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Release of surfactants from organo-modified montmorillonite into solvents: Implications for polymer nanocomposites

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ABSTRACT

A liquid chromatography-tandem mass spectrometry (LC-MS/MS) method was developed to measure the surfactant released from organo-modified montmorillonite (OMMt) into different solvents used as food simulants. Two types of OMMt (Nanomer I.44P and Cloisite 93A) containing different quaternary alkylammonium surfactants were selected. The release of surfactant from clay suspensions was investigated by taking three factors into consideration: temperature, sonication and simulant type. At room temperature (22 °C), the amount of surfactant (in percentage) released from the OMMt into pure ethanol was about 25% (from the I44P clay) and 11% (from the Cloisite clay). However, more surfactant was released into ethanol when the clay suspensions were held at higher temperatures, and a two-fold amount of surfactant was released when the suspensions were sonicated. The maximum surfactant release from both types of OMMt was achieved when the clays were dispersed in pure ethanol, while significantly less surfactant was released into 50% ethanol (ethanol/water, 1:1) or pure water. Finally, the affinity between the solvent and the surfactant was discussed based on solubility parameters and correlated with the surfactant release into different solvents.

1. Introduction

Clays, including montmorillonite (Mt) and silicates of nano-size dimensions, are extensively used as engineered nanoparticles in polymer nanocomposites. The addition of clays at small loadings can significantly improve the performance of polymer materials, thereby expanding their application in consumer goods (Alexandre and Dubois, 2000). Mt is a type of naturally occurring clay with a crystal structure consisting of two silica tetrahedral sheets fused to an edge-shared alumina octahedral sheet (Sinha Ray and Okamoto, 2003). Each Mt layer has a thickness of about to 1 nm and a diameter of 20–200 nm (Ajayan et al., 2003). The clay layers are usually parallel stacked to form tactoids with up to 1 nm interlayer space containing hydrated exchangeable cations (e.g., Na^+ or K^+). Mt can be organically modified by replacing the exchangeable cations with organic cationic surfactants (e.g., alkylammonium cations) changing its nature from hydrophilic to hydrophobic, which improves the compatibility of the clay with the polymers (De A Prado et al., 2005).

Polymer nanocomposites with organo-modified montmorillonite (OMMt) as the nanofiller account for over half of total nanocomposite consumption (estimated at 225,000 metric tons in 2014), and the primary application is in the packaging industry (Patel et al., 2006; BCC Research, 2014). There is increasing concern about the potential release of clay particles and surfactants from nanocomposites, either into foods when used as food packaging materials in direct contact with foods or into the surrounding environment (Chaudhry et al., 2008; Gottschalk and Nowack, 2011; Szakal et al., 2014). Although a few studies have addressed the release of clays from nanocomposites (Schmidt et al., 2009; Mauricio-Iglesias et al., 2010; Diaz et al., 2013), to the best of the authors' knowledge, no attention has been given to the release of surfactants. Some surfactants have been shown to be toxic to ecosystems, animals and humans (Lewis, 1991; Talmage, 1994; Ying, 2006). Therefore, it is critical to understand the release of surfactants from the OMMt under different conditions before further investigation of their transport within different environmental or biological systems takes place.

The surfactant used as the organo-modifier of Mt is usually not a single compound but a mixture of different components with similar structures. For example, one type of the most commonly used surfactants is quaternary alkylammonium salt with varied alkyl chain lengths. The instrumental method used for the measurement of surfactant should enable the separation of different components in an efficient manner and the subsequent detection of each component. Meanwhile, the measurement should be relatively rapid, which is critical for real-time transport studies. There are some studies on the analysis of surfactants by liquid chromatography (Ferrer and Furlong, 2001; Nishikawa et al., 2003; Li and Brownawell, 2009); however, the separation of various components in the quaternary alkylammonium surfactants was difficult, and the analysis time was long in order to achieve a good separation, which will make the method difficult to use for migration studies. In addition, the analysis of surfactant was usually from

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Table 1
MS parameters for multiple reaction monitoring of surfactant components.

Component	Precursor ion (m/z)	Daughter ion (m/z)	Dwell (s)	Cone voltage (V)	Collision voltage (eV)
$C_{16}C_{16}$-Arquad	494.55	270.34	0.3	60	44
$C_{16}C_{18}$-Arquad	522.60	270.33	0.3	60	44
$C_{18}C_{18}$-Arquad	550.65	298.40	0.3	60	44
$C_{16}C_{16}$-Armeen	480.33	256.33	0.3	60	38
$C_{16}C_{18}$-Armeen	508.38	256.29	0.3	60	44
$C_{18}C_{18}$-Armeen	536.38	284.28	0.3	60	44

environmental samples (sewer water, soil, etc.) not from food or food simulants.

The objectives of this study were to (1) develop a liquid chromatography-tandem mass spectrometry (LC-MS/MS) method to identify and quantify surfactants in solution, (2) to apply the method to measure and describe the release of surfactants from OMMt into solvents used as food simulants and (3) to investigate the effect of different factors (temperature, sonication and simulant type) on surfactant release.

2. Materials and methods

2.1. Clays and surfactants

Two types of OMMt were used in this study. Nanomer® I.44P (herein referred to as I44P clay) was obtained from Nanocor (Aberdeen, MS, USA) containing 65 wt% Mt and 35 wt% surfactant. It is normally included in nanocomposites with polyolefins such as polyethylene (PE) and polypropylene (PP). Cloisite® 93A (herein referred to as Cloisite clay) was obtained from Southern Clay Products (Gonzales, TX, USA) containing 60 wt% Mt and 40 wt% surfactant. It is commonly used in nanocomposites with nylon. The surfactant for I44P clay (dimethyl dihydrogenated tallow ammonium chloride or Arquad® 2HT-75, around 75 wt% purity and the rest includes water, isopropanol and free amine) and the surfactant for Cloisite clay (methyl dihydrogenated tallow amine sulfate or Armeen® M2HT, around 90 wt% purity and the rest includes water, primary and secondary amines) were obtained from AkzoNobel (Chicago, IL, USA). According to the supplier and the MSDS, both surfactants consist of two alkyl chains (hydrogenated tallow) ranging from 12 to 18 carbons with mainly C_{16} and C_{18} (>96 wt%). Therefore, only the three main components of each surfactant were considered for analysis, designated as $C_{16}C_{16}$-Arquad/Armeen, $C_{16}C_{18}$-Arquad/Armeen and $C_{18}C_{18}$-Arquad/Armeen.

2.2. Thermogravimetric analysis

The heat stability of the surfactant within each clay was characterized by thermogravimetric analysis (TGA) with a Q-50 thermogravimetric analyzer (TA Instruments Inc., New Castle, DE, USA). A heating cycle from room temperature to 700 °C at a ramp rate of 10 °C min^{-1} was used. The experiment was conducted in a high-purity flowing nitrogen atmosphere (70 cm^3 min^{-1}) to avoid oxidation, and the weight loss was recorded.

2.3. Release experiments

The release of surfactant from OMMt into food simulants was evaluated as a function of temperature, sonication or simulant type and detected by using an LC-MS/MS method. No stirring was applied during the release experiment to avoid any impact of stirring on surfactant release. The food simulants used included ethanol (100%), 50% ethanol (ethanol/water = 1:1, v/v) and water. Both solvents and combinations are commonly used to simulate a wide variety of food systems: water for aqueous foods, ethanol for fatty foods, and water-ethanol combinations for fatty foods and alcoholic foods (FDA, 2007).

For the first test to assess the effect of temperature, clay suspensions (60 mg L^{-1}, containing about 21 mg L^{-1} surfactant for I44P clay and 24 mg L^{-1} surfactant for Cloisite clay) were prepared by carefully weighing 2.4 mg of I44P or Cloisite clay into amber glass vials (25 × 95 mm) and adding 40 mL ethanol into each vial. For each clay type, a total of 9 vials were prepared, which were then divided into three groups (3 vials per group), and each group of vials was held in an oven set at 22, 40 or 70 °C for up to 24 h. For another temperature test, Cloisite clay was heated in a Q-50 thermogravimetric analyzer at 240 °C for 7 min and then dispersed in ethanol at a concentration of 60 mg L^{-1}. The suspension was transferred to 3 vials (40 mL per vial), and the vials were stored at 40 °C for up to 24 h.

To assess the effect of sonication on the release of surfactant, clay suspensions were prepared in ethanol (60 mg L^{-1}) as described above. For each clay type, 3 vials were prepared and sonicated (Model FS30 ultrasonic cleaner, 35 kHz, Fisher Scientific Co., Pittsburg, PA, USA) at 40 °C for up to 6 h. Special care was taken to maintain the temperature at 40 °C in the sonicator. The concentration of surfactant released from the sonicated samples and the unsonicated samples exposed to 40 °C (in the temperature effect test) were compared.

To evaluate the effect of simulant type, clay suspensions in ethanol, 50% ethanol or water (60 mg L^{-1}) were prepared in amber glass vials, in triplicate, as described above. All vials were held at 40 °C for up to 24 h.

2.4. LC-MS/MS analysis

The measurement of the surfactant released from the OMMt into solution was carried out by an LC-MS/MS method. A Waters Quattro micro API Tandem Quadrupole mass spectrometer (Waters Co., MA, USA) coupled to a Shimadzu LC-20 AD HPLC system (Shimadzu Scientific Instruments, MO, USA) and an SIL 5000 auto-sampler was used. The system was operated by using Waters MassLynx 4.0 software.

The separation of different components of the surfactant with the HPLC was achieved on a Waters Symmetry C18 column (3.5 μm, 2.1 × 100 mm) with a Symmetry guard column operated at 30 °C. A gradient elution was performed at a flow rate of 0.2 mL min^{-1} for 15 min with a binary mobile phase consisting of (A) 0.1% formic acid in water and (B) methanol. The gradient program was set as follows: 0–2 min, 20% B; 2–3 min, 20–80% B; 3–5 min, 80–95% B; 5–13 min, 95% B; and 13–15 min, 20% B.

Composition analysis of each surfactant standard was conducted by setting the MS detector at electrospray ionization in positive mode

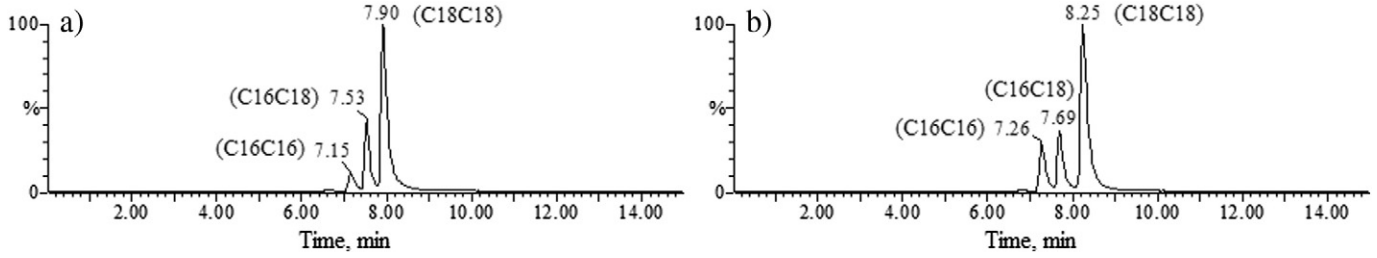

Fig. 1. LC-MS/MS chromatograms obtained for the three main components of (a) Arquad 2HT-75 and (b) Armeen M2HT surfactants in 5 mg L^{-1} standard solution.