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

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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

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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 alumino-silicate 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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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

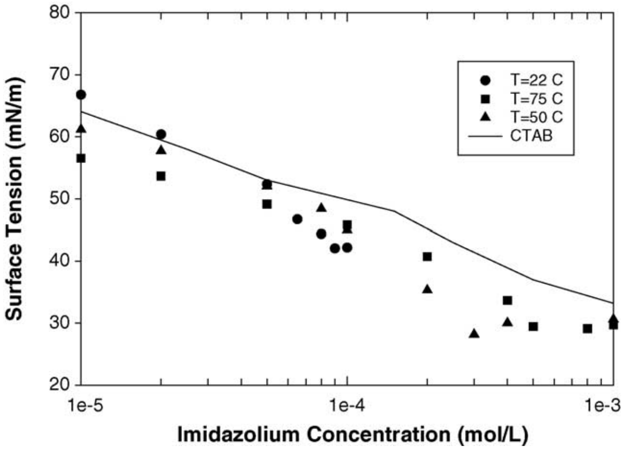

Fig. 1. Surface tension measurements of Im BF_4 surfactant as a function of concentration. The circles, triangles, and squares represent measurements taken at 22, 50 and 75 °C, respectively. The solid line represents corresponding measurements of the surface tension of CTAB taken from the literature [13]. The values of the surface tension were measured to ±2 mN/m.

$4 \times 10^{-4} \pm 1 \times 10^{-4}$ mol/L. The deflection in the slope of surface tension versus concentration is associated with aggregate formation in solution.

The presence of aggregates in solution was confirmed by SANS. To obtain structural information, i.e. the size of the aggregate, the SANS data has been fitted to a model [7,8]. The scattered intensity $I(q)$ will generally have contributions from both the form factor $P(q)$ and the structure factor $S(q)$. At the low concentrations studied, however, the volume fraction of micelles is shown to be on the order of 10^{-4} and hence, scattering arising from interactions between particles as given by $S(q)$ will be negligible and the scattered intensity will depend solely on $P(q)$. The decoupling approximation is assumed to be valid in the analysis [9].

To calculate $P(q)$, the micelles were modeled as being a hydrocarbon core surrounded by a shell (composed of the headgroups and counterions) in solution [7]. For such a model, the intensity is given by:

$$I(q) = n_\mathrm{p} P(q) = n_\mathrm{p}[V_\mathrm{C}(\rho_\mathrm{C} - \rho_\mathrm{M}) P_0(qR_\mathrm{C}) + V_\mathrm{M}(\rho_\mathrm{M} - \rho_\mathrm{S}) P_0(qR_\mathrm{M})]^2 \quad (2)$$

where n_p is the average number density of micelles, V_C is the volume of the core, R_C is the radius of the core, ρ_C and ρ_S are the scattering densities of the core and solvent, respectively, R_M is the outer radius of the shell, V_M is the volume of the micelle and ρ_M is the scattering density inside the shell. $P_0(x)$ is the expression for the form factor of a sphere and is given by $P_0(x) = 3(\sin x - x\cos x)/x^3$. D_2O was used instead of water for two reasons: (1) the contrast, or difference in scattering length densities (given below for each component), is larger between the hydrophobic micelle core and D_2O and (2) water contributes more incoherent scattering to the total intensity than D_2O. Since the volume fraction of micelles in solution is low, the increased incoherent scattering from water may hide the details of the micelle scattering. We assume that the micelles are similar in D_2O and H_2O. The aggregation number M is related to the inner core radius since the total volume of the core must equal M times the volume per chain [7]. The volume per chain, υ, is obtained from the relationship υ (Å^3) = 27.4 + 26.9n, where n is the carbon length of the chain [10]. Both shell thickness and M are varied to fit the data. The scattering densities of the core, shell, and solvent are assumed to be −3.6 e–7, 3.0 e–6, 6.3 e–6 Å^{-2}, respectively [7].

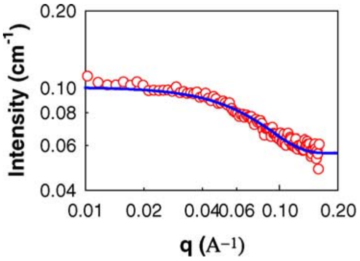

Fig. 2. SANS data of the scattering intensity of a solution of 6×10^{-4} mol/L Im BF4 at 50 °C as a function of the scattering vector q. The solid line is a fit to the data assuming the model described in Eq. (2).

The data in Fig. 2 shows the log of the absolute intensity I versus log of the scattering vector q, where $q = (4\pi/\lambda)\sin(\theta/2)$, where λ is the wavelength of the neutrons and θ is the scattering angle for Im BF_4 concentration of 6×10^{-4} mol/L. Using Eq. (2) to fit the data, the core radius and shell thickness were found to be 20.5 and 8.6 Å, respectively. The measured core radius corresponds to the extended length of a C_{16} chain. The aggregation number is found to be ≈83 and the critical packing parameter is 0.314 for Im BF4 micelles at 50 °C, which is what is expected for spherical micelles [11].

There appears to be only minimal change in the surface tension with temperature, as has been observed with other surfactants, at least for the temperatures studied in this experiment [12]. The surface tension of Im BF_4 can be compared to the surface tension of hexadecyl trimethyl ammonium bromide CTAB (Fig. 1, solid line) taken from the literature [13]. A lower surface tension at each concentration is measured for the Im BF_4 surfactant than the CTAB surfactant, indicating that the Im BF_4 surfactant is more surface active than the CTAB surfactant. In addition, the critical micelle concentration (CMC) for CTAB $\approx 1 \times 10^{-3}$ mol/L, whereas micelles appear to be forming at a concentration near $(4 \pm 1) \times 10^{-4}$ mol/L for the Im BF_4. Hence, the solubility of the Im BF_4 molecule is less than the solubility of the CTAB molecule. Since the hydrophobic tail on each molecule is the same (hexadecyl), the difference in solubility must be related to the properties of the head group as well as the corresponding counterion.

Fig. 3 shows typical contact angle versus immersion depth plots for a concentration of 1×10^{-5} mol/L Im BF_4. In Fig. 3a, the mica has been equilibrated with surfactant solution prior to immersion into the aqueous surfactant solution. Both the advancing and receding angles are independent of

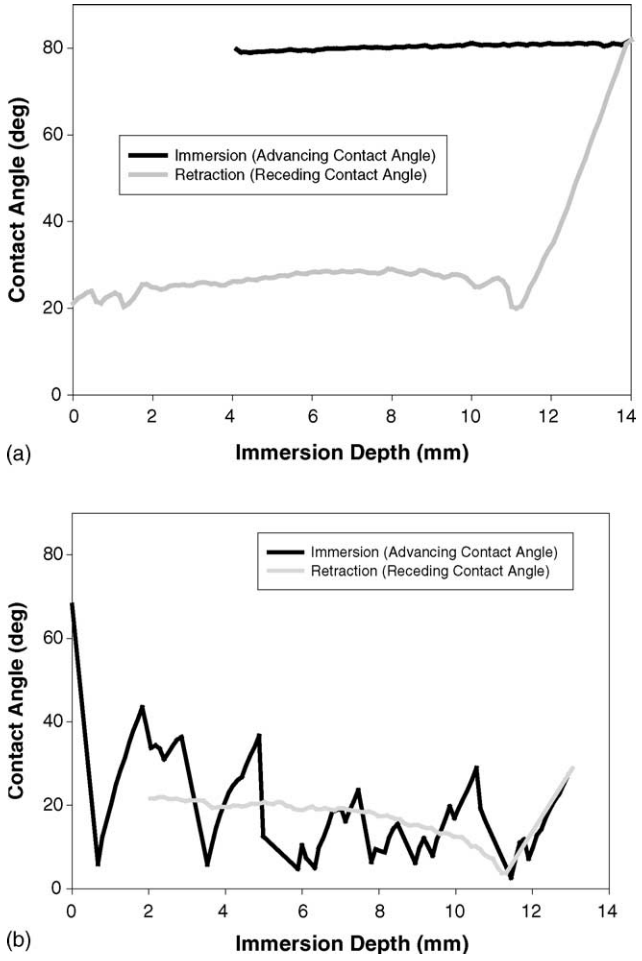

Fig. 3. (a) Advancing and receding contact angles as a function of immersion depth for pre-equilibrated mica immersed in 1×10^{-5} mol/L Im BF_4 surfactant solution. The immersion speed was 5 mm/min. (b) Advancing and receding contact angles as a function of immersion depth for bare mica immersed in 1×10^{-5} mol/L Im BF_4 surfactant solution. The immersion speed was 5 mm/min.

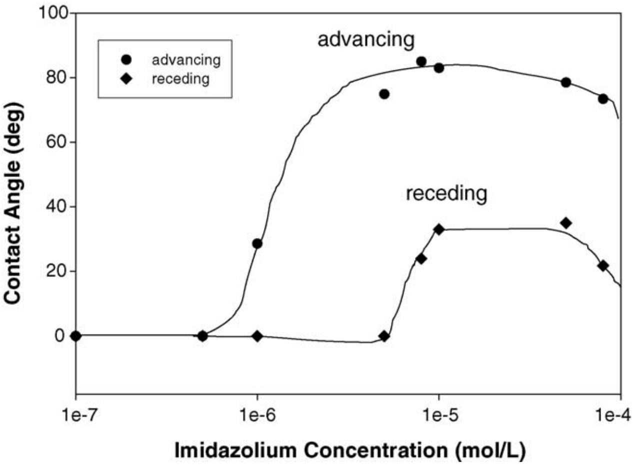

Fig. 4. Advancing (circles) and receding (diamonds) contact angles of Im BF_4 surfactant solution on pre-equilibrated mica surfaces measured as a function of Im BF_4 concentration. The values of the contact angle were measured to ±3°. The immersion speed was 5 mm/min. The solid lines are drawn through the data and are meant to guide the eye.

immersion depth. In Fig. 3b, unequilibrated (bare) mica is immersed in the surfactant solution, and the contact angle data exhibits stick-jump behavior as the depth is increased. This behavior has been observed for other systems including bare mica immersed in aqueous solutions of CTAB [14]. Clearly, the advancing and receding contact angles cannot easily be extracted from experiments using bare mica as a substrate and this justifies our use of pre-equilibrated mica in all contact angle experiments.

Fig. 4 shows the dynamic advancing (circles) and receding (diamonds) contact angles of aqueous imidazolium BF_4 surfactant solutions wetting a pre-equilibrated mica surface. The wetting solution and the pre-equilibrated solution were the same concentration. The contact angle data shows measurable adsorption onto the mica surface beginning at approximately 10^{-6} mol/L and forms a hydrophobic surface at approximately 7×10^{-5} mol/L. A contact angle of 84° ± 2° was measured at this concentration. We assume a monolayer has formed at this concentration. At higher concentrations, the measured contact angle decreased, presumably due to bilayer formation. Similar measurements on CTAB surfaces show adsorption occurs at slightly higher concentrations, beginning around 10^{-5} mol/L [15].

Recent measurements of self-assembled imidazolium ion-terminated monolayers on gold have shown the contact angle of these surfaces to be 35° ± 1° [16]. In those experiments, the imidazolium head group is adjacent to the wetting solution, and the contact angle is relatively low. In the experiments reported here, a much larger contact angle is measured, confirming that the monolayer is adsorbed with the head group next to the mica surface and the hydrophobic tail oriented away from the surface, as expected.

The mica sheets were also treated by the same method used for previous melt processing experiments [5]. The mica was pre-equilibrated in a 50/50 ethanol/water mixture at 60 °C for 2 h, as described in the experimental section. The advancing contact angle of an aqueous solution measured on a pre-equilibrated mica sheet was 75° ± 3°. Thus, this method also produces a hydrophobic surface.

While mica is not easily swelled, montmorillonite can be swelled by incorporation of surfactants between the layers. For alkylammonium ions containing alkyl groups with more than eight methylene groups, the number of adsorbed alkylammonium ions were found to be fixed in excess of the cation-exchange capacity (CEC). [2] In addition, the spacing between the basal plane of the montmorillonite increased from 1.24 nm for NH^+ treated montmorillonite to 1.77 nm for dodecylammonium treated montmorillonite [2]. This indicates that the alkyl tails of the surfactant monolayers are laying adjacent to the mica, and that two layers reside in the layers. This is shown schematically in Fig. 5. For Na montmorillonite, the interlayer spacing was measured to be 1.19 nm

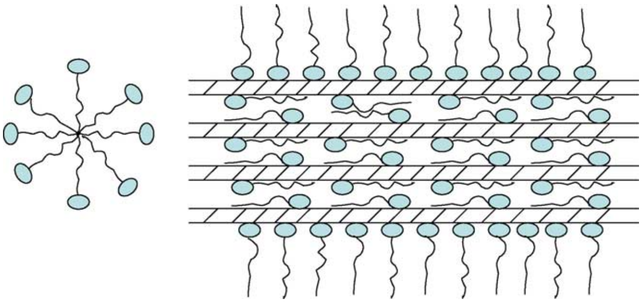

Fig. 5. Schematic diagram of the orientation of surfactant ions on the surface of montmorillonite clays. A typical micelle is also shown. The micelle is too large to fit between the layered clay. Hence, adsorption can only occur via surfactant monomer or dimer diffusion between the clay layers and displacing the native cations.

which increased to 1.82 nm when treated with imidazolium BF_4 [17]. Hence, the interlayer spacing for montmorillonite treated with either alkyl ammonium cations or alkyl imidazolium cations are similar and thus the imidazolium BF_4 surfactant must be also lying adjacent to the montmorillonite surface, with two surfactant layers in each layer.

The diffusion of surfactants into the interstitial layers of the montmorillonite must occur via monomer or dimer adsorption since the layer spacing is too small to allow larger aggregates (see Fig. 5). Since aggregates appear at 7×10^{-4} mol/L, and monomer concentration is relatively constant once aggregates occur, little is to be gained by using higher concentrations, as long as the amount of surfactant depletion is taken into account. In fact, the contact angle results indicate that full monolayer coverage occurs around 1×10^{-5} mol/L. Thus, the optimum surfactant concentration to use should be in the range 1×10^{-5} to 7×10^{-4} mol/L.

The interlayer spacing is much less than expected if the monolayers were fully packed and oriented away from the mica surface. In that case the interlayer spacing should be more like 3 nm (1.5 nm per surface). It should also be noted that the outer montmorillonite surface which is exposed to solution and is representative of the measurements reported here may be different than the interstitial surface. On the outer surface, a fully packed monolayer can occur with the hydrophobic tail oriented away from the clay surface. The interlayer spacing consists of surfactants laying flat against the montmorillonite surface. If these inner layers are exposed in the extruder, the surfactant molecules in these inner surfaces are likely not as tightly packed as the outer surface. However, as the contact angle data suggest, even a small amount of surfactant adsorbed on the clay surface can make it hydrophobic.

Studies of the adsorption of surfactants onto clay surfaces have shown that adsorption occurs via electrostatic interaction between the surface and the monomer. Usually, it is the interaction of the charged head group with the surface that acts to anchor the molecule to the surface. For hexadecylpyridinium ions, the pyridinium ring adsorbs to the mica surface at 34° angle to the mica basal plane [18]. In solution, spherical admicelles of CTAB and hexadecylpyridinium ions have been observed at concentrations above the CMC [19,20]. The adsorption and orientation of hexadecyl imidazolium ions adsorbed onto clay surfaces may behave similarly to the hexadecylpyridinium ions.

The results presented here give insight into the wetting behavior of an imidazolium surfactant onto a clay surface. The Im BF_4 surfactant produces a hydrophobic surface which can easily mix with a polymer melt. The wetting of mica by Im BF_4 is similar to the wetting behavior of CTAB, however a hydrophobic surface occurs at lower concentrations for the imidazolium surfactant than the CTAB surfactant. Given that the Im BF_4 surfactant produces a hydrophobic surface and that the surfactant is more stable at processing conditions than the alkyl ammonium surfactants, it appears that this surfactant might be a better choice for organic modifiers.

4. Conclusions

The imidazolium BF_4 surfactant adsorbs onto a mica surface, giving a hydrophobic surface. The surface tension data suggest that the imidazolium surfactant is more surface active and less soluble than the CTAB surfactant. Micelle formation appears to occur at a concentration near 4×10^{-4} mol/L with the aggregation number of the micelle measured to be 83. This concentration is about half the concentration needed for micelles to appear in CTAB solution.

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