5-Alkyl-1,2,4-triazole-3-thiones as stabilizers in the synthesis of silver nanoparticles

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Introduction / Objectives / Aims

The development of synthetic procedures for the formulation of metal nanoparticles (NPs) is a mainstream of the modern nanoscience [1]. Undoubtly, the stabilization of metal NPs is a key factor for their long term exploration and especially widespread usage. Often, as general stabilizers surfactants can be used. The role of surfactants in NPs synthesis have been detailed discussed in the recent work of Song et al., where authors have suggested that the review can open up new avenues for the synthesis of nanocrystals [2].

Several novel 5-alkyl-4-methyl-1,2,4-triazole-3-thiones (alkyl can be pentyl, heptyl, pentadecyl, and heptadecyl) were synthesized from hydrazides of corresponding acids. It is known from the literature that structurally similar 4-amino-5-hexyl- 1,2,4-triazole-3-thione can be used as a flotation collector in the treatment of malachite [3]. The authors note that the surface activity is due to the interaction of sulfur and nitrogen atoms with the surface of malachite. Moreover, it was shown a strong binding of thiolate-containing stabilizers to silver nanoparticles [4]. Considering all the above, it was decided to investigate the possibility of using alkaline solutions of 5-alkyl-4-methyl-1,2,4-triazole-3-thiones as stabilizers in the chemical synthesis of silver nanoparticles.



Results

In the present work, we have focused on the improvement of the synthesis of Ag-NPs via the reduction of silver ions (in the form of silver nitrate) with sodium borohydride in the presence of new anionic triazole surfactants **3a-d**. The synthesis of **3a-d** is presented in Scheme 1, and it includes the transformation of fatty acids hydrazides into thiosemicarbazides **1a-d** via the reaction with methyl isothiocyanate. Further treatment of **1a-d** with a base causes the cyclization and formation of triazoles **2a-d**, which were separated by the neutralization of the reaction medium with acetic acid. NMR spectra unequivocally confirmed the formation of the triazole ring. The further desolution of triazole3-thiolate salts **3a-d**, which have structural fragments of surfactants – triazole-3-thiolate core acts as a "polar head", whereas the alkyl substituent in position 5 acts as a "lipophilic tail".

Fig.1 shows the ¹H-NRM spectrum of triazole 2a, in which the signals of the pentyl substituent in the fifth position, the methyl group in position 4 of the triazole cycle, and the signal of the N-H proton in position two are observed. Namely, a triplet with a relative intensity of 2, characterized by a spin-spin interaction constant of 7.6 Hz, at 2.63 ppm corresponds to the α -methylene group of the pentyl chain. Compared with the original thiosemicarbazide, we observe a chemical shift to a weaker field of the spectrum for 0.52 ppm, which confirms the formation of an aromatic cycle, which leads to even greater deshielding of this methylene group, compared to the effect of the carbonyl group of the original thiosemicarbazide 1a. Other components of the pentyl substituent undergo a much smaller shift. Thus, the β -methylene group multiplet is observed at 1.62 ppm, and at 1.31 ppm, the multiplets of γ - and δ -methylene groups are overlapped. The triplet at 0.87 ppm with a spin constant of 6.9 Hz and the relative intensity of 3 corresponds to the terminal methyl group of pentyl fragment.

Figure 1. ¹H-NMR spectrum of compound 2a.

Varying the experimental conditions, we have succeeded in developing new simple methods for synthesizing Ag-NPs by using new triazole surfactants. Corresponding UV-VIS spectra are presented in Figure 2. The absorption maxima range of 410-430 nm corresponds to the formation of classical spherical silver nanoparticles. It should be noted that in the case of compounds 3c and 3d narrower peaks were obtained (Figure 2a), whereas compounds with shorter "lipophilic tail" produce more wide peaks (Figure 2b). Moreover, it should be highlighted that Ag-NPs obtained with C15 (3c) and C17 (3d) triazoles were stable during 3-4 days, whereas Ag-NPs stabilized with 3a and 3b were decomposed during 4-8 hours.



Figure 2. UVVIS spectra of Ag-NPs stabilized with 3c (a) and 3b (b).

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Scheme 1. Synthesis of the new surfactants **B**.

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