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Photon Correlation Spectroscopy and SAXS Study of Mixture of NaCl with AOT Microemulsion at X = 6.7

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ABSTRACT

Photon Correlation Spectroscopy is used to study the AOT microemulsion with and without NaCl. Collective diffusion coefficient was investigated by Photon Correlation Spectroscopy technique. We have studied effect of charge on dynamic of water-in-oil microemulsion (nano-droplet of water to the oil), which stabilized by AOT and dispersed in n-Decane at water/AOT with 6.7 molar ratio. The small angle X-ray scattering technique and hard sphere model were used to study the structural information of AOT microemulsion with and without NaCl. The structural investigation of samples shows a decrease of length scale of cylindrical droplets with increasing of NaCl concentration in AOT microemulsion.

1. Introduction

The microemulsions are consisting nano-meter size of water droplets in the oil [1-3]. Microemulsion have attracted interest for the delivery of single drug substances with low water solubility and stabilization of drugs in combination due to their preferential solubility in either the water or oil phases [4,5]. Microemulsions can be regarded as reverse-micellar solutions that have solubilized water into the polar surfactant tail region (L$_2$ phase). The anionic surfactant Aerosol OT (sodium bis-(2-ethylhexyl) sulfosuccinate, AOT) together with water and oil readily forms ternary microemulsions. The aqueous part of microemulsion is usually water or a solution of water with salts. The dynamic properties of microemulsions and colloidal systems are studied by photon correlation spectroscopy (PCS) [6-8] and the structure of AOT microemulsions are well investigated at water to the surfactant molar ration 6.7 [9]. A study shown, for AOT/H$_2$O/ Decane microemulsion, at the low droplet mass fractions (0.01< m$_f$ <0.1 and molar ratio 40) the collective diffusion coefficient has a linear behavior as function of the mass fraction [10]. It is well known that at high water concentration with a water to surfactant molar ratio of X = 40 the collective diffusion coefficient D$_c$ depends on the droplet mass fraction (droplet concentration) due to inter-particle interactions [10]. This study is an attempt to understand the collective diffusion coefficient of AOT/ H$_2$O/Decane microemulsion at low water concentration

X = 6.7 construct with photon correlation spectroscopy. Our previous work on AOT microemulsion at 6.7 shows a spherical to cylindrical transition [9]. In the present work, we studied the behavior of the collective diffusion coefficient (D_c) at the fix water to oil ratio (X = 6.7) and low mass fraction, by means of photon correlation spectroscopy and SAXS techniques. Moreover, we study the effect of NaCl on the D_c and structure of the AOT/H$_2$O/ Decane microemulsion.

2. Experimental

Photon Correlation Spectroscopy measurements were performed using an ALV single-detector version compact goniometer system, from ALV-GmbH, Langen, Germany. The light source is a He-Ne laser, operating at a wavelength of 632.8 nm with vertically polarized light. The beam was focused on the sample cell through a temperature-controlled cylindrical quartz container (with two plane-parallel windows), which is filled with a refractive index matching liquid (toluene). All the correlation functions in this work were fitted by a single stretched exponential function [10-13].

$$g_1(t,q) = \exp\left[-\left(\frac{t}{\tau}\right)^\beta\right] \qquad (1)$$

The stretched exponential function describes the decay processes that have a distribution of relaxation times (τ). The parameter β ($0 \leq \beta \leq 1$) shows width of the distribution function. Small-angle X-ray scattering (SAXS) measurements were performed using the pinhole SAXS in-

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strument at the Aarhus [14]. The instrument consists of an X-ray camera (NanoSTAR, Bruker AXS) with a rotating anode X-ray (Cu Kα radiation) source, cross-coupled Göbel mirrors, collimation using three pinholes, an evacuated beam path, and a 2D position-sensitive gas detector (HiSTAR). The experiments were done at a fixed wavelength of $\lambda = 1.54$ Å and two different sample-detector distances. In the current experiments small pinholes were used, giving a range of scattering vectors as $0.004 < q(1/Å) < 0.2$, ($q = 4\pi \sin\theta/\lambda$ where θ is half the scattering angle.

n-Decane, NaCl and Sodium-2-diethylhexyl sulfosuccinate, or AOT 99% were obtained from Sigma-Aldrich. Chemicals were used as received and MilliQ water was used in preparing all samples. The bottles of AOT, which are hermetically sealed, have always been stored in a refrigerator well below the melting point (23˚C). After a container was opened, the surfactant was stored in a nitrogen environment; it was still found that the surfactant did not remain stable for more than a month. The samples were prepared by mixing the components directly in glass ampoule in order to minimize the number of transfers and the glass ampoules were tightly sealed with a gas flame. The composition of each system is determined by the molar ratio X of water to surfactant molecules, $X = [H_2O]/[AOT]$ where $[H_2O]$ and $[AOT]$ are molarities of water and surfactant. The droplet mass fraction $m_f = (m_{AOT} + m_{H_2O})/(m_{AOT} + m_{H_2O} + m_{Dec})$ Which varies by the respective mass of the components water (m_{H_2O}), decane (m_{Dec}), and AOT(m_{AOT}). The microemulsions were prepared by weight, in terms of $X = 6.7$ and the different mass fraction of droplets ($m_{f,drop} = (m_{H_2O} + m_{AOT})/(m_{Dec} + m_{H_2O} + m_{AOT})$), which varies by the respective mass of n-decane (m_{Dec}), AOT(m_{AOT}). The samples were thoroughly shaken to ensure homogenization and then kept at the temperature 20˚C in a water bath for several days before the experiment. We observed that all samples were transparent at 20˚C. The mixing of NaCl with microemulsions is described by molar ratio of NaCl to AOT, $Y = [NaCl]/[AOT]$, for this experiments, $Y = 0.005$.

3. Results and Discussion

Microemulsions were formulated by mixing AOT with water and n-Decane at constant molar ratio of water to AOT ($X = 6.7$) at the different mass fraction ($0.01 < m_f < 0.3$ dilute regime).

Dynamic behavior of the AOT/H$_2$O/Decane microemulsion was probed with photon correlation spectroscopy. The correlation function shows a single stretch exponential decay at all concentrations, **Figure 1**. The AOT/H$_2$O/Decane/NaCl microemulsion at $X = 6.7$ and [NaCl]/[AOT] = 0.005 and different mass fraction is studied by photon correlation spectroscopy, **Figure 2**.
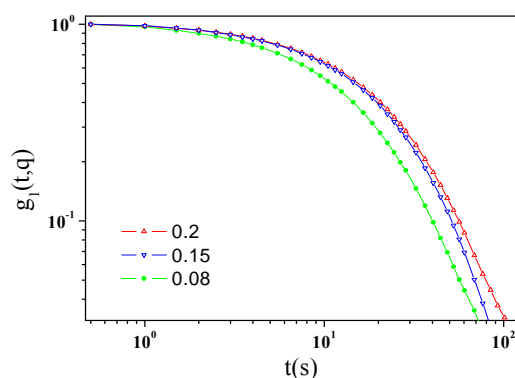

Figure 1. Correlation function as function delay time for AOT/H$_2$O/Decane microemulsion at X = 6.7 and different mass fraction at 20˚C.
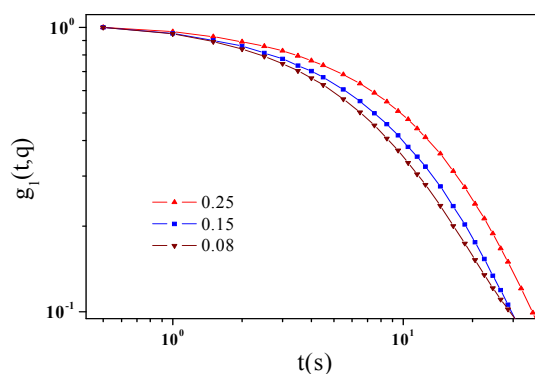

Figure 2. Correlation function as function delay time for AOT/H$_2$O/Decane/NaCl microemulsion at X = 6.7 and [NaCl]/[AOT] = 0.005, and different mass fraction at 20˚C.

All the correlation functions in this work were fitted by a single stretched exponential function, Equation (1). The collective diffusion coefficient D_c were extracted from $D_c = 1/q^2 \langle \tau \rangle$ as the function of the mass fraction for the AOT/H$_2$O/Decane and AOT/H$_2$O/Decane/NaCl microemulsion illustrated in **Figure 3**. The normalized collective diffusion coefficient show a liner behavior with negative slop between $0.01 < m_f < 0.75$. Our results show after adding NaCl to the AOT/H$_2$O/Decane microemulsion, diffusion increase clearly, **Figure 3**.

In this work, SAXS is used for the determination of the structure of AOT/H$_2$O/Decane microemulsions at 293.15 K. The SAXS method was used because the scattering of X-rays of wavelengths of a few angstroms through small angles provides a q range which is particularly appropriate for the determination of both the size of discrete reverse micelles and their interactions. The scattered intensity as a function of q for AOT/H$_2$O/Decane and AOT/H$_2$O/Decane/NaCl microemulsion is presented in the **Figure 4**, which the lines are fits to a power law, $I(q) \approx q^{-1}$, with properties of a cylindrical object. At small q, the scattering is only sensitive to the
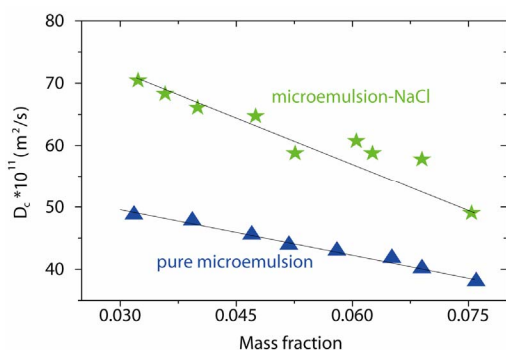
Figure 3. The normalized collective diffusion coefficient as function of mass fraction for AOT/H₂O/Decane with X = 6.7 (up triangle points) and AOT/H₂O/Decane/NaCl with X = 6.7, [NaCl]/[AOT] = 0.005 molar/l (Star points) at the temperature 20°C.
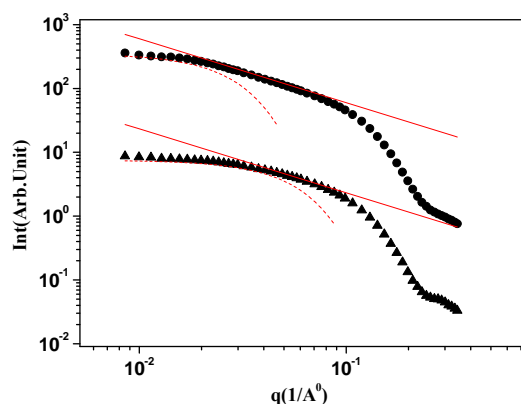

Figure 4. SAXS intensity *I(q)* of a AOT/H₂O/Decane microemulsion (▲ up triangle points) with X = 6.7 and droplet mass fraction (m_f = 0.1) and AOT/H₂O/Decane/NaCl microemulsion (● circle points) with X = 6.7 at constant droplet mass fraction (m_f = 0.1) and [NaCl]/[AOT] = 0.005. The red line is the line with slop (−1) that shown cylinder behavior of the SAXS experiments and dot line at low *q* is the fit of Guinier's law, *I(q)* ≈ exp(−(qξ)²/3) and ξ change from 50 Å to 30 Å with adding NaCl at 20°C.

overall dimension of the scattering particles, and we analyzing with Guinier's law, $I(q) \approx \exp(-(q\xi)^2/3)$, where ξ is a correlation length.

The correlation length was changed from 60 Å to 30 Å with adding NaCl to the AOT/H₂O/Decane microemulsion, **Figure 4**. The change in the correlation length of microemulsion can increase the collective diffusion coefficient of droplets. For analyzing the data, we applied a model for a mixture of core-shell spheres with an added depletion attraction due to dissolved non-adsorbing polymer. The scattering intensity as a function of scattering vector $I(q)$ of spherical Monodisperse particles can be describe with a form factor component $F(q)$, which is proportional to the scattering of a single particle, and a structure factor $S(q)$, which describes the interaction ef-

fect [15,16]:

$$I(q) = c F^2(q) S(q) \qquad (2)$$

c being a prefactor, which contains density of scattering particles. For the general case of n shells around a spherical droplet core the form factor reads.

$$F(q) = 4\pi \sum_{i=0}^{n} \Delta\rho_i \left(\frac{\sin(qR_i) - qR_i \cos(qR_i)}{q^3} \right) \qquad (3)$$

Where R_i is the radius of the ith shell or, respectively, the core R_0 and $\Delta\rho_i$ is the electron density contrast between the shells i and $I + 1$ with ρ_{n+1} and ρ_0 being the electron density of the solvent and the core, respectively. The structure factor is the Fourier transform of the pair correlation function $g(r)$.

$$S(q) = 1 + 4\pi n \int_0^\infty (g(r) - 1) \cdot r^2 \frac{\sin(qr)}{qr} dr \qquad (4)$$

The pair correlation function gives the probability to find another particle at a distance r from the center of a given particle, relative to the probability to find a particle at this distance in an ideal gas.

It is closely related to the total correlation function $h(r)$ = $g(r) -1$ and it can by means of the Ornstein-Zernike equation [17,18]. The **Figure 5** shows the compare of the SAXS experiment with the results of the hard sphere model, the points are experiments data of SAXS and the red lines are hard sphere model with core-shell radius 30nm. This results show that AOT/H₂O/Decane/NaCl microemulsion at X = 6.7 and m_f = 0.1 isn't hard sphere and more similar to cylinder shape. The increase of the NaCl to the microemulsion decrease the length scale of
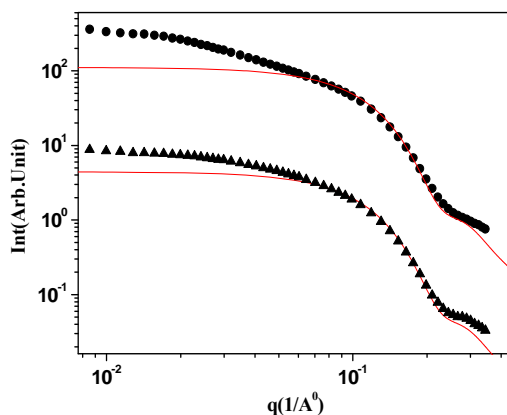

Figure 5. SAXS intensity *I(q)* of a AOT/H₂O/Decane microemulsion (▲ up triangle points) with X = 6.7 and droplet mass fraction (m_f = 0.1) and AOT/H₂O/Decane/NaCl microemulsion (■ cubic points) with X = 6.7 at constant droplet mass fraction (m_f = 0.1) and [NaCl]/[AOT] = 0.005 at temperature 20°C. The red line is the hard sphere with core shell model with the core radius 25 nm, core-shell radius 30 nm.

the cylinder and droplets become more similar to the sphere. So, the NaCl can change the cylindrical AOT/H$_2$O/Decane microemulsion to the spherical microemulsion.

Our results show that the length scale of the droplet changes from 60 Å to 30 Å and shape of droplets changed from spherical to cylindrical by increasing the mass fraction. The study of the C$_{12}$E$_5$ microemulsion at different droplet mass fraction shows a repulsive behavior that with increase of concentration of PEG on the C$_{12}$E$_5$ microemulsion, system become attractive [19,20]. In the AOT microemulsion, the collective diffusion coefficient shows a negative slop at mass fraction and so shows a attractive interaction that with add NaCl the interaction stay attractive.

4. Conclusion

The study of the collective diffusion coefficients of AOT/H$_2$O/decane microemulsions showed a negative slope as a function of droplet mass fraction at the low mass fraction. Small-angle X-ray scattering measurements revealed that AOT microemulsions show cylinder behavior at X = 6.7 and mass fraction 0.1. The NaCl can change the shape of nano-droplets from cylindrical to the spherical and the shape changing of nano-droplets can describe the increasing of collective diffusion coefficient as a function of the mass fractions.

5. Acknowledgements

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