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Electrophoretic Mobility and Size Determination of Aerosol OT Inverse Micelle in Decane Using Phase Analysis Light Scattering (PALS) and Dynamic Light Scattering (DLS) Respectively

Suparno

Abstract—**Aerosol OT is a well known surfactant used as negative charging agent. When dissolved in a solvent an Aerosol OT molecule is ionized to become negatively charged head group (RSO_3^-) and a positively charged sodium ion (Na^+). The head groups are supposed to adsorb onto the surface of dispersed particles leaving positively charged counter-ions in the solution. However, silica particles are positively charged when suspended in the dispersion of Aerosol OT in decane. Only at concentrations below approximately 0.5mM the data showed that silica particles are negatively charged.**

In searching for strong evidences supporting the above fact, inverse micelles of Aerosol OT in decane were observed in term of their charge and size growth using Phase Analysis Light Scattering (PALS) and Dynamic Light Scattering (DLS) respectively. The results showed that inverse micelles of Aerosol OT in decane were negatively charged. This evidence strongly support that the positive ions adsorb onto the particle to impart positive charge. Further measurement on electrophoretic mobility of silica particles in the system show that at Aerosol OT concentrations 100mM-1000mM silica particles are positively charged. The negativity of Aerosol OT inverse micelle in decane is growing along with the growth of the size of micelles and the growth of Aerosol OT inverse micelles was aboserved at Aerosol OT concentration 100-1000mM.

Index Terms—**Aerosol OT inverse micelle, decane, dynamic light scattering (DLS), phase analysis light scattering (PALS).**

I. Introduction

Colloid particle surface charge has an extremely important role in stabilization of colloidal solutions. In aqueous solutions most particle surface molecules are ionized, so that the particles have sufficient charges to produce electrostatic force that prevent the particles from coagulation. However, that is not the case for nonpolar solutions. The level of ionization in nonpolar solutions is relatively low, due to their low dielectric constant, so that the electrostatic force is weak and not sufficient to prevent from coagulation. This means that the solution is unstable. To overcome this problem researchers impart charges onto the surface of the dispersed particles and most of them use surfactant molecules as charging agents.[1]-[4] John F. Miller introduced and used *Phase Analysis Light Scattering* (PALS) technique to detect low mobility due to low concentration of particle surface charge [5], [6] This technique was developed based on Yoshimura's [7] crossed beam *Laser Doppler Electrophoresis* (LDE). The LDE technique for the measurements of low particle mobility in its simple form was used by H. Z. Cummins and N. Knable, [8] and modified by B. R. Ware and H. Flygare [9].

Drew Myers [10] explained that as charging agent surfactant molecules are characterized by their head group charge. Surfactants are called anionic when their head groups carry negative charges. Sulfonate (RSO^-3M^+), sulfate ($ROSO^-3M^+$) and carboxyl ($RCOO^-M^+$) belong to anionic surfactant, since their hydrophilic groups carry negative ions. On the other hand, when the hydrophilic head groups of surfactant molecules carry positive charges, these type of surfactants are called cationic. Quaternary ammonium halide ($R_4N^+X^-$) falls into this group. Some other surfactant may not carry any charge. This surfactant is then called non-ionic surfactant. The hydrophilic head groups may adsorb onto the surface of target particles in the dispersions. Therefore, particles are supposed to be negatively charged when suspended in the dispersion of anionic surfactant.

Aerosol OT (RSO_3Na) is a well known anionic surfactant. When dissolved in a solvent it produces negatively charge head groups (RSO_3^-) and positively charged sodium ions (Na^+).[1],[2] Therefore, silica (SiO_2) particle is supposed to be negatively charged when suspended in the dispersion of Aerosol OT in decane. Consequently, to meet the electro-neutrality law positively charged sodium ions stay in the solution as counter-ions to produce electrical double layer. The negativity of the silica particle surface charge should increase with the increase of Aerosol OT concentration. However, this is not the case Kier et al showed that the above explanation is only correct at concentrations below 0.5mM. At concentrations above 0.5mM to 10mM silica particles are positively charged [1], [2]. The magnitude of positive charge tends to increase, reaches its maximum value at concentration 5mM, and then decreases [1], [2].

On one hand, since the charge of silica is positive at concentrations above 5mM and the magnitude tends to decreases. Measurements of the charge of silica at concentrations above 10mM should show some consistence in sign of the charge and the trend. On the other hand, since silica particles are positively charged at concentrations higher than 0.5mM, negative charge carriers (RSO_3^-) must stay in the solution and at relatively high Aerosol OT concentrations they may create inverse micelles. If inverse micelles of Aerosol OT surfactant molecules are produced

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during silica particles charging process, the size of inverse micelles will increase with the increase of Aerosol OT concentration. Furthermore, the increase in the size of inverse micelle must be followed by the increase of the magnitude of micelle's charge. This may be observed using Dynamic Light Scattering (DLS). Suparno and his coworkers used DLS for latex particle size determination at 90° scattering angle [11]. X. Liu and his coworkers modified this technique for multiangle scattering observation.[12], [13]. J. Shen and his coworkers presented their technique for noise reduction in DLS for particle determination [14]. T. Ito and his colleagues successfully applied DLS for nanosize determination [15].

II. The Charge of Inverse Micelle of Aerosol OT in Decane

In order to gain a more comprehension of the strange behavior of silica particle charging process in the suspension of Aerosol OT in decane, a relatively large range measurement on the electrophoretic mobility of silica particles as a function of Aerosol OT concentration were performed. These measurements were done at concentration of Aerosol OT from 100mM to 1000mM using a fiber optic Phase Analysis Light Scattering (PALS). The results of the measurement are presented in Fig. 1 [1]-[4].

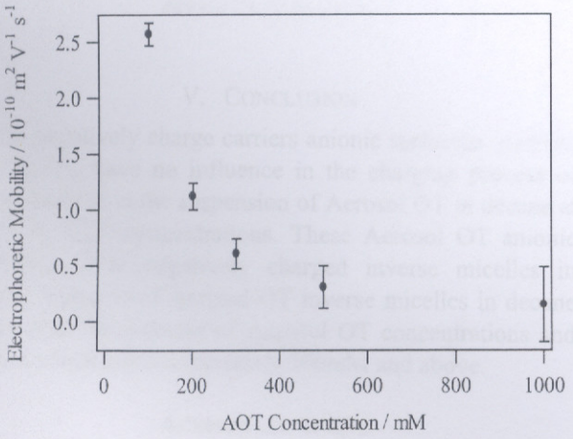

Fig. 1. Measurement of electrophoretic mobility of silica particles in the suspension of Aerosol OT in decane.

The data in Fig. 1 shows that Silica particles are positively charged at Aerosol OT concentrations between 100mM to 1000mM. It should be noted that the mobility of the particle is proportional to the magnitude of surface charge of the particle. For spherical particles with radius R the proportionality of the mobility and the charge is given by

$$q = 6\pi\eta R\mu$$

where q is the magnitude of the charge, η is viscosity, and μ is the electrophoretic mobility of the particle. A relatively comprehensive study on this topic may be found in these reference [16]-[18].

These data are consistent with those of Keir *et al.*[1] However, there is no maximum or minimum at this range of data. The Fig. 1 also shows that the magnitude of the positive charge decreases with the increase of Aerosol OT concentrations. At Aerosol OT concentration 1M the standard of deviation is quite large, so that at this point the charge might be negative. Some change in charge sign from positive to negative is likely to happen at concentrations of Aerosol OT above 1M. However, it is beyond the reach of this paper and left to the reader to investigate. Consequently, the negative charge carriers, RSO^-_3 must stay in the solution. If this is the case, the negatively charge surfactant counter-ions may form inverse micelles in nonpolar solvent, [10] decane at relatively high concentrations of Aerosol OT.

III. Negatively Charged Inverse Micelle

The negatively charge inverse micelle were detected using PALS. The data are presented in Fig. 2. The data show that at Aerosol OT concentrations up to 10mM inverse micelles are negatively charged. The magnitude of the charge increases with the increase of Aerosol OT concentration. This means that the relative number of negatively charge carriers forming each inverse micelle increases. Consequently the size of each inverse micelle should increase with the increase of Aerosol OT concentration.

The data in Fig. 2 also show that the standard deviations of the measurements of electrophoretic mobility of inverse micelles are relatively large at Aerosol OT concentration 0.5mM and below. This might be caused by rapid dynamic change of micelle formation at very low concentrations of Aerosol OT. Surfactant counter-ions are easily come and easily go to form inverse micelle at concentrations far below critical micelles concentration (CMC). The number of negatively charged head group forming each inverse micelle nearly the same with the number of positively charge carriers trapped inside the inverse micelle. However, the fact that the inverse micelles are negatively charged at Aerosol OT concentrations above 0.5mM strongly support that it is Na^+ and not RSO^-_3 that adsorb onto the surface of silica particle to give positive surface charge.

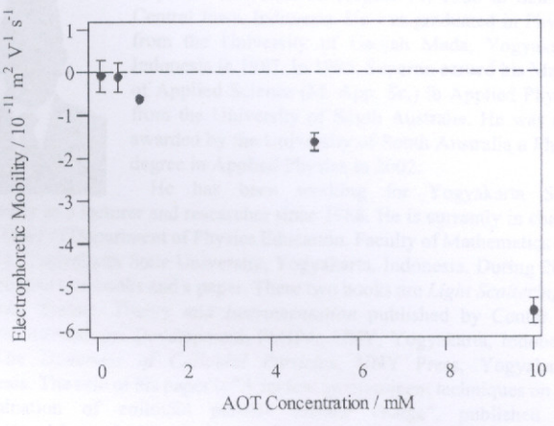

Fig. 2. Electrophoretic mobility of inverse micelle as a function of Aerosol OT concentration.

IV. Measurements of the Size of Aerosol OT Inverse Micelles

The growth of the size of inverse micelle was observed using Dynamic Light Scattering (DLS). The data are presented in Fig. 3. This figure shows that the size of inverse

micelle Aerosol OT in decane increases with the increase of Aerosol OT concentration. This is in line with the previous data (Fig. 1) showing that silica particles are positively charged at Aerosol OT concentrations 100mM – 1000M. This means that relatively higher concentrations of surfactant counter-ions stay in solution to form inverse micelles. The more surfactant counter-ion available in the solution the greater the size of inverse micelle formed. Finally the size of inverse micelle reaches plateau at approximately concentration of Aerosol OT 500mM. At this stage the size of inverse micelle is approximately 0.7nm.

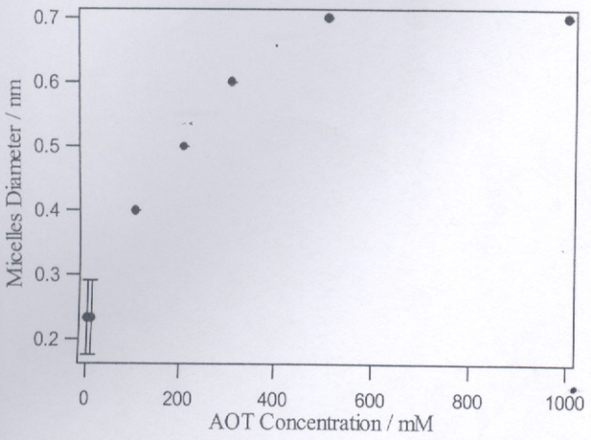

Fig. 3. The measurements of the diameter of inverse micelle as a function of Aerosol OT concentration.

V. Conclusion

The negatively charge carriers anionic surfactant Aerosol OT, RSO^-_3, have no influence in the charging process of silica particles in the suspension of Aerosol OT in decane at relatively high concentrations. These Aerosol OT anionic molecules form negatively charged inverse micelles in decane. The size of Aerosol OT inverse micelles in decane grows with the increase of Aerosol OT concentrations and reaches plateau at concentration 500mM and above.

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