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Synthesis, adsorption and aggregation properties of trisiloxane room-temperature ionic liquids

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ABSTRACT

Three amphiphilic trisiloxane room-temperature ionic liquids, [(Si(3)N(2)-AC(2), Si(3)N(2)-PC(2), Si(3)N(2)-BC(2))], were designed and synthesized. Their surface activity and aggregation behavior in aqueous solution were systematically investigated through measurements of surface tension, conductivity, and transmission electron microscopy (TEM). Surface activity measurements indicate that the trisiloxane ionic liquids can significantly reduce the surface tension of water, as shown by the γ_{cac} values of about 20 mN/m. Aggregation behavior studies reveal that the aggregates formed in Si(3)N(2)-AC(2) and Si(3)N(2)-PC(2) solutions are observed to be small spherical aggregates, while those formed in Si(3)N(2)-BC(2) solutions are found to be large necklace-like aggregates.

1. Introduction

Ionic liquids (ILs) have unique and high performance properties such as insignificant vapor pressure, high ion conductivity, outstanding catalytic properties, nonflammability, and stability at temperatures up to or greater than 300 °C [1–5]. In view of these improved properties, their utilization in organic synthesis, chemical separation, nanomaterial preparation, and polymer gel electrolytes has been widely reported [6–8]. The ILs that consist of a charged hydrophilic headgroup and a nonpolar hydrophobic tail are expected to be surface active and are referred to as surface active ionic liquids (SAILs). Similar to normal surfactants, SAILs can form an aggregation in aqueous solution, and their aggregation behavior has been a focus of recent investigations [9–13]. Numerous SAILs based on imidazolium, pyridinium, and quarternary ammonium cations with a variety of anions such as halides, ClO_4^-, BF_4^-, and $CF_3SO_3^-$ have been successively synthesized. Structural effects of anions and cations on the aggregation behavior of 1-alkyl-3methylimidazolium ILs have been described by Wang and colleagues [14]. The adsorption and aggregation of a chiral long-chain IL ([C_{16}hpim] Br) have also been reported [15]. The Luis Laboratory has studied the self-aggregation behavior of the double-chained IL 1, 3-didecyl-2-methylimidazolium chloride [$C_{10}C_{10}$mim]Cl) in aqueous solution [16]. Even so, the development of SAILs is generally confined to N-alkyl ILs. Moreover, their melting points begin to rise dramatically once an appended N-alkyl group exceeds seven carbon atoms in length [17], which restrict the applications of SAILs.

Siloxane surfactants have attracted considerable attention due to their remarkable properties such as flexibility, high surface activity, low toxicity and biocompatibility. In particular, trisiloxane surfactants are under the spotlight, because they have abilities to decrease the surface tension of water to approximately 20 mN/m [18–20]. In this paper, three novel room-temperature SAILs (RT-SAILs), comprising the trisiloxane cations and the well-known homologous series of carboxylate anions (Si(3)N(2)-AC(2), Si(3)N(2)-PC(2), Si(3)N(2)-BC(2)), were synthesized. The trisiloxanes were introduced as hydrophobic group to improve the surface activity of the ILs while keeping melting points below room temperature. Their adsorption properties were studied using surface tension and electrical conductivity measurements, while the aggregation behavior was monitored by transmission electron microscopy (TEM). However, up until now, research on organosilicon RT-SAILs has not yet been reported. Therefore, the findings obtained in the present study will be useful in understanding the fundamental properties of organosilicon RT-SAILs in aqueous solutions and in designing novel RT-SAILs in colloid and interfacial science.

2. Experimental

2.1. Materials and characterization

N-(2-aminoethyl)-3-aminopropylmethyldimethoxysilane (AAMDS), hexamethyldisiloxane (HMDS) and tetramethylammonium hydroxide

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(TMAH) were obtained from Aldrich. Dichloromethane, acetic acid, propionic acid and n-butyric acid were purchased from the Beijing Chemical Reagent Company. All the reagents are of analytical grade and were used without further purification.

Fourier transform infrared spectroscopy (FT-IR) was performed with a Hitachi 270-30 spectrometer. The examples were smeared directly onto a KBr plate for measurement.

Proton nuclear magnetic resonance (^{1}H and ^{13}C NMR) spectroscopy was recorded in $CDCl_3$ with a Varian INOVA-400 MHz spectrometer. Since TMS cannot easily be used as internal standard because of the overlapping with other methyl signals, we used the residual protons of the solvent $\delta^1H = 7.26$ and $\delta^{13}C = 77.00$.

2.2. Synthesis

The three trisiloxane RT-SAILs were synthesized according to Scheme 1.

2.2.1. Synthesis of N-(2-aminoethyl)-3-aminopropyltrisiloxane, Si(3)N (2), (**2**)

The mixture of AAMDS (28.72 g, 0.15 mol), HMDS(121.80 g, 0.75 mol) and TMAH (0.742 g,0.008 mol) was stirred at reflux temperature for 2 h under nitrogen atmosphere. After the solvent was removed by evaporation, the residue was purified by vacuum distillation. Yield: 44.73% (colorless liquid). bp 142 °C/7 mm Hg.

IR (KBr, cm^{-1}): 3296 ν(N–H), 2958 ν(C–H), 1257 ν(Si–Me_3), 1050 ν(Si–O–Si), 841 ν(Si–Me_3), 754 ν(Si–Me_3); ^{1}H NMR ($CDCl_3$, ppm) δ: 0.008 (s, 3H, $SiCH_3$), 0.03 (s, 18H, $Si(CH_3)_3 \cdot 2$), 0.40 (t, 2H, $SiCH_2$), 1.21 (m, 3H, –NH and $-NH_2$), 1.43 (m, 2H, CH_2CH_2NH), 2.51 (m, 2H, $-CH_2NH$), 2.61 (m, 2H, $-CH_2CH_2NH_2$), 2.72 (m, 2H, $-CH_2CH_2NH_2$).

2.2.2. Synthesis of the trisiloxane RT-SAILs (**3**, **4**, **5**)

Neutralization reactions were conducted with Si(3)N(2) (5.59 g,0.02 mol) and carboxylic acid (1.27–1.85 g,0.021 mol) dissolved in around 40 mL dichloromethane. Then the mixture was refluxed for 6 h. After the solvent was removed by rotary evaporation, the pure product was obtained.

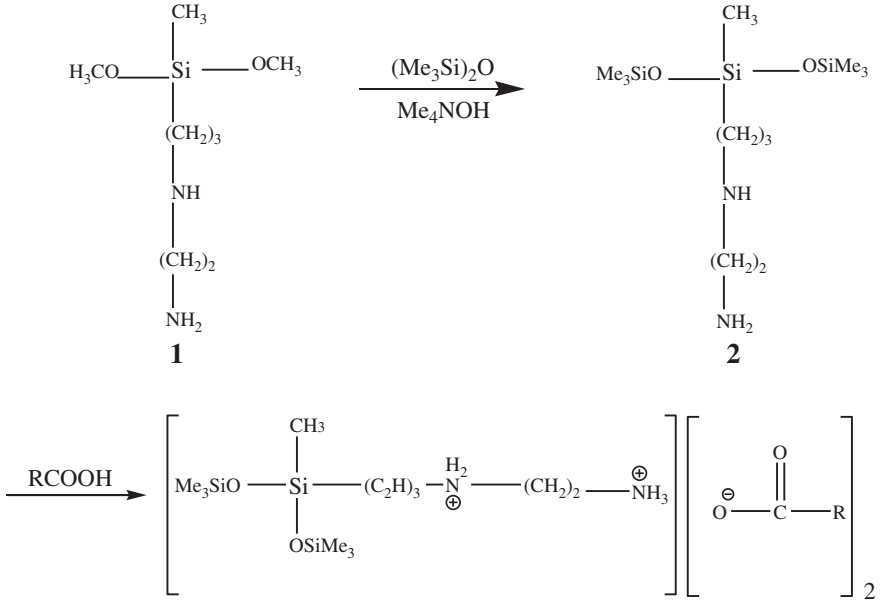
Si(3)N(2)-AC(2), (**3**) Yield: 96.16%, ^{1}H NMR ($CDCl_3$, ppm): δ:0.01 (s, 3H, $SiCH_3$), 0.06 (s, 18H, $Si(CH_3)_3 \cdot 2$), 0.44 (t, 2H, $SiCH_2$), 1.68 (m, 2H, $SiCH_2CH_2CH_2$), 1.91 (s, 3H, CH_3COO^-), 2.81 (m, 2H, $-CH_2NH_2$), 3.08 (m, 2H, $-CH_2CH_2NH_3$), 3.18 (m, 2H, $-CH_2CH_2NH_3$), 9.24 (m, 5H, $-NH_2$ and $-NH_3$); ^{13}C NMR ($CDCl_3$, ppm) δ: 0.56 ($SiCH_3$), 2.11 ($Si(CH_3)_3 \cdot 2$), 14.41 ($SiCH_2$), 20.25 ($SiCH_2CH_2$), 23.54 (CH_3COO^-), 36.62 (CH_2NH_2), 45.63 ($CH_2CH_2NH_3$), 50.67 ($CH_2CH_2NH_3$), 178.01 (COO^-).

Si(3)N(2)-PC(2), (**4**) Yield: 96.70%, ^{1}H NMR ($CDCl_3$, ppm): δ:0.02 (s, 3H, $SiCH_3$), 0.04 (s, 18H, $Si(CH_3)_3 \cdot 2$), 0.48 (t, 2H, $SiCH_2$), 1.03 (t, 3H, CH_3CH_2 CH_2COO^-), 1.68 (m, 2H, $SiCH_2CH_2CH_2$), 2.14 (s, 3H, CH_2COO^-), 2.78 (m, 2H, $-CH_2NH_2$), 3.08 (m, 2H, $-CH_2$ CH_2NH_3), 3.21 (m, 2H, $-CH_2CH_2NH_3$), 9.41 (m, 5H, $-NH_2$ and $-NH_3$); ^{13}C NMR ($CDCl_3$, ppm) δ: 0.47 ($SiCH_3$), 1.56 ($Si(CH_3)_3 \cdot 2$), 9.78 ($CH_3CH_2COO^-$), 14.24 ($SiCH_2$), 20.31 ($SiCH_2CH_2$), 29.63 ($CH_3CH_2COO^-$), 36.42 (CH_2NH_2), 45.48 ($CH_2CH_2NH_3$), 51.09 ($CH_2CH_2NH_3$), 180.42 (COO^-).

Si(3)N(2)-BC(2), (**5**) Yield: 93.79%, ^{1}H NMR ($CDCl_3$, ppm): δ:0.03 (s, 3H, $SiCH_3$), 0.07 (s, 18H, $Si(CH_3)_3 \cdot 2$), 0.44 (t, 2H, $SiCH_2$), 0.92 (t, 3H, CH_3CH_2 CH_2COO^-), 1.56 (m, 2H, $CH_3CH_2CH_2COO^-$), 1.68 (m, 2H, $SiCH_2CH_2CH_2$), 2.14 (t, 2H, CH_2COO^-), 2.75 (m, 2H, $-CH_2NH_2$), 3.07 (m, 2H, $-CH_2CH_2NH_3$), 3.19 (m, 2H, $-CH_2CH_2NH_3$), 9.10 (s, 5H, $-NH_2$ and $-NH_3$); ^{13}C NMR ($CDCl_3$, ppm) δ: 0.05 ($SiCH_3$), 2.21 ($Si(CH_3)_3 \cdot 2$), 13.96 ($CH_3CH_2CH_2COO^-$), 15.17 ($SiCH_2$), 19.80 ($CH_3CH_2CH_2COO^-$), 20.95 ($SiCH_2CH_2$), 37.14 (CH_2NH_2), 39.12 ($CH_3CH_2CH_2COO^-$), 46.47 ($CH_2CH_2NH_3$), 51.76 ($CH_2CH_2NH_3$), 180.84 (COO^-).

2.3. Apparatus and procedures

Surface tension measurements were carried out by the ring method with a KRUSS K12 Processor Tensiometer at 298 ± 0.1 K. Concentrated stock solutions of surfactants were prepared in doubly distilled water, and then diluted to appropriate concentrations. The solutions were aged for at least 24 h before the determinations. All measurements were repeated until the values were reproducible.



R=C_nH_{2n+1}(n=1,2,3)

3 n=1 (Si(3)N(2)-AC(2))

4 n=2 (Si(3)N(2)-PC(2))

5 n=3 (Si(3)N(2)-BC(2))

Scheme 1. Synthetic route of trisiloxane RT-SAILs.