fluorescence technique and z-potential measurements. The emission spectra of pyrene excimer around 475 nm appear in the NaDEHP fluorescence spectroscopy but are not found in the AOT system, and the decrease of I_1/I_3 experiences a more limited concentration range for AOT than that for NaDEHP. This is attributed to the smaller aggregates formed in the NaDEHP system compared with the AOT system. The negative z-potential of the aggregates formed by AOT is larger than that formed by NaDEHP in the absence of PVP, while the case is the inverse in the presence of PVP, which proves that the interaction between AOT and PVP is larger than that between NaDEHP and PVP.

ACKNOWLEDGMENTS

The authors gratefully acknowledge financial support from the NSF of Shandong Province (Y2001B08) and National Microgravity Laboratory, Institute of Mechanics, CAS, Beijing, China.

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