Historical perspective

The role of acid–base effects on particle charging in apolar media

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ABSTRACT

The creation and stabilization of electric charge in apolar environments (dielectric constant ≈ 2) have been an area of interest dating back to when an explanation was sought for the occurrence of what are now known as electrokinetic explosions during the pumping of fuels. More recently attention has focused on the charging of suspended particles in such media, underlying such applications as electrophoretic displays (e.g., the Amazon Kindle® reader) and new printing devices (e.g., the HP Indigo® Digital Press). The endeavor has been challenging owing to the complexity of the systems involved and the large number of factors that appear to be important. A number of different, and sometimes conflicting, theories for particle surface charging have been advanced, but most observations obtained in the authors' laboratory, as well as others, appear to be explainable in terms of an acid–base mechanism. Adducts formed between chemical functional groups on the particle surface and mono-mers of reverse micelle-forming surfactants dissociate, leaving charged groups on the surface, while the counter-charges formed are sequestered in the reverse micelles. For a series of mineral oxides in a given medium with a given surfactant, surface charging (as quantified by the maximum electrophoretic mobility or zeta potential ob-tained as surfactant concentration is varied) was found to scale linearly with the aqueous PZC (or IEP) values of the oxides. Different surfactants, with the same oxide series, yielded similar behavior, but with different PZC crossover points between negative and positive particle charging, and different slopes of charge vs. PZC. Thus the oxide series could be used as a yardstick to characterize the acid–base properties of the surfactants. This has led directly to the study of other materials, including surface-modified oxides, carbon blacks, pigments (charge transfer complexes), and polymer latices. This review focuses on the acid–base mechanism of particle charging in the context of the many other factors that are important to the phenomenon, including the presence of water, of other components (e.g., synergists and contaminants), and of electric field effects. The goal is the con-struction of a road map describing the anticipated particle charging behavior in a wide variety of systems, assisting in the choice or development of materials for specific applications.

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1. Introduction

There are a number of key factors that must be accounted for in the study of particle charging in apolar media, but none as important as the mechanism by which particles obtain charge. Identifying and understanding the nature of particle charging in these systems have been of central focus in this area of study for decades and it appears that a unifying mechanism has emerged: that of acid–base interactions. It appears that, for most systems, the magnitude and polarity of charge are dependent on the relative acid–base properties of the surfactant and the particle surface, the "hard" or "soft" nature of the surfactant head group, and the ability for the surfactant to stabilize charges in reverse micelles. There have been three recent reviews published in the area of charge stabilization in nonpolar fluids [1–3]. The review by Lyklema details the energetics of micelle and particle interactions in nonpolar systems [1], the review by Dukhin and Parlia focuses on the presence of ion pairs and reverse micelles [2], and the review by Smith and Eastoe [3] provides a comprehensive overview of the current theories of charge stabilization for reverse micelles and colloidal particles as well as the current techniques used to explore charging behavior in apolar systems. The current work is intended to supplement these reviews with a focused evaluation of the validity of an acid–base charging mechanism in apolar systems.

The study of charge generation in nonpolar systems has remained an active area of interest over 100 years after it was initially investigated [4–6]. Interest in the subject was sporadic until the 1950s as the control of conductivity became important for preventing electrokinetic explosions in the petroleum industry [7]. Over time, the idea of generating and manipulating charge on particle surfaces has been applied to a number of different applications [8], particularly as it applies to electrostatic particle stabilization in media of low dielectric constant [9–15]. Some specific applications include the stabilization of carbon particles in motor oil [16–19], stabilization of pigment in paints and inks [8], electrophoretic displays [20–23], and full color "digital press" electronic lithographic printers (http://www8.hp.com/us/en/commercial-printers/indigo-presses/overview.html). For many applications it is desirable for the medium to be insulating, limiting power consumption and providing long battery life in many of the e-reader devices available today. Such applications have helped drive research to better understand the phenomena of stabilizing charge in apolar (dielectric constant of approximately 2 or lower) fluids.

The generation of stable charge in apolar systems is less probable than in aqueous systems due to the low dielectric constant of the medium. A simplistic energetic explanation of this is the Bjerrum length (λ_B) which is defined as the ratio of the force of coulombic attraction to the thermal energy in the system:

$$\lambda_B = e^2/4\pi\varepsilon\varepsilon_0 k_B T \qquad (1)$$

where e is the elementary charge, ε is the dielectric constant of the medium, ε_0 is the permittivity of free space, k_B is the Boltzmann constant, and T is the absolute temperature. In essence, λ_B characterizes the

effective distance of separation needed for charges to be stable. In room temperature water λ_B is only about 0.7 nm. This is of the order of the size of a hydration sheath of water molecules, allowing most ions to freely dissociate. In an apolar environment of a dielectric constant of 2.0 the Bjerrum length is of the order of 28 nm, preventing free dissociation of most ions. Some level of spontaneous dissociation can be achieved for very large organic ions [24]. More commonly, charge stabilization is achieved through the addition of surfactants that form reverse micelles or similar aggregates. A reverse micelle has a polar core of large dielectric surrounded by a shell of the hydrophobic surfactant tail groups. The high dielectric core is a region that is more energetically favorable to house charge. An interesting aspect of reverse micelles is that the critical micelle concentration (CMC) does not appear always to be a distinct concentration as it is in aqueous systems [25,26]. There may be surfactant doublets, triplets, and "pre-micellar" aggregates that form near the CMC [27], and it has been suggested that the presence of some water may be required for reverse micelles to form at all [28–30]. Reverse micelles are believed to be capable of acquiring charge through the process of disproportionation, where two neutral micelles collide and exchange charge to yield a positively charged micelle and a negatively charged micelle, as opposed to a single micelle expelling an ion via dissociation [8,31–35]. The reason for this is that it is more energetically favorable for both positive and negative ions to be housed in a reverse micelle as opposed to one bare ion being in the apolar medium. The charging of reverse micelles has been studied extensively using transient current measurements [35–40]. In addition, there is some evidence that near the CMC pre-micellar aggregates may engage in some amount of dissociation as the concentration of micelles is not large enough to engage in disproportionation. This is demonstrated by conductivity measurements of solutions of dioctyl sodium sulfosuccinate, more commonly known as Aerosol OT (AOT), in hexane as shown in Fig. 1 [34].
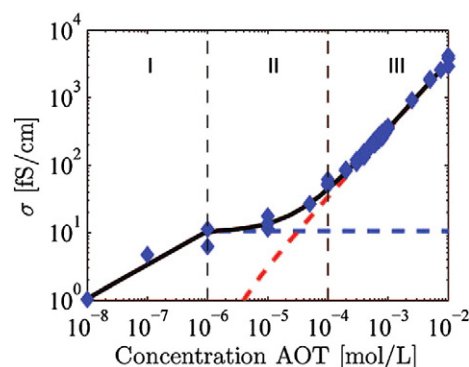

Fig. 1. Conductivity of AOT/hexadecane solutions without particles. Symbols indicate measurements. Red dashed line indicates reverse micelle contribution to conductivity. Reprinted with permission from [Sainis SK, Merrill JW, Dufresne ER, Langmuir, 2008; 24: 13334]. Copyright [2008] American Chemical Society.