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Polyamine-based spin probes for the study of siliceous structures

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ABSTRACT

Three new spin probes containing polyamine chains (2 or 3 nitrogen atoms) and nitroxide were synthesized. These compounds are stable in aqueous media at pH 5–10, and shape and intensity of their ESR spectra do not depend on pH in this range. The involvement of the spin probes in association in solution results in decrease of the spin mobility which appears as spectral anisotropy. The polyamine spin probes bind to siliceous nanoparticles in solution resulting in a reversible decrease in spectral intensity. These observations open a new way for monitoring silicic acid condensation. Sorption of the spin probes on solid silica gives rise to anisotropic spectra. The polyamine spin probes penetrate into growing cells of diatom algae in a similar manner to polyamine-containing fluorescent dyes.

1. Introduction

Condensation of silicic acid in aqueous medium is actively studied nowadays. Biosilicifying organisms such as diatoms can store a lot of silicon as these single-cell algae build their siliceous exoskeleton (Fig. 1). The structure and properties of biogenic silica are close to those of amorphous quartz glass [1] in spite of formation at ambient temperatures. Study of the biosilicification mechanism is aimed at invention of ecology-friendly approaches to new siliceous and composite materials. Condensation of silicic acid in solution results in sols, gels and solid products [2,3]. Several methods are used to study this process: colorimetric determination of monomeric $Si(OH)_4$ with molybdenum blue assay [2,4], ^{29}Si NMR to measure siliceous structures of various degrees of condensation [5] and IR spectroscopy for studying silanol groups in solid materials [5]. Formation of the primary poly(silicic acid) particles is a very important step in the pathway from silicic acid to siliceous gels and solid materials. These primary particles are poorly visible via light scattering due to their small size and a refractive index close to that of water value. ^{29}Si NMR is not an appropriate method for these objects too because of low sensitivity with the low, natural ^{29}Si content.

Spin probes, which contain moieties capable of interacting with various surfaces, nano- and microparticles [6,7], mesoporous materials [8–12], and membranes [13], allow monitoring of the formation of the corresponding structures and thus permit study of the properties of these objects [6–16]. Electron spin resonance (ESR) gives information about the microenvironment around a spin probe because polarity, viscosity and dynamics of the environment alter ESR spectra [17,18]. The nitroxide in aqueous solution undergoes fast and isotropic spinning. Restrictions to this spinning result in anisotropic broadening of the spectral lines, change of the spectral component amplitudes and shift of the outside components [13,17,18]. Spin probes can be covalently bonded with the materials being studied or they can bear moieties capable of association with active particles by means of ionic, covalent or hydrophobic interactions.

Siliceous materials interact with amines and tertiary amine salts through hydrogen and/or ionic bonds [3] which allows the use of amine containing spin probes in the study of these materials.

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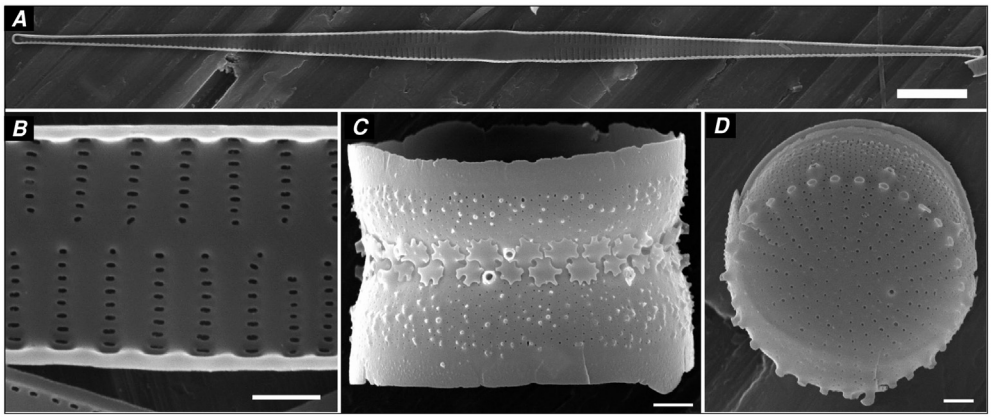

Fig. 1. SEM images of siliceous valves of diatoms *Ulnaria ferefusiformis* Kulikovskiy & Lange–Bertalot (A and B) and *Stephanodiscus meyerii* Genkal & Popovskaya (C and D) from Lake Baikal. Scale bars are 10 μm (A) and 1 μm (B–D).

Investigation of the interaction of these positively charged spin probes with silica gel samples showed that the spin probe is not associated with silica gel surface but placed in surface boundary area [19]. pH-Sensitive spin probes were studied in canals and pores of mesoporous siliceous materials [6]. Nitroxyl spin probes with phenyl and pyridyl moieties were found to be able to interact with hydrophobic and hydrophilic surface domains which allows monitoring of acidity and electric potential in the canals of mesoporous materials. Covalent immobilization of 4-amino-2,2,6,6-tetramethylpiperidine-1-oxyl (4-amino-TEMPO) onto siliceous particles was used to study the particles' mobility [20] and to monitor interaction between negatively and positively charged nanoparticles [21].

The known amine containing spin probes have one amino group only which does not allow strong interactions with siliceous materials. We have found [22] that oligomeric propylamines containing 2–3 nitrogen atoms can catalyze condensation of silicic acid and associate with siliceous particles. These propylamines are synthetic analogs of biogenic amines from siliceous frustules of diatom algae [23] and of spermine. Spermine plays an important role in cell division [24]. This work is aimed at synthesis of TEMPO (2,2,6,6-tetramethylpiperidine-N-oxyl) [25] derivatives containing two or three amino groups (Fig. 2). We have studied paramagnetic properties of the new probes and composite systems including the probes and solid silica, soluble and gel-like poly(silicic acid) and frustules of the living diatoms after culturing them in the presence of the spin probe.

2. Experimental section

2.1. Reagents and materials

Toluene, acetic and formic acids, aqueous ammonia (25%), 1-methylimidazole, NaOH, $Na_2SiO_3 \cdot 5H_2O$, 1 M HCl, reagents for the molybdenum blue assay (ammonium molybdate, oxalic acid, 4-methylaminophenol sulfate, sodium sulphite, standard silicate solution, hydrochloric acid (35%), and sulphuric acid (98%)) were purchased from Aldrich, Fisher, Panreac, or Acros chemicals and used without further treatment. Polyamines N,N-Bis[3-(methylamino)propyl]methylamine (N3), N^1-[3-(Dimethylamino) propyl]-N^1,N^3-dimethyl-1,3-propanediamine (N3–H) and N,N-Bis [3-((3-methylaminopropyl)methylamino)propyl]methylamine (N5) were synthesized according to the methods in our previous publications [22,26]. Nitroxides TEMPONE [27], and 4-Iodoacetamido-TEMPO [28] were prepared according to the protocols given in those papers. 20 mM buffer solutions were prepared in deionized water by adjusting pH with 0.1, 1 M NaOH and HCl (sodium formate – pH 3, sodium acetate – pH 5, 1-methylimidazole - pH 7, aqueous ammonium solution – pH 10). The following solid siliceous materials were used for

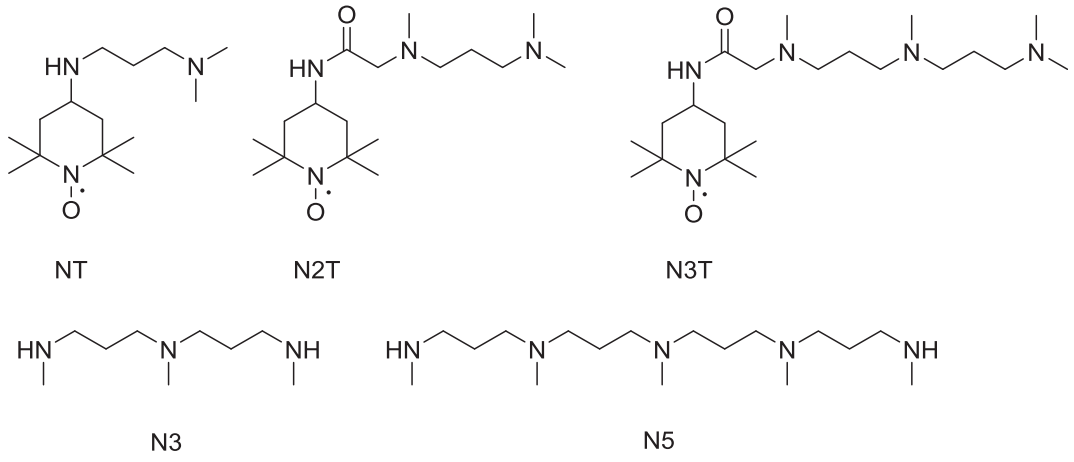

Fig. 2. New spin probes and polyamines.