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New chiral metal-mesogenic nanosystems "silver - thiocholesterol" and their adsorption properties

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ABSTRACT

New chiral matrices for thin film chromatography were obtained using hybrid metal-mesogenic nanosystems «silver – thiocholesterol» with different metal to ligand ratio, immobilized on silica gel particles. It was shown, that heteroatomic derivative of cholesterol – thiocholesterol and its composition with small silver nanoparticles formed in the system by the chemical reduction of silver ions possess liquid crystalline cholesteric mesophase. Molar ratio between thiocholesterol ligand molecules (L) and silver (Ag) insignificantly influenced on the size of silver nanoparticles formed in the system: for molar ratio Ag : L = 1:5 the main diameter of nanoparticles was equal to (2,7 ± 0,4) nm, for molar ratio Ag : L = 1:2 – (2, 2 ± 0,4) nm, for molar ratio Ag : L = 1:0,5 – (2,1 ± 0,6) nm. The new chiral matrices for thin film chromatography possess enantioselectivity related to optical isomers of 2,2′-diamino-1,1′-binaphtol (DABN) and trifluoroantranylethanol (TFAE). We have succeeded to select optical isomers of TFAE with selecting factor equal to 1,56.

KEYWORDS

hybrid metal-mesogenic nanosystems; thiocholesterol; silver nanoparticles; thin layer chromatography; chiral matrices; modified silica gel

1. Introduction

The chirality of active compounds is important for many biochemical processes [1], the study and separation of optical isomers drug substances is principal for pharmaceutical applications, and control of optically purity is necessary for production pharmaceutical components [2]. In this connection it is obvious the rising interest of many researchers to the development of new approaches for effective separation of optically active compounds isomers. Last years the new methods were developed for chromatographic separation of optically active compounds – chiral chromatography [3–5]. One of the directions of such investigations is the development of stationary phase suitable for separation of produced raceme mixtures to optical pure compounds. Nowadays the development of new chiral stationary phases and matrices is very important task of chiral chromatography.

The tasks of creation of new chiral matrices on the base of hibrid metal – mesogenic nanosystem, including silver nanoparticles covered by stabilising layers of chiral liquid crystalline ligands cholesterol and it's heteroatomic derivative thiocholesterol immobilised on silica gel plates, study of the adsorbtive properties of such system and their testing as stationary phases in thin layer chromatography were included in the goal of this work.

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2. Experimental methods

The synthesis of silver nanoparticles was performed by the modified method of borohydride reduction of silver ions [6] in a biphase aqueous-organic medium with a phase transfer tetra-n-octylammonium bromide in the presence of a stabilizing ligand thiocholesterol. The following reagents were used in this method: $AgNO_3$ (Merk, 99.99%), $NaBH_4$ (Merk, 99.99%), $C_{27}H_{46}S$ (Merk, 99.99%), tetra-n-octylammonium bromide (Merk, 99.99%), toluene (analytical grade). Hybrid nanosystems "silver-thiocholesterol" with a molar ratio of Ag:L 1: 5, 1: 2 and 1: 0.5 were synthesized by varying the concentration of the initial reactants.

The TEM micrographs of silver nanoparticles were used by transmission electron microscope (TEM) (accelerating voltage 100 kV, «Carl Zeiss SMT AG Oberckochen», Germany). The calibration absorbance spectra were obtained for solutions of silver nanoparticles in toluene with different concentration. The measurements were performed with a UV spectrophotometer SPECORD M 40 (Carl Zeiss, Germany).

«Polysorb», SiO_2, 10 micrometers was used as the substrate for preparing chiral matrices for thin layer chromatography (TLC). The impregnation of plates for thin layer chromatography was carried out by the double spray technique using toluene sols of hybrid silver - thiocholesterol nanoparticles.

The following optical active compounds were used in this work: TFA, 1,1′-bi-2- naphthol, 2,2-diamino-1,1-binaphlene. The solutions were prepared by dissolving of accurate mass in the mixture of ethanol-water (1:1), the concentration was equal to 100 micrograms/ml. A mixture of acetonitryle and water (AcN : H_20) in a volume ratio of 1: 1 was used as a mobile phase. The modified plates were treated by video-densitometry (densitometer "Sorbfil ", software version 1.1.0.100). For the visualization of tested compounds were used their ability to fluorescence upon exposure to UV radiation at 360 nm. The diffusion reflectance optical spectra were obtained for constructing the adsorption isotherms in the visible region of the modified silica gel plates by hybrid nanoparticles of silver stabilized by thiocholesterol (spectrophotometer with a set up for diffusive reflection Shimadzu CS-9001PC, Japan).

3. Results and discussion

Cholesterol and it's mesogenic (liquid crystalline) derivatives are natural and modified chiral matrices, which adsorbtive and selective properties only begin to study [7]. Thiocholesterol is the heteroatomic derivative of cholesterol, it's chemical structure is presented in Fig. 1. Cholesterol and it's derivatives are optically active molecules and form at definite conditions helical liquid crystalline structures – cholesteric mesophases. It is known that the effects «guest-host» interactions are very important for the practical applications of composite liquid crystalline systems, including guest molecules of organic and inorganic compounds [8, 9]. At the same time these compounds contain such functional groups as -OH, -SH, which are able to the effective interaction with the surface atoms of metal nanoparticles and form liquid crystalline stabilising and selecting layers on the surface of metal nanoparticles. Last several years we have intensively developed the investigations on creation of new methods of production hybrid metal-mesogenic nanosystems and study of their physical and chemical properties [10–12]. The use of optically active cholesteric ligands allow us to produce chiral hybrid nanosystems, including silver nanoparticles covered by optically active ligand layers and connected with silica particles formed active layers on the plates for chromatography. The scheme of hybrid nanoparticles and nanosystems formed in this case is also presented in Fig. 1. The use of cholesteric liquid crystalline systems as chiral matrices for chromatography can improve the

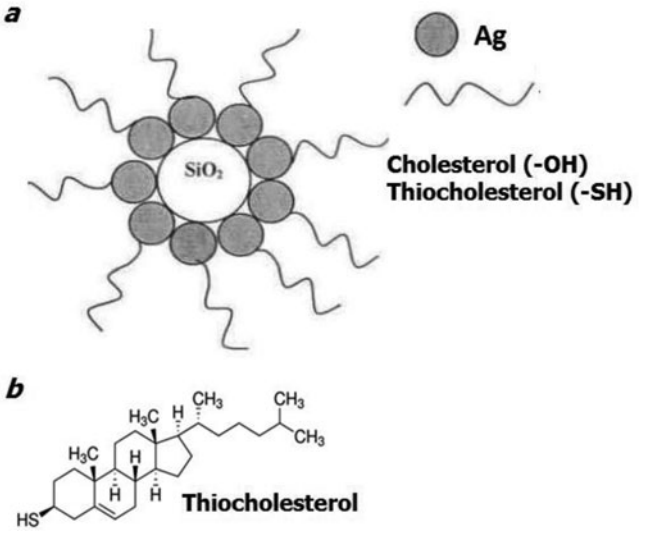


Figure 1. Schematic structure (a) of silica gel modified by silver nanoparticles stabilized by thiocholesterol (b).

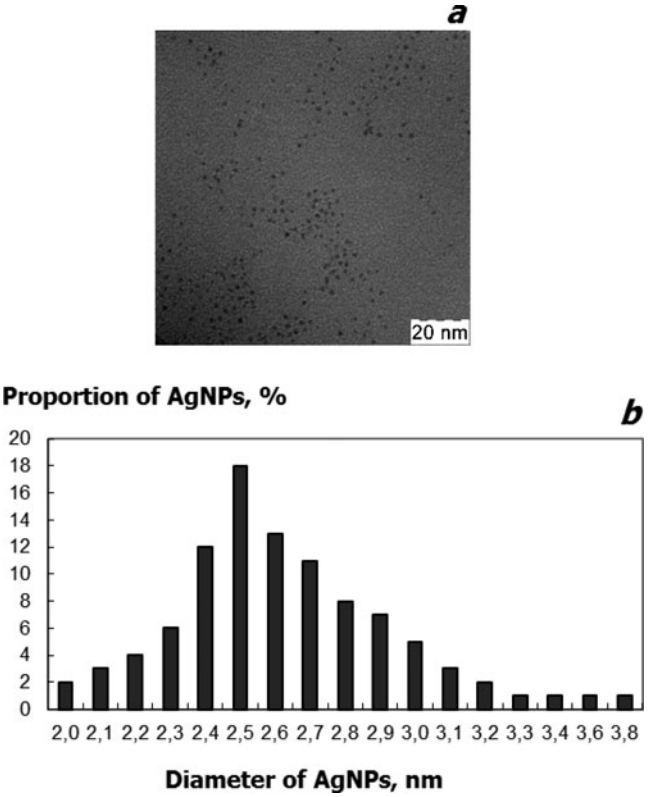
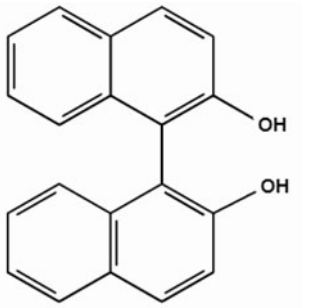
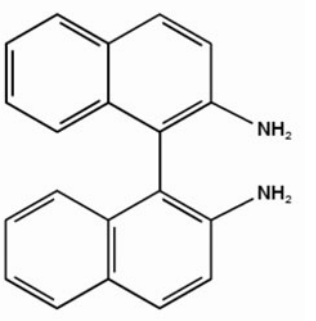
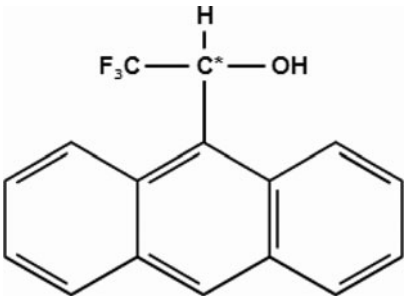


Figure 2. TEM-micrograph (a) and a histogram of the size distribution for silver nanoparticles (molar ratio Ag:L = 1:5 (b).

Table 1. The structures of the test compounds.

1,1-bi-2-naphthol	
1,1-binaphtyl-2,2-diamine	
TFA	

procsses of optical isomers selection and "guest-host" interactions can play the main role in the selective adsorbtion and partition of optical isomers.

Then histograms of the distribution of silver nanoparticles in size were obtained for molar ratios of Ag - NPs: L 1:5, 1:2 and 1:0.5, respectively. Molar ratio between thiocholesterol ligand molecules (L) and silver (Ag) insignificantly influenced on the size of silver nanoparticles formed in the system: for molar ratio Ag : L = 1:5 the main diameter of nanoparticles was equal to (2,7±0,4) nm, for molar ratio Ag : L = 1:2 – (2,2±0,4) nm, for molar ratio Ag : L = 1:0,5 – (2,1±0,6) nm. The results of the samples studies by TEM method for the system Ag : L = 1:5 is presented in Fig. 2(a) and hystogram of size distribution for silver nanoparticles in Fig. 2(b). This system was used for impregnition of silica gel plates for thin layer chromatography. The UV-Vis spectra of toluene sols of the hybrid system silver: thiocholesterol (Ag / L = 1:5) were recorded in silver concentration range 0,2–2,0 mg/ml and show the characteristic for silver nanoparticles plasmonic band at 450 nm. The intensity of absorbance is growing linear by rising the concentration of nanoparticles.

For producing of silica gel plates modified by the layers of hybrid metal-mesogenic system "silver: thiocholesterol" toluene sols of silver nanoparticles were prepared and silica plates were covered by double spray technique. The spectra of diffusion reflection of the thin films

Table 2. The retention times and separation factors of test compounds.

Substance	Rf	α
1,1′-binaphtyl 2,2′-diamine (R)	0.57	1.56
1,1′-binaphtyl 2,2′-diamine (S)	0.46	
1,1-bi-2-naphthol (R)	0.49	1.07
1,1-bi-2-naphthol (S)	0.51	
TFA (R)	0.43	1.56
TFA (S)	0.54	

of hybrid silver-thiocholesterol nanoparticles adsorbed on the silica gel plates were recorded for rising concentration of nanoparticles and of isoterms of adsorbtion were obtained. It was shown the metal-mesogenic system (Ag / L = 1:5) that silver plasmonic band absorbance grows up on metal nanoparticles concentration in the range of 0,2–2,0 mg/ml). Maximal covering of silica plates by monolayet of hybryd "silver-thiocholester" was reached at concentration of toluene sol of 1,2 mg/ml. The spectral characteristics of the plates were stable for several days during storage at lower temperatures and in the dark place. Thus, the selection of optical isomers of tested compounds were made using silica plates modified with hybrid silver-thiocholesterol (Ag/L = 1/5) nanoparticles with concentration of 1,2 mg/ml.

The structures of tested compounds used for selection are presented in Table 1. The chromatographic separation of tested substances were made using modified and unmodified silica plates for comparison of the results. The eluent phase for the selection was choisen from the several solvents differed by their chemical structure and polarity – methanol, isopropanol, acetonitryl, aceton, butylacetete. It was shown that the most suitable eluent was the mixture acetonitryl/water (50:50 v/v), the yield mobility was rising in the row 1,1′-bi-2-naphtol < 1,1′-binaphtyl-2,2′-diamine (BNDA) ≈ trifluoro antranylethanol (TFAE). The difference of the values of R_f was observed for S- and R-isomers of BNDA and TFAE. The detection of the spots of separated enanthiomers BNDA and TFAE was made by UV-irradiation with wavelength of 360 nm of the chromatographic plates using the ability of these compounds for fluorescence.

The chromatographic separation was estimated by the value of R_f, which was calculated using the relation $R_f = x/L$, where x – the length, passed by the substance from the start line, L – the length, passed by solvent up to front line. The efficiency of separation was estimated by the value α (selection factor), which was calculated using the relation $\alpha = \frac{1/Rf_2 - 1}{1/Rf_1 - 1}$, where Rf_1 and Rf_2 – parameters of two substances retention. The data wee presented in Table 2. It was shown, that hybrid nanosystems based on silver nanoparticles covered by stabilising layerof mesogenic molecules of thiocholesterol show the enantioselectivity in relation to optical isomers of BNDA and TFAE.

4. Conclusions and perspectives

Thus, the new approach was proposed and realized in this work for formation of optically active metal-mesogenic nanosystem, based on silver nanoparticles stabilized by optically active cholesteric mesogenic ligands – cholesterol and it's heteroatomic derivative thiocholesterol. The hybrid metal-mesogenic nanosystems obtained were used as liquid crystalline component for modification of silica gel nanoparticles and production of chiral matrix for thin film chromatography. The size and morphology properties of the systems obtained with different metal to ligand (Ag/L) ratio were studied. For molar ratio Ag : L = 1:5 the main diameter of nanoparticles was equal to (2,7 ± 0,4) nm, for molar ratio Ag : L = 1:2 – (2,2 ± 0,4) nm,

for molar ratio Ag : L = 1:0,5 – (2,1 ± 0,6) nm. The conditions allowed the production of silica-gel plates modified by chiral hybrid metal-mesogenic nanosystem in toluene sols were developed. The new chiral matrices for thin film chromatography possess enantioselectivity related to optical isomers of 1,1′-binaphtyl 2,2′-diamine (BNDA) and trifluoroantranylethanol (TFAE). We have succeeded to select optical isomers of TFAE with selecting factor equal to 1,56.

In future the hybrid silver-thiochlesterol systems obtained in the work can be used as chiral stationary phase also for high performance liquid chromatography (HPLC). One can expect the higher values of selecting effects due to the increasing pathway for selecting compounds in comparison to thin layer chromatography technique.

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