



A new zwitterionic siloxane compound: structural characterization, the solution behavior and surface properties evaluation



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ABSTRACT

1,3-Bis(3-ammonium-propyl)tetramethyldisiloxane carbamate, APCO, was unexpectedly formed in a solution containing the proper diamine besides 4-imidazolecarboxaldehyde in methanol solution maintained for long time at room temperature. The compound separated as colourless crystalline one was investigated by single-crystal X-ray diffraction and spectral (FT-IR, $^1\text{H-NMR}$) analysis. Due to the co-existence of both hydrophobic bis(propyl)tetramethyldisiloxane fragment and telechelic hydrophilic groups, the obtained compound shows surface activity proved by tensiometry. Self-assembly in solution was emphasized by dynamic light scattering (DLS) and confirmed by atomic force microscopy (AFM) images taken on the spin coated films, both revealing closed values for size of the micelles (few hundred nanometers). The behavior of the carbamate in wet atmosphere was studied by water vapor sorption analysis in dynamic regime (DVS). Thermal analysis revealed almost a complete decomposition of the compound occurring in a two-steps process.

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1. Introduction

A variety of silicone-based materials have been examined as CO_2 -capture media since 1972 when silicone oils were patented for this application. Silicones having different substituents have also been subsequently explored. Between them, amino-silicones proved recently to be highly effective as CO_2 adsorbers [1–3]. It was well-established that primary and secondary amines react with CO_2 to form carbamates, under anhydrous conditions [3–7]. The amine compounds can be used as sensing CO_2 sensors [3]. Ammonium carbamates are a class of compounds with interesting structure, molecular aggregation and thermal behaviour [8,9].

The siloxane-containing amines offer several advantages in comparison with classical organic amines: thermal stability of Si-O-Si bond, lower volatility, low viscosity that permits their using as such without water or other solvents. This decreases the energy needed to heat the mixture and to recover the solvent upon CO_2 release [3]. On the other hand, the presence of amine and more the carbamate attached to the siloxane, confers its amphiphile character taking into account the high hydrophobicity of the dimethylsiloxane moieties. Such compounds could behave as a surfactant.

It has been proved that siloxane surfactants can perform better than most of the organic ones [10,11]. This property is due to its flexibility which enables it to adopt proper conformations (close and efficient packing at various interfaces) and its low cohesive energy [12]. Surface active agents based on silicones are known in a lot of domains, as polyurethane foam additives, textile manufacture, cosmetics, agricultural adjuvants and paint additives [13,14]. Carbohydrate-modified siloxane

surfactants were used to increase the solubility for the hydrophobic drugs, improving transdermal penetration drugs [5]. Usually nonionic silicone polyether copolymers are used as surfactants due to their low critical micelle concentration and to their maximum capacity to reduce surface tension [15]. For improving the wettability of a polyester material, an amphiphilic polysiloxane was modified with multi-cationic groups. Due to this change, the surface activity of the material was improved. When the cationic degree increases, the surface energy of the polymer solution decreases [16,17].

In this paper we report a silicone derivative, 1,3-bis(3-ammonium-propyl)tetramethyldisiloxane carbamate, APCO, formed by atmospheric CO_2 capture in the presence of slight basic environment conferred by the presence of an imidazole derivative. Its structure was evaluated by spectral analysis (FTIR, $^1\text{H NMR}$) and X-ray single crystal diffraction. Having both cationic and anionic centers attached to the same molecule, it was expected as this to behave as a zwitterionic (amphoteric) surfactant. This was followed by tensiometry, dynamic light scattering, and atomic force microscopy. The behavior in wet and nitrogen atmosphere thermostability were also evaluated.

2. Experimental

2.1. Materials

1,3-Bis(3-aminopropyl)tetramethyldisiloxane (AP_0), $[\text{H}_2\text{N}(\text{CH}_2)_3(\text{CH}_3)_2\text{Si}]_2\text{O}$, was purchased from Fluka with main characteristics: b.p. = $142^\circ\text{C}/11.5\text{ mmHg}$, $d_{20}^4 = 0.901$.

4-Imidazolecarboxaldehyde ($\text{C}_4\text{H}_4\text{N}_2\text{O}$), IC, purity > 98%, was purchased from Sigma-Aldrich.

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Methanol and chloroform (Chemical Company-Romania) were used as solvents.

2.2. Measurements

The infrared spectra were registered on a Bruker Vertex 70 FT-IR instrument, in transmission mode, in the 300–4000 cm^{-1} range (resolution 2 cm^{-1} , 32 scans), at room temperature.

The $^1\text{H-NMR}$ spectra were acquired in CDCl_3 at 25 °C with a Bruker Avance DRX 400 MHz spectrometer operating at 400.13 MHz for ^1H . The spectrometer was equipped with a 5 mm four nuclei, direct detection z-gradient probe head. Chemical shifts are reported in ppm and are referenced to chloroform $\delta^1\text{H} = 7.26$ ppm.

Surface tension was measured in aqueous solution (1 g/dl) with an automatic tensiometer, Sigma 700 from KSV, using the Wilhelmy plate method and adequate software.

Electronic absorption spectra were measured in chloroform solution (concentration 1 g/dl) by Analytik Jena SPECORD 200 spectrophotometer in 10 mm optical path quartz cells fitted with polytetrafluoroethylene stoppers.

The luminescence spectrum was recorded at room temperature with a Perkin Elmer LS55 spectrometer in chloroform solution (concentration 1 g/dl).

Water vapour sorption capacity of the sample has been determined by using the fully automated gravimetric analyzer IGA_{sorp} produced by Hidden Analytical, Warrington (UK).

Particles size and distribution in aqueous solution was determined by dynamic light scattering (DLS) using a Malvern Instruments Autosizer Lo-C 7032 Multi-8 Correlator (Malvern Instruments, UK). The solution previously filtered through 0.5 μm filter, without further dilution was irradiated with red light (HeNe laser, wavelength $\lambda = 632.8$ nm) and the intensity fluctuations of the scattered light were analyzed to obtain an autocorrelation function.

The atomic force microscopy (AFM) measurements were done on films cast from aqueous and chloroform solutions by using a Scanning Probe Microscope Solver Pro-M platform (NT-MDT, Russia), in air, in semi-contact feedback error mode, using a rectangular NSG03 cantilever with a resonance frequency of 92 kHz. The cantilever's tip radius of curvature was 10 nm. The scanning area was $5 \times 5 \mu\text{m}^2$. The AFM images processing and the calculations of the parameters were realized by the Nova Software (NT-MDT, Russia). In order to obtain nanometer-scale resolution images without any artifacts, beside the calibration of the optical detection system, a full set of calibration standards was used for: AFM simultaneous calibration in X, Y and Z directions, lateral and vertical calibration, detection of lateral non-linearity, detection of hysteresis, creep, and cross-coupling effects, detection of angular distortion, 3-D visualization of the scanning tip, determination of tip sharpness parameters (aspect ratio and curvature radius), tip degradation and contamination control.

Thermogravimetric measurements (TGA) were performed on a Mettler Toledo TGA851e derivatograph under a flow of nitrogen (20 ml/min), in the temperature range 25–900 °C, with a heating rate of 10 K min^{-1} .

Crystallographic measurements were performed with an Oxford-Diffraction XCALIBUR E CCD diffractometer with graphite-monochromated Mo- $\text{K}\alpha$ radiation. The crystal was placed 40 mm from the CCD detector. The unit cell parameters determination and data integration were done using the CrysAlis package of Oxford Diffraction [18]. The structure was solved by direct methods using SHELXS-97 [19] and refined by full-matrix least-squares on Fo^2 with SHELXL-97 [19] with anisotropic displacement parameters for non-hydrogen atoms. All H atoms attached to carbon were introduced in idealized positions ($\text{dCH} = 0.96$ Å) using the riding model with their isotropic displacement parameters fixed at 120% of their riding atom. Positional parameters of the H attached to N

Table 1

Crystallographic data, details of data collection and structure refinement parameters for APCO sample.

Compound	APCO
Empirical formula	$\text{C}_{11}\text{H}_{28}\text{N}_2\text{O}_3\text{Si}_2$
Molecular weight, g/mol	292.53
Temperature, (K)	293
Wavelength, (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
a , (Å)	16.8847(18)
b , (Å)	6.3849(7)
c , (Å)	16.4378(13)
α , (°)	90
β , (°)	91.972(9)
γ , (°)	90
V , (Å ³)	1771.0(3)
Z	4
D_{calc} (g/cm ³)	1.097
μ , (mm ⁻¹)	0.203
θ_{min} , θ_{max} (°)	4.96 to 52°
Crystal size (mm)	0.35 × 0.15 × 0.15
Reflections collected	7610
Independent reflections	3484 [$R_{\text{int}} = 0.0221$]
R_1^a ($I > 2\sigma(I)$)	0.0952
wR_2^b ($I > 2\sigma(I)$)	0.1909
GOFC ^c	1.015
$\Delta\rho_{\text{max}}$ and $\Delta\rho_{\text{min}}$ (e/Å ³)	0.25/-0.19

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$, ^b $wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$.

^c $\text{GOFC} = \{ \sum [w(F_o^2 - F_c^2)^2] / (n - p) \}^{1/2}$, where n is the number of reflections and p is the total number of parameters refined.

atom were obtained from difference Fourier syntheses and verified by the geometric parameters of the corresponding hydrogen bonds.

CCDC 938660 contains the supplementary crystallographic data for this contribution. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.ca.ac.uk).

The main crystallographic data together with refinement details are summarized in Table 1.

2.3. Procedure

A solution consisting in 0.1242 g (0.50 mmol) 1,3-bis(3 aminopropyl) tetramethyldisiloxane in 10 mL methanol was added to a solution of 4-imidazolecarboxaldehyde 0.0961 g (1 mmol) in 2.5 mL methanol, in a 50 mL one-necked round-bottom flask. The reaction mixture was stirred for 4 h at 60 °C, after which was allowed to stay in a closed flask at room temperature. Formation of colorless crystals was observed after about 5 days. These were separated by filtration washed with diethyl ether, dried and analyzed further. Crystalline compound was labeled as APCO: $\text{C}_{11}\text{H}_{27}\text{N}_2\text{O}_3\text{Si}_2$.

FT-IR (KBr pellet, cm^{-1}): 3553w, 3416 m, 2955 m, 2926 m, 2872w, 1638 m, 1618s, 1574s, 1487s, 1435 m, 1410w, 1387 m, 1327 m, 1296 m, 1254s, 1182w, 1142w, 1116 m, 1057vs, 959w, 893w, 841 m, 797 s, 779 s, 739w, 708 m, 685w, 631w, 602w, 474w, 444w.

Table 2

Bond lengths (Å) for the synthesized compound.

Si1-O3	1.602(4)	O2-C11	1.268(5)
Si1-C3	1.831(5)	N2-C11	1.368(6)
Si1-C4	1.845(6)	N2-C10	1.445(6)
Si1-C5	1.850(6)	C3-C2	1.523(6)
Si2-O3	1.604(4)	C10-C9	1.509(7)
Si2-C8	1.832(6)	C1-C2	1.501(6)
Si2-C7	1.834(6)	C8-C9	1.514(7)
Si2-C6	1.846(6)	O1-C11	1.255(6)
N1-C1	1.474(6)	-	-

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