Colloids and Surfaces A: Physicochem. Eng. Aspects 262 (2005) 8–13

COLLOIDS AND SURFACES A

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Surface tension and contact angle measurements of a hexadecyl imidazolium surfactant adsorbed on a clay surface[☆,☆☆]

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Received 16 November 2004; received in revised form 31 March 2005; accepted 31 March 2005
Available online 31 May 2005

Abstract

The surface tension of 1,2-dimethyl-3-*N*-hexadecyl imidazolium tetrafluoroborate (Im BF_4) as a function of concentration has been measured. Between 10^{-5} and 4×10^{-4} mol/L, the surface tension decreases with increasing imidazolium concentration. Aggregate formation appears to occur at a concentration near 4×10^{-4} mol/L for temperatures between 50 and 75 °C. Small angle neutron scattering measurements show the aggregates to be micelles with an aggregation number ≈83. Advancing and receding contact angles of Im BF_4 surfactant solutions wetting pre-equilibrated mica surfaces show surfactant adsorption occurring at 10^{-6} mol/L. At 7×10^{-5} mol/L, a maximum in the hydrophobicity of the surface is measured, with a contact angle of $84^\circ \pm 2^\circ$. The results show that the Im BF_4 surfactant adsorbs onto the mica surface and produces a hydrophobic surface, similar to the behavior of cetyl trimethyl ammonium bromide (CTAB). However, a hydrophobic surface forms at lower concentrations for the Im BF_4 surfactant than the CTAB surfactant.

Keywords: Contact angle measurements; Hexadecyl imidazolium; Surface tension; Nanocomposite; SANS

1. Introduction

The physical properties of polymeric materials can be varied through the incorporation of micrometer or nanometer sized particles to give a composite. If the particles are nanoscale in at least one dimension, the composite is called a nanocomposite. Polymer–clay nanocomposites have demonstrated improved mechanical, thermal, and flame-retardant properties compared to the neat polymers [1]. The amount of performance enhancement is determined by the size of the clay particles and the quality of the dispersion of the clay in the polymer matrix. Clays with large aspect ratio particles where the particles are well dispersed are desired, as these give the best performance enhancement.

Layered silicate clays, such as montmorillonite are commonly used in nanocomposites since they can be exfoliated. The exfoliation process involves separating the layers of the clay into large, thin platelets. Often, the clay is first swelled by the intercalation of surfactants or polymers between the layers. These swelled sheets can then be easily cleaved apart by mechanical mixing.

The tendency for the clay to be swelled is determined by the balance of the intermolecular forces between the layers of the clay. Montmorillonite clays are composed of aluminosilicate sheets. The sheets are 1 nm in thickness and are negatively charged due to a charge deficiency within the layers. Sodium or potassium ions are adsorbed between the layers and act to balance the charge.

A cationic surfactant can diffuse between the sheets and replace the adsorbed ions. If a cationic surfactant replaces the adsorbed ions, the surfactant further acts to change the charge

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doi:10.1016/j.colsurfa.2005.03.019

and chemistry of the montmorillonite surface. The surfactant will adsorb with its positively charged head group next to the negatively charged clay surface, forcing the hydrophobic surfactant tail to adsorb and be exposed to the solution. Thus, while the native montmorillonite surface is hydrophilic, the adsorption of a small amount of surfactant on the surface can render it hydrophobic [2]. This hydrophobic surface can more easily mix with a polymer melt. Hence, the surface properties of the organically modified clay dictate the dispersion and ultimately the performance of the nanocomposite.

Quaternary ammonium surfactants are commonly used to organically modify montmorillonite clays. Recent measurements, however, have shown that these surfactants do not have high thermal stability at the polymer processing temperatures [3]. In addition, the imidazolium cation has been found to be more thermally stable than the alkyl ammonium cation [4]. Also, montmorillonite clay treated with imidazolium surfactants show superior thermal properties compared to the quaternary alkyl ammonium treated montmorillonite [5].

While the adsorption of quaternary ammonium surfactants onto clay surfaces has been extensively studied [2,6], the adsorption properties of imidazolium surfactants have not been investigated. In addition, the surface tension, which gives insight into surfactant behavior, has not been measured for imidazolium surfactants. In this study, we report measurements of the surface tension and adsorption properties of Im BF_4 onto mica. Mica is used as a model clay substrate since it has similar surface properties to montmorillonite and can be cleaved along the basal plane to produce smooth, uniformly crystalline surfaces.

2. Experimental procedure

Im BF_4 was kindly supplied by Gilman et al. [5]. The surfactant was used as received. Solutions of Im BF_4 were prepared in deionized water by heating the solution to 70 °C for at least half an hour in order to dissolve the surfactant. The solutions were then left to equilibrate at room temperature for at least 1 day prior to use.

A dynamic contact angle apparatus (Krüss K121 tensiometer, Charlotte, NC) was used to measure the surface tension. The apparatus was fitted with a jacketed water bath using a Julabo circulator (model MP-BASIS, Germany) which allowed measurements at higher temperatures. Surface tension measurements were made at three temperatures: 22, 50 and 75 °C. The temperature in the circulating bath could be controlled to ±0.2 °C. Unless otherwise noted, the ± refers to the standard uncertainty in the measurements and is taken as one standard deviation of the observed values.

The Wilhelmy plate method was used to measure the surface tension of the surfactant solutions. A roughened Platinum plate was heated in a flame to clean. The plate was then hung from a microbalance. The surfactant solution was placed under the plate and gradually raised until the solution touched the bottom of the plate. The force of the liquid at the plate is monitored by the microbalance. The surface tension γ of the liquid is related to the force F on the plate according to:

$$\gamma = \frac{F}{L\ \cos\theta} \tag{1}$$

where L is the wetted length and θ is the contact angle. For clean Pt surfaces, $\theta \approx 0\cdot$

For contact angle measurements of surfactant solutions on mica, mica was cut into rectangular plates 25 mm wide. The mica was then cleaved to thicknesses ranging from 0.05 to 0.15 mm. The dimensions of the plates were measured using a caliper to ±0.025 mm. The mica plates were pre-equilibrated by immersing the mica in the surfactant solutions for at least half an hour, removed, and then blown dry with nitrogen gas to prevent evaporative deposition.

The surfactant equilibrated mica plates were clamped into the tensiometer balance and immersed into the solution at a speed of 5 mm/min. The plates were immersed to a depth of 10–12 mm and then retracted in order to get advancing and receding contact angle measurements. The contact angle can be calculated from the force measurements, knowledge of the surface tension of the solution, the wetted length of the plate, and the buoyancy.

For comparison, mica was also pre-equilibrated using a method previously described in the literature [5] A surfactant solution was prepared by dissolving 0.27 g of Im BF_4 in 2 mL of a 50/50 water/ethanol mixture. The solution was heated to 60 °C. Mica was immersed in this solution and kept at 60 °C for 2 h. The mica was then removed from the hot solution, rinsed with deionized water and blown dry with nitrogen.

small angle neutron scattering (SANS) was performed on the 8 m NG1 beamline at the National Institute of Standards and Technology in Gaithersburg, MD. The incident neutrons had a wavelength of 6 Å with a 12% spread. Surfactant solutions were prepared in D_2O (Cambridge Isotopes, 99.9%) and were equilibrated for 4 h at a temperature of 50 °C before being transferred into demountable titanium cells with 2 mm path lengths. The cells were then placed in a temperature-controlled sample chamber. One sample to detector distance was employed, yielding a range of 0.01 to 0.167 $Å^{-1}$ in the scattering vector q. The data was corrected for detector efficiency, background radiation, empty cell scattering and sample transmission.

3. Results and discussion

Measurements of the surface tension of aqueous solutions of Im BF_4 as a function of concentration are shown in Fig. 1. The circles, triangles, and squares represent measurements taken at 22, 50 and 75 °C, respectively. At 22 °C, no measurements of the surface tension of Im BF_4 were made above 1×10^{-4} mol/L since the surfactant was no longer soluble. For the temperature range 50–75 °C, the surface tension appears to be constant above a concentration of